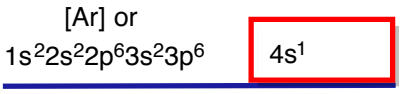
Hybridization: The Shape Of Things To Come

A. Intro

B. Electron Counting

In Atoms

neon



potassium

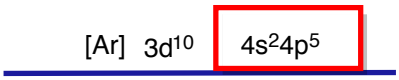
silicon

nitrogen

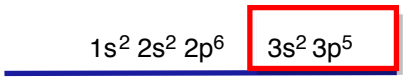
carbon

hydrogen

fluorine

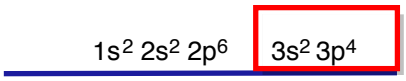


bromine



chlorine

oxygen



sulfur

boron

In Molecules, and Valency

2 electrons in the first shell,
8 in the second,
8 in the third.

share
completely donate or receive electrons.

each hydrogen atom has *2* first shell electrons
One bond containing *2* electrons is formed in this sharing process
valency of hydrogen in H_2 is *1*

He

C ___4____ *N* ___3____ *O* ____2___ *F* ___1____ *Cl* ___1____ *Br* ___1____ *S* ___2____

may only bring *1*
common molecules is *1*.

C ___CH_4__ *N* __NH_3___ *O* __H_2O___ *F* __HF____ *Cl* ___HCl___ *Br* __HBr____ *S* __H_2S___

N $2s^2 2p^1 2p^1 2p^1 1s^1 1s^1 1s^1$ H_3

The blue and red electrons are shared in bonds, two per bond, so ammonia has two electrons that are not in bonds, *ie* a lone pair.

H_2 $1s^1 1s^1 2p^1 2p^1 2p^1 2p^1 2s^2$ *O*	2	2	
water electronic structure	*bonds*	*lone pairs*	

H $1s^1 2p^1 2p^1 2p^1 2p^1 2p^1 2s^2$ *F*	1	3	
hydrogen fluoride electronic structure	*bonds*	*lone pairs*	

H $1s^1 4p^1 4p^1 4p^1 4p^1 4p^1 3d^{10} 4s^2$ *Br*	1	3	
hydrogen bromide electronic structure	*bonds*	*lone pairs*	

C $2s^2 2p^1 2p^1 1s^1 1s^1 1s^1 1s^1$ H_4	4	0	
methane electronic structure	*bonds*	*lone pairs*	

favored electron count for that is *8*

B $2s^2 2p^1 1s^1 1s^1 1s^1$ H_3	3	0	
borane electronic structure	*bonds*	*lone pairs*	

H_2 $1s^1 1s^1 3p^1 3p^1 3p^1 3p^1 3s^2$ *S*	2	2	
hydrogen sulfide electronic structure	*bonds*	*lone pairs*	

Si $3s^2 3p^1 3p^1 1s^1 1s^1 1s^1 1s^1$ H_4	4	0	
tetrahydrosilane electronic structure	*bonds*	*lone pairs*	

P $3s^2 3p^1 3p^1 3p^1 1s^1 1s^1 1s^1$ H_3	3	1	
phosphine electronic structure	*bonds*	*lone pairs*	

electrons *is* lost

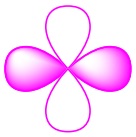
C. Mixing Atomic Orbitals To Maximize Overlap In Molecules

Combining *s*- and *p*-Orbitals

called *atomic* orbitals.

have *different* shapes as atomic orbitals.

s-



d-

d-

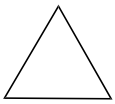
p-

hybridized to make them.
2 molecular orbitals, of three gives *3*, and of *n* gives *n*.

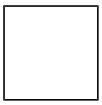
denoted as *sp*, whereas sp^2 surfaces are formed if *two p*-orbitals are mixed with one *s*-.
a ___sp^3___ hybrid.

Geometric Shapes

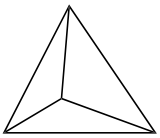
straight line connecting three dots



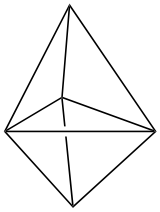
a triangle



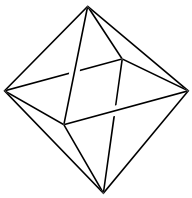
a square



a tetrahedron



a trigonal bipyramid



an octahedron

the boy *in the middle*.
girl-boy-girl angle is *180*
ideal bond angle.

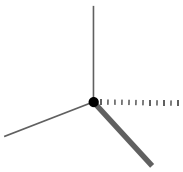
middle of a *triangle* with
then *120°*.

a *tetrahedron*,
109°.

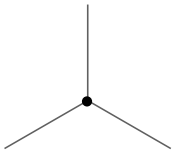
Shapes Of Molecules Based On Geometric Shapes

2 *sp*-hybrid orbitals.
3 hybrid orbitals, and
4 arise from.

Bold lines mean
dashed lines



sp^3



sp^2

sp

will be sp^2 hybridized.
A tetrahedron of sp^3 hybrids
if *4* bonds
sp hybrid orbitals.

0 lone pairs
it is *tetrahedral*.

Fluorine in HF is surrounded by one atom, with which it shares one electron, and it has *6* electrons that it did not share, *ie* *3* lone pairs.

4 entities
hydrogen fluoride is approximately *tetrahedral*.

Water
4 objects
tetrahedral

hydrogen chloride, *4*
Cl is *tetrahedral*

ammonia, *4*
tetrahedral

hydrogen sulfide, *4*
tetrahedral arrangement; and,

borane, *3*
triangular arrangement.

C in methane is *tetrahedral* with a dihedral angle of *109°*

O in water is *tetrahedral* with a dihedral angle of *109°*

Br in hydrogen bromide is *tetrahedral* with a dihedral angle of *109°*

N in ammonia is *tetrahedral* with a dihedral angle of *109°*

S in H_2S is *tetrahedral* with a dihedral angle of *109°*

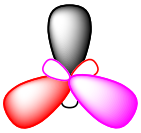
B in BH_3 is *trigonal* with a dihedral angle of *120°*

an *sp* hybrid consisting of *2* MOs in a *linear* arrangement with a dihedral angle of *180°*

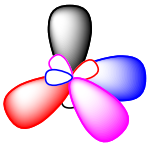
3 sp^2 MOs, and these arrange in a *trigonal* arrangement with a dihedral angle of *120°*

4 sp^3 MOs, and these arrange in a *tetrahedral* arrangement with a dihedral angle of *109°*

sp

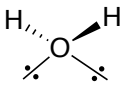


sp^2

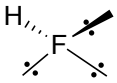


sp^3

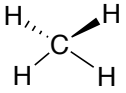
eg



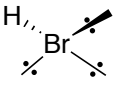
water



hydrogen fluoride

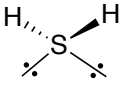


methane

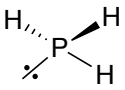


HBr

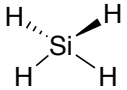
BH_3



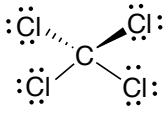
hydrogen sulfide



PH_3



SiH_4



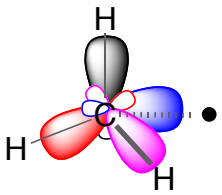
CCl_4

D. Multiple Bonds

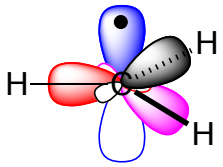
8 electrons in its second shell

7 electrons in its second shell; this *is not* a *are* relatively reactive.

sp^3 hybridized

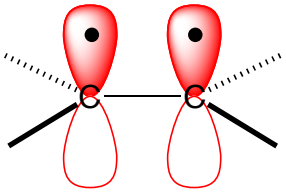


sp^3

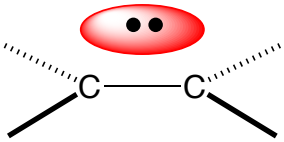


sp^2

σ-bonded *sp* hybridized *C*-atoms



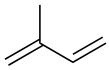
*ethene **before** mixing p-orbitals*



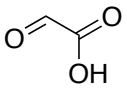
*ethene **after** mixing p-orbitals*

are called *sigma*.
pi bond.
Maximal overlap *is* achieved
Perpendicular *p*-orbitals *do not* interact.

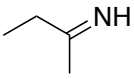
of a *π* bond.
1 line(s), and π-bonds are represented by adding *2* parallel line(s).



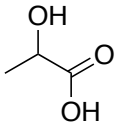
__2__
isoprene



__2__
pyruvic acid

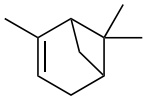


__1__
an imine



__1__
lactic acid

_3___
benzene



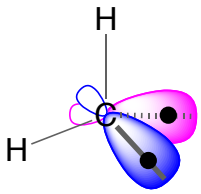
__1__
β-pinene

because they *would not* contribute to the binding interaction.
Atoms in molecules *can* selectively

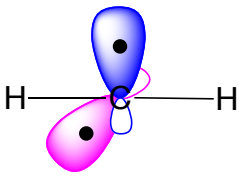
Carbene, CH_2, *6* shared electrons in the *C*-second shell.

this is called the *singlet* state.

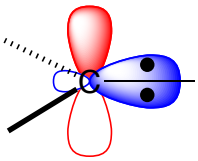
Alternatively, carbenes can be sp^2-hybridized with one electron in each of the hybrid lobes that does not point to a hydrogen; this is a *triplet* state.



triplet

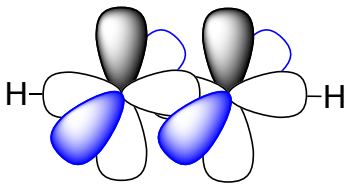


unstable triplet

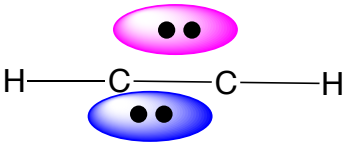


singlet

σ-bonded *sp* hybridized *C*-atoms



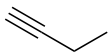
*ethyne **before** mixing p-orbitals*



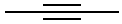
*ethyne **after** mixing p-orbitals*

two π bonds surrounding the σ bond
called a *triple* bond.

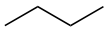
__1__
propyne



__1__
1-butyne

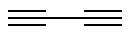


__1__
2-butyne



__0__
butane

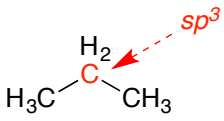
__1__
acetonitrile



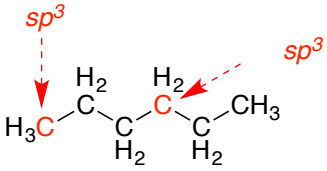
__2__
1,3-butadiyne

it *does not* matter if.

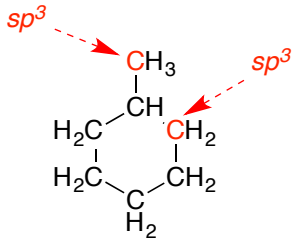
are *sp* hybridized, three sp^2, and four sp^3.



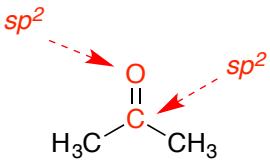
propane



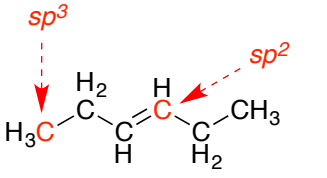
hexane



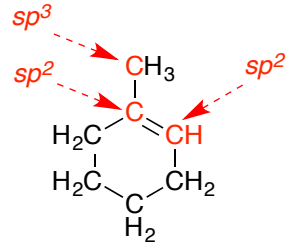
methylcyclohexane



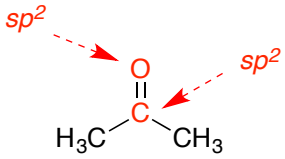
acetone



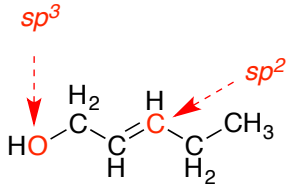
1-pentene



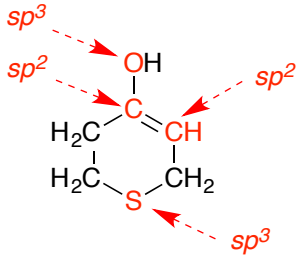
1-methylcyclohexene

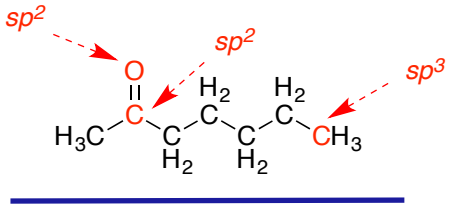


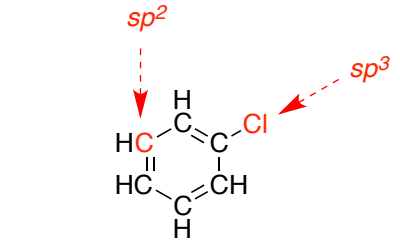
acetic acid

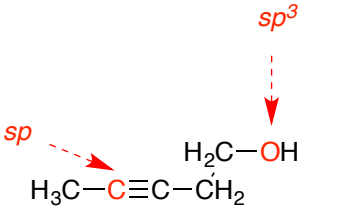


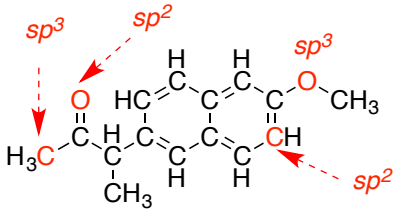
cis-1-hydroxy-2-butene



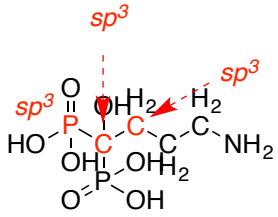




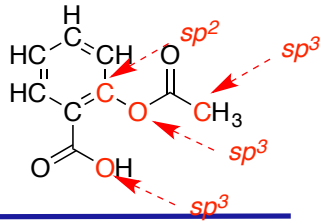




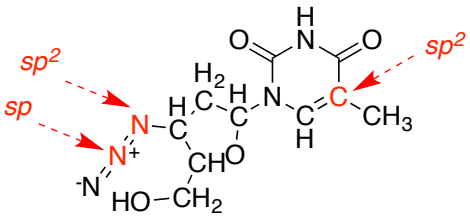
naproxen



alendronate



aspirin



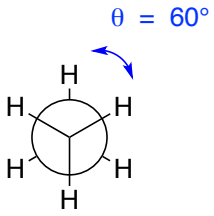
zidovudine (AZT)

Saturated Acyclic Hydrocarbons

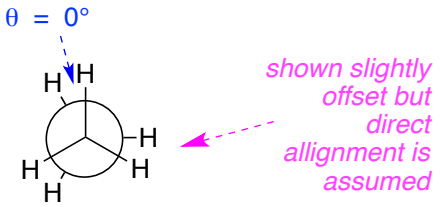
A. Introduction

B. Conformations Of Acyclic Hydrocarbons

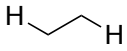
Ethane



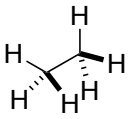
staggered



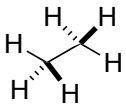
eclipsed



staggered



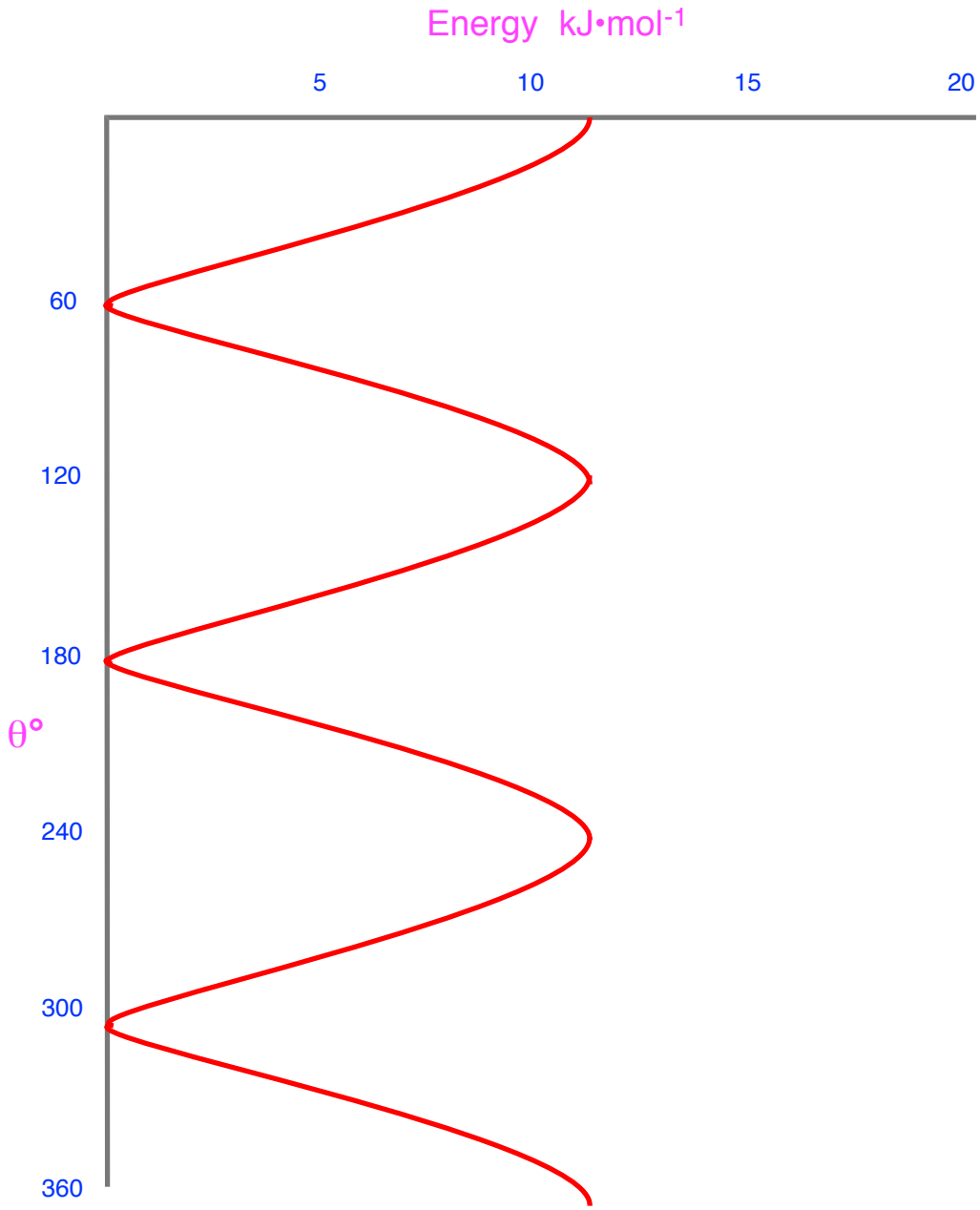
eclipsed

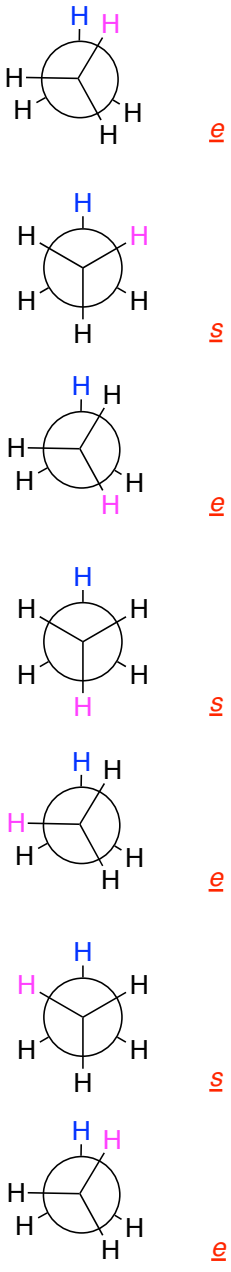


staggered

eclipsed

The *staggered* ethane conformer is more stable





called *torsional* strain.

indicate *destabilizing* interactions

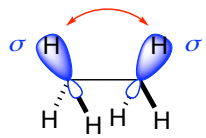
stabilizing interactions between empty and filled orbitals in staggered conformations.

if both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital are filled, this is slightly *destabilizing*.

contributes *2* *e*

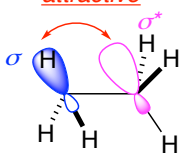
empty one donates *0* *e*.

repulsive

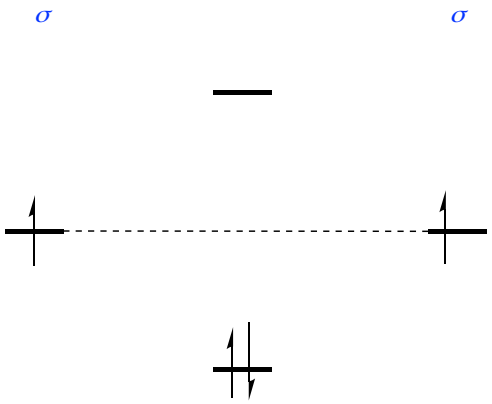


torsional strain

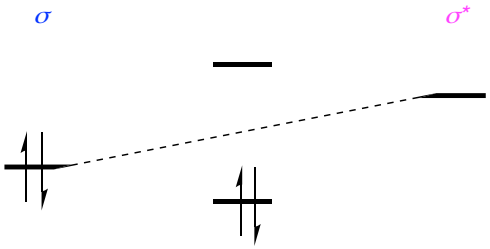
attractive



add electrons to the diagrams below and indicate bond orders:



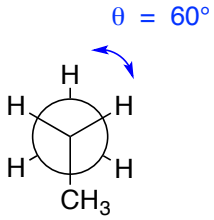
bond order = _1__



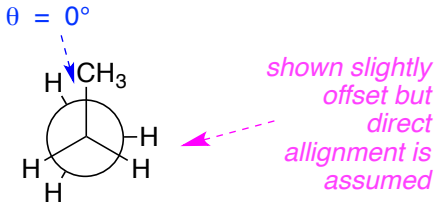
bond order = _1__

(but not strictly so since this is a secondary orbital interaction)

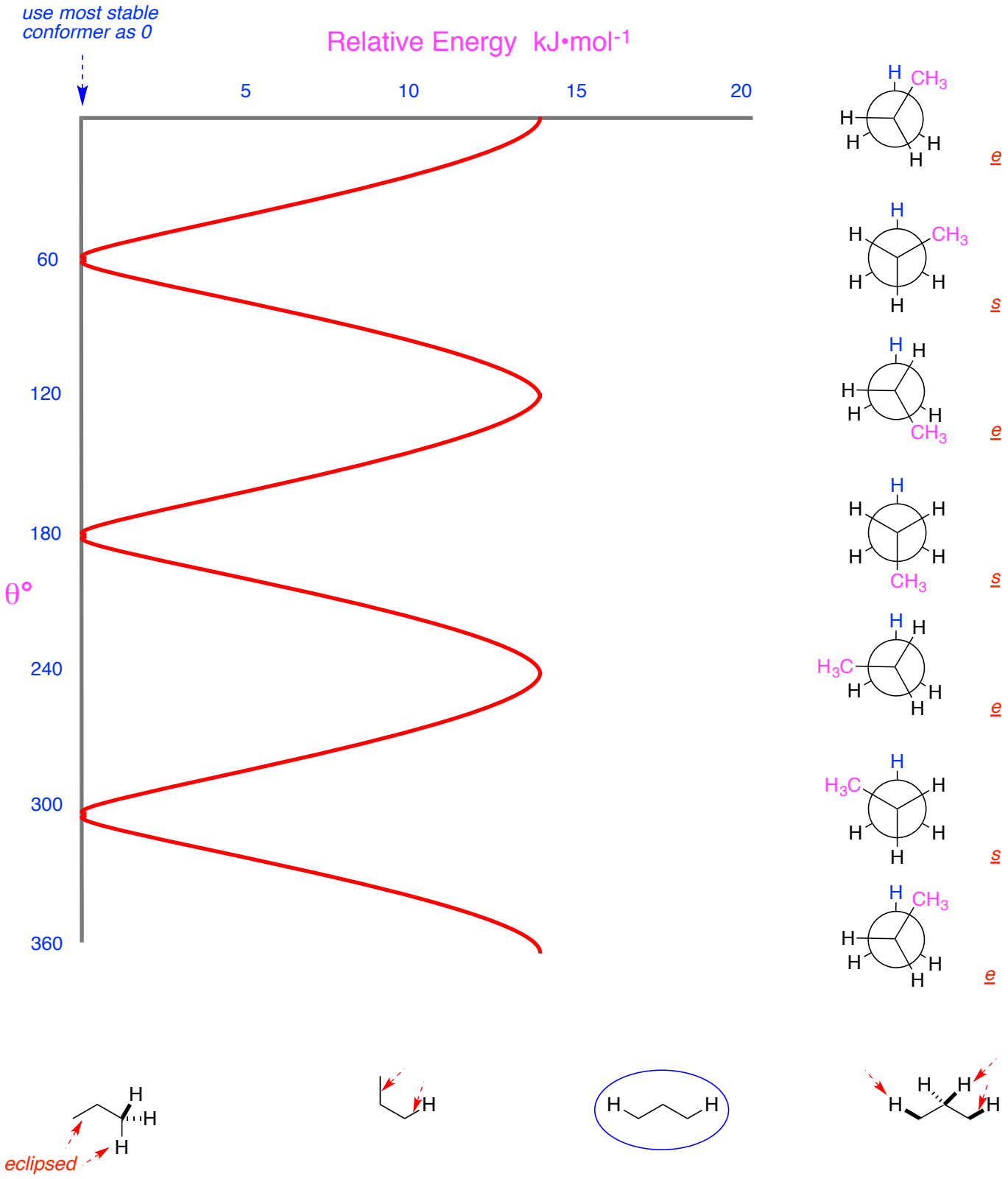
Propane



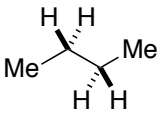
staggered



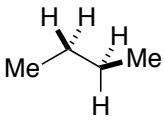
eclipsed


use most stable conformer as 0
Relative Energy kJ•mol-1
5
10
15
20
60
120
180
240
300
360
θ°
e
s
e
s
e
s
e
eclipsed

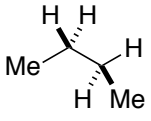
Butane



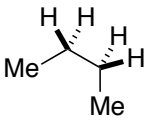
very low



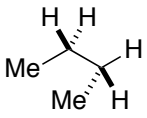
high



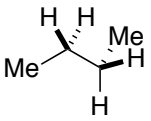
low



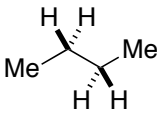
very high



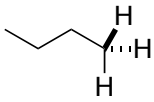
low

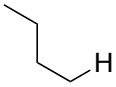


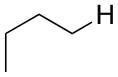
high

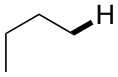


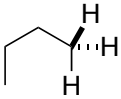
very low

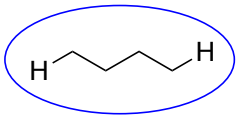


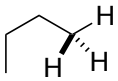


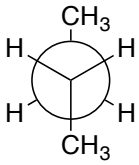












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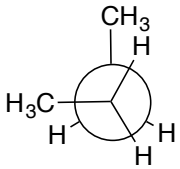

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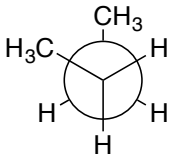

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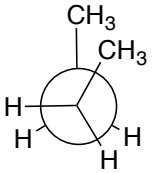

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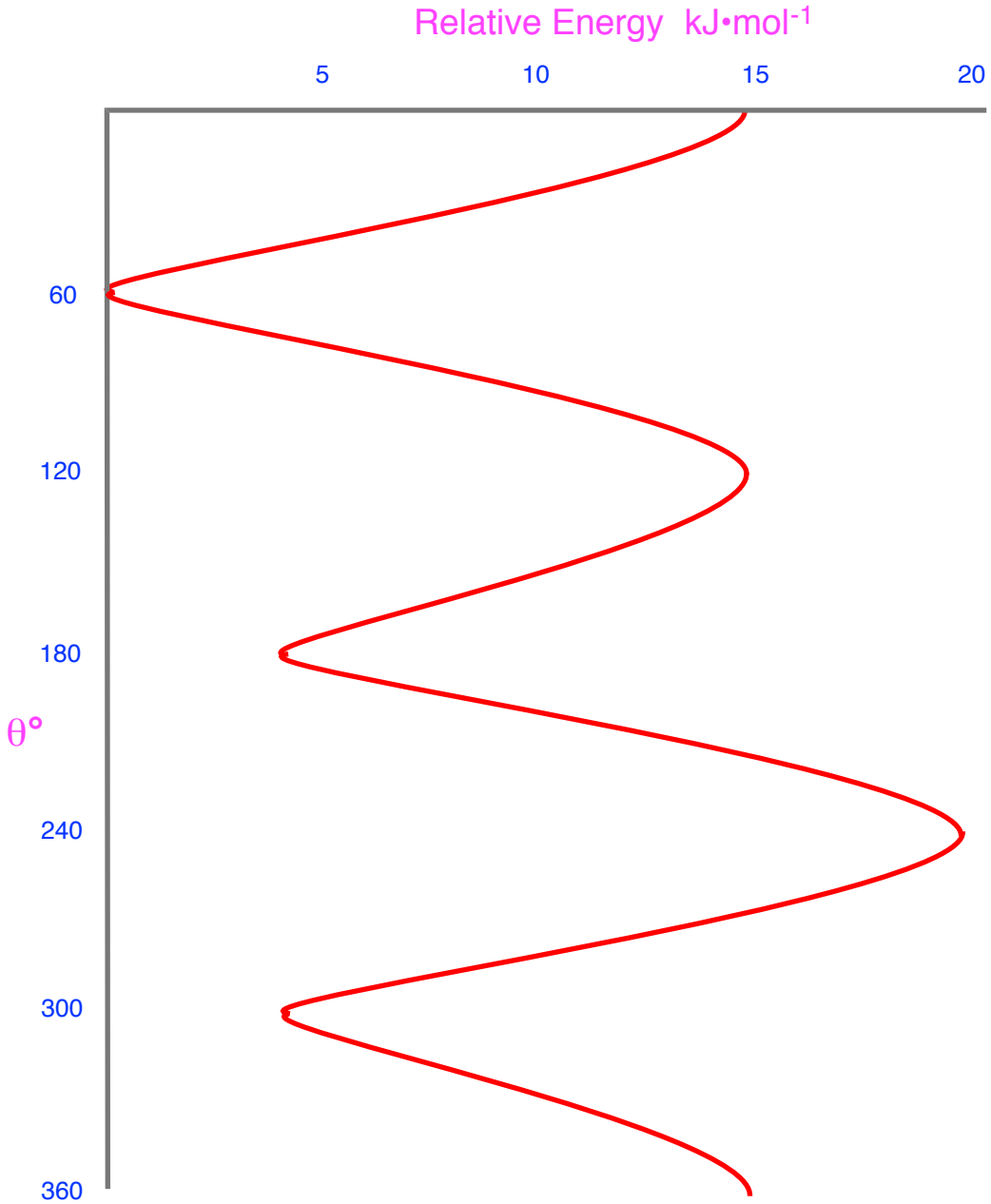

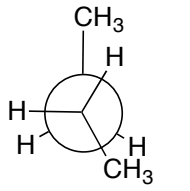

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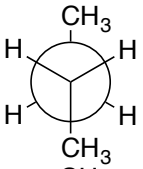

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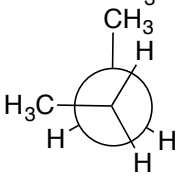

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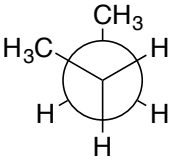

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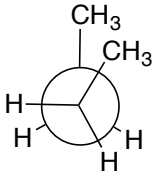

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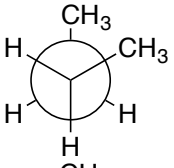

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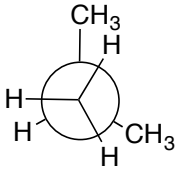
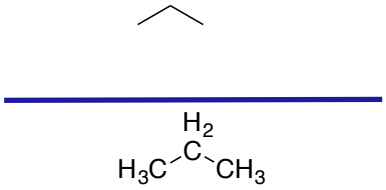


pe

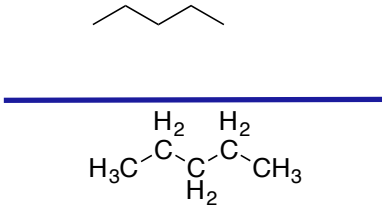
C. Art In Organic Chemistry

represents *CH₃*, two bonds to an apex means it is a *CH₂*, and three bonds to a branch point represent *CH*. If there are four bonds to a central point, this means there are *0* hydrogen atoms on that carbon.

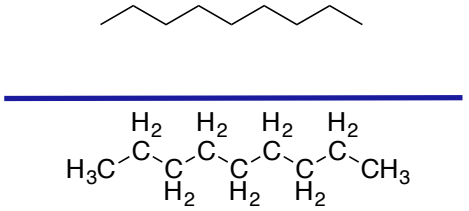
propane



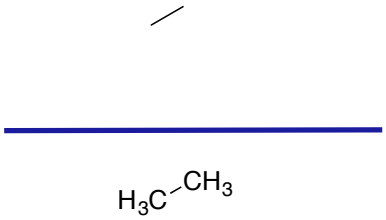
pentane



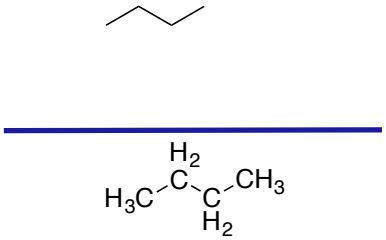
nonane



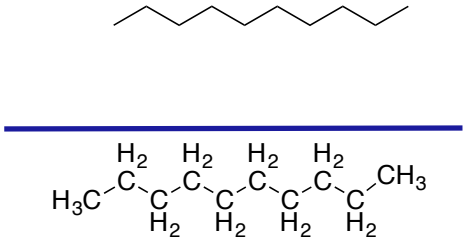
ethane



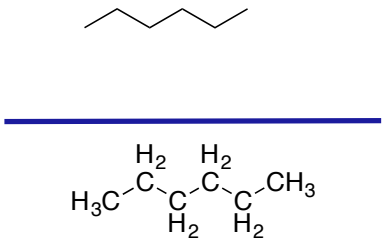
butane



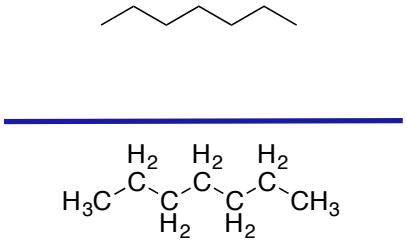
decane



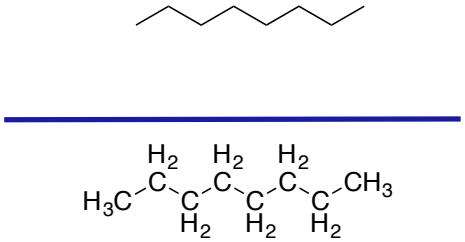
hexane



heptane



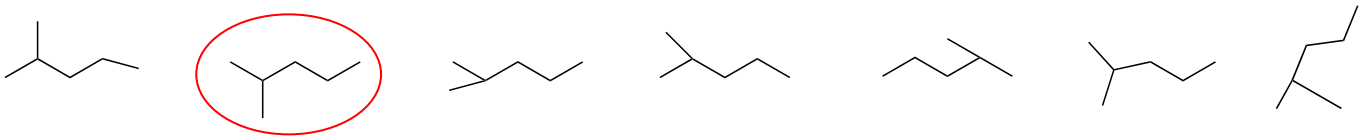
octane



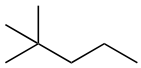
sp^3 hybridized carbons are *109°*.
has *4* bonds to other atoms.
structures *always* have this number

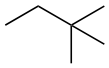
never have five or more atoms attached to them.
sp^3 because they have *4* atoms attached.

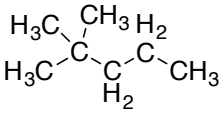
tetrahedral shape
about *109°*

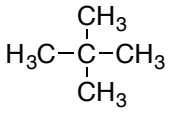


2,2-dimethylpentane *2,2-dimethylpropane* *2,2-dimethylbutane*

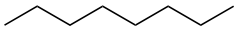






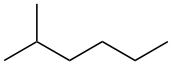


$CH_3CH_2C(CH_3)_2CH_3$



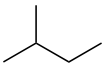
octane

heptane

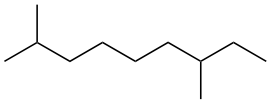


2-methylhexane

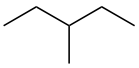
methylpropane



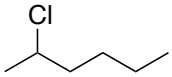
2-methylbutane



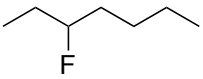
2,7-dimethylnonane



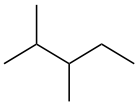
3-methylpentane



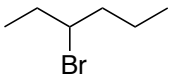
2-chlorohexane



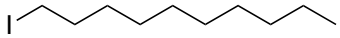
3-fluoroheptane



2,3-dimethylpentane

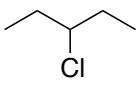


3-bromohexane

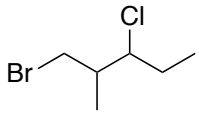


1-iododecanane

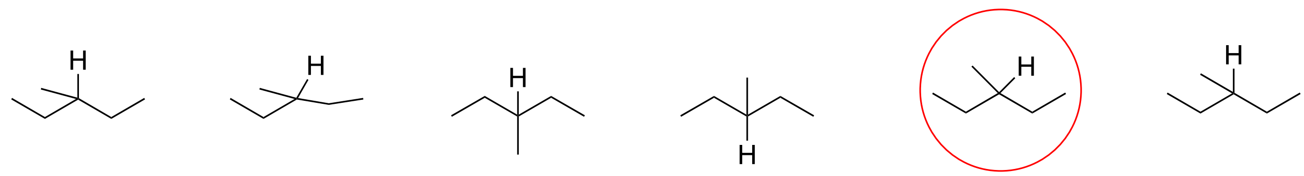
$CH_3CH_2CH_2CH_2CH_3$

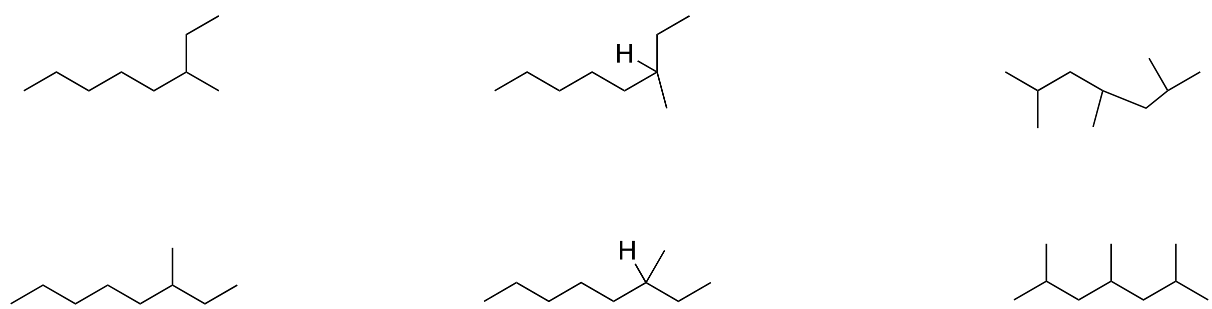


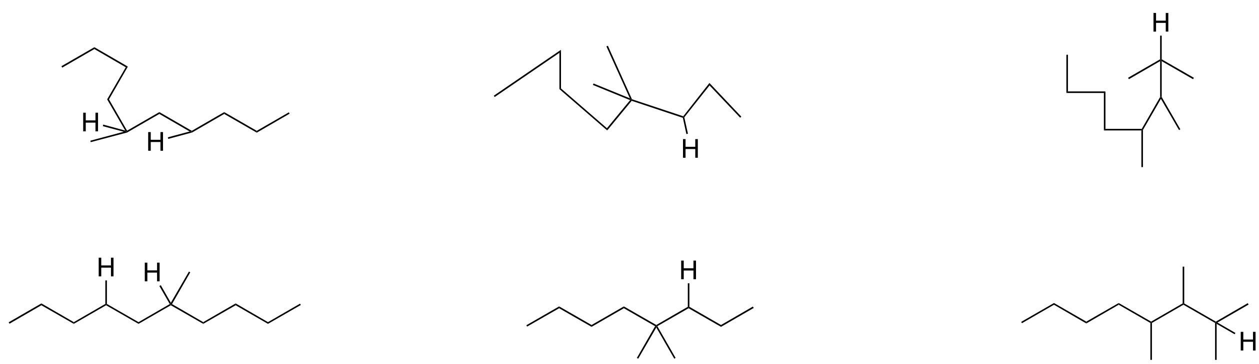
$CH_3CH_2CHClCH_2CH_3$

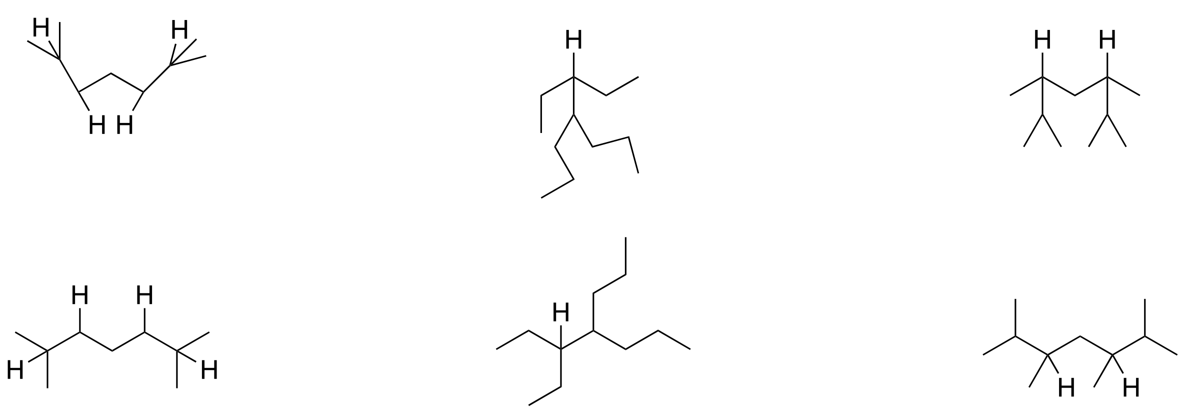


$BrCH_2CH(CH_3)CHClCH_2CH_3$

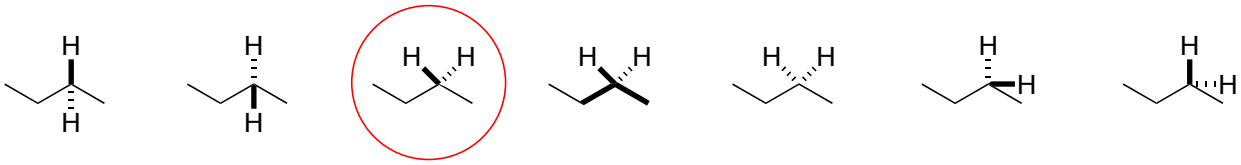


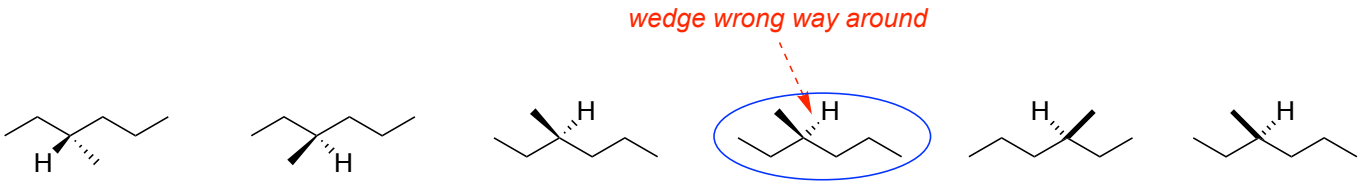


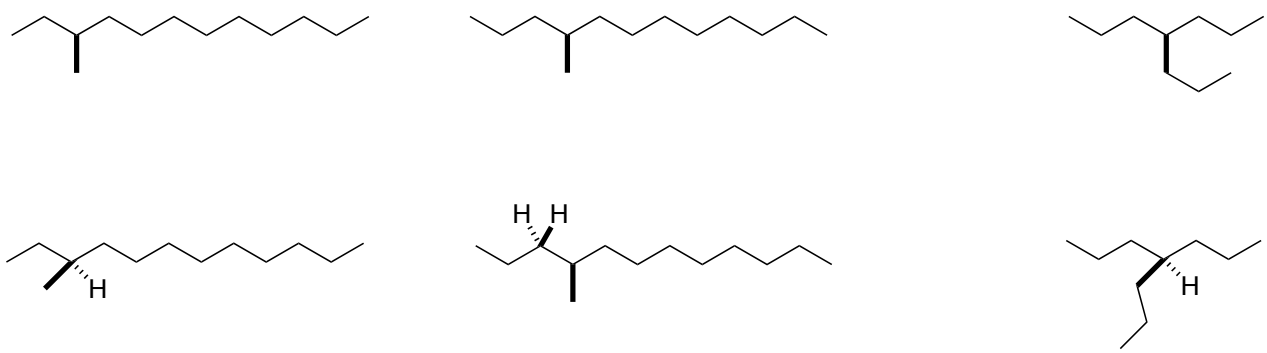




Three Dimensional Diagrams Of Organic Molecules







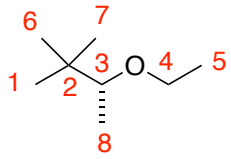
.... the C^3 hydrogen

.... both hydrogens on C^3

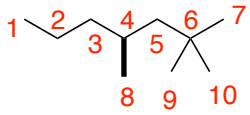
.... the H on unique C

Alkyl Fragments

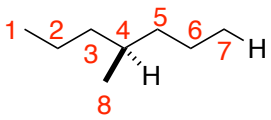
is called a *methyl*.
that have CH_2 connected to
Methine is the name given to *CH* fragments.
is called a *methyl*.
A quaternary *C* has *0* hydrogen atoms attached.



C1, C5, C6, C7, C8 methyl
C2 quarternary
C3 methine
C4 methylene



C1, C7, C8, C9, C10 methyl
C2, C3, C5 methylene
C4 = methine
C6 = quarternary



C1, C7, C8 methyl
C2, C3, C6 methylene
C4 = methine

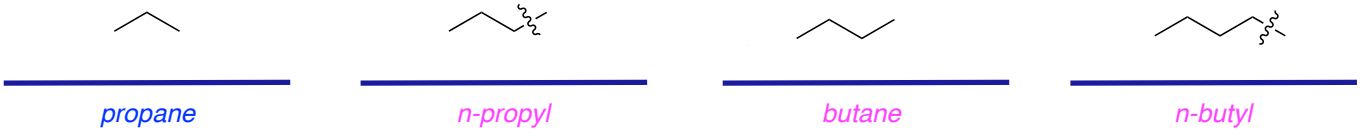
ie *substituted*
CH_3, Me

CH_3CH_2, Et (circle all correct).

cannot be isolated
is not a discrete compound,
is a molecular fragment.

A jagged line drawn perpendicularly across a bond means the fragment *is / is not* attached to something else.

2 types of hydrogen atoms
different outcomes.
Replacement of a hydrogen at the end of the chain gives a *normal*-propyl
$MeCH_2CH_2$, $EtCH_2$, ^nPr (circle all correct).
Conversely, removal of a proton at C^2 gives a(n) *iso-* propyl
as *^iPr, $(CH_3)_2CH$* (circle all correct



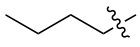
3 types of hydrogen atoms
gives a *normal* butyl group
as *$MeCH_2CH_2CH_2$, $^nPrCH_2$, $CH_3CH_2CH_2CH_2$*

a *sec-* butyl group that can be represented as *$CH_3CH_2CHCH_3$*

isomer of butane: it has __2___

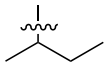
an *^{i}Bu* group.

something, *ie* a *^{t}Bu* group.

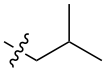


n-butyl

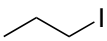
tert-butyl



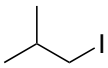
sec-butyl



iso-butyl

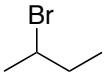


^{n}PrI



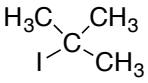
^{i}BuI

^{i}PrCl

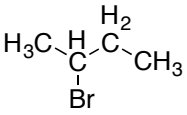


^{s}BuBr

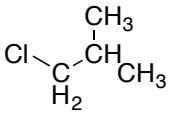
MeBr



^{t}BuI

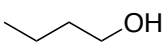


^{s}BuBr

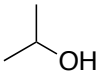


^{i}BuCl

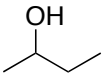
^{t}BuOH



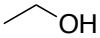
^{n}BuOH



^{i}PrOH

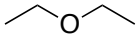


^{s}BuOH

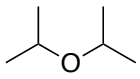


EtOH

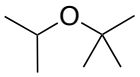
^{t}BuOMe



EtOEt
an anesthetic



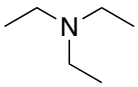
^{i}PrO^{i}Pr



^{t}BuO^{i}Pr

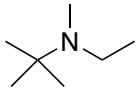
MeOMe

^{t}BuNHMe



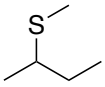
Et_3N

^{i}PrNH$_2$

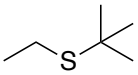


^{t}BuNMeEt

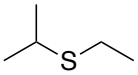
MeNH$_2$



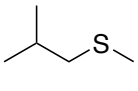
^{s}BuSMe



EtS^{t}Bu

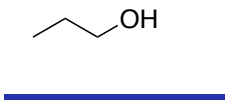


^{i}PrSEt



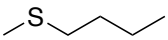
^{i}BuSMe

Me_2S



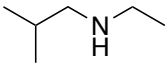
$HO^{n}Pr$

alcohol



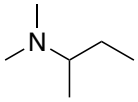
$MeS^{n}Bu$

thioether



$^{i}PrNHEt$

amine



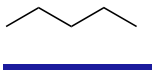
$^{i}BuNMe_2$

amine

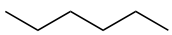
name functional groups as alcohol, amine, ether, or thioether on the dashed lines

D. Conclusion

These *are* zig-zag conformations.



pentane



hexane

heptane

decane

can be

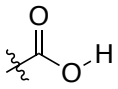
Molecular Fragments And Functional Groups

A. Introduction

Being unable to name compounds accurately is often that restrictive, but correctly interpreting molecular drawings, *eg* as an ester with the intended substituents, is usually vital. The problem is that there are a few ways to draw each functional group, and several widely used abbreviations for fragments that simply must be learned; chemists frequently draw the same molecule in different ways, and different chemists tend to favor different abbreviations. This sucks for you.

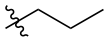
B. Fragments

a *molecular fragment* *cannot* be isolated.

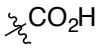


carboxyl

name of fragment

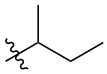


n-propyl

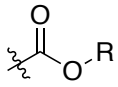


carboxyl

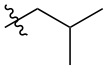
carboxylic acid



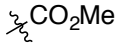
s-butyl



carboxyalkyl

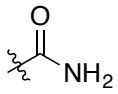


i-butyl



carboxymethyl

i-propyl



carboxamide

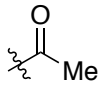
amide

t-butyl

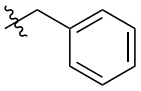
carboxamide

amide

ethyl

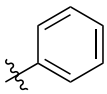


acyl



benzyl

acyl

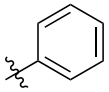


phenyl

acyl

vinyl

acyl

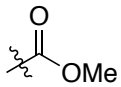


phenyl

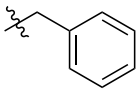
acyl

carbonyl chloride

acid chloride



carboxyalkyl



benzyl

$-CO_2Et$

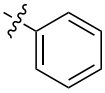
carboxyethyl

Ac

acyl

Bn

benzyl



phenyl

cyano or nitrile

$CH_2C_6H_6$

benzyl

Ph

phenyl

-COMe

acyl

$-C_6H_5$

phenyl

-OMe

methoxy

cyano or nitrile

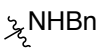
i-propyl

ethyl

t-butyl

acetyl

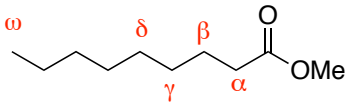
phenoxy

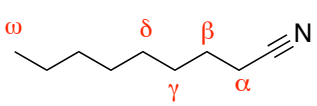


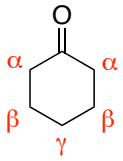
benzylamine

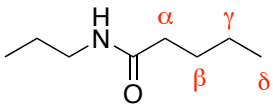
acyl

means *last*.



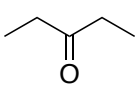




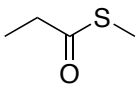


ω is last, δ is more specfic

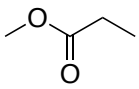
C. Expanded Forms Of Functional Groups



ketone

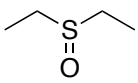


thioester

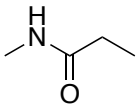


ester

aldehyde

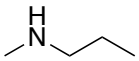


sulfoxide

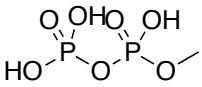


amide

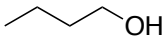
ester



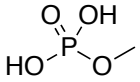
amine



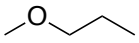
diphosphate



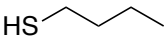
alcohol



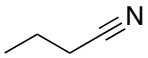
monophosphate



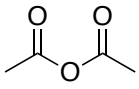
ether



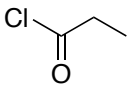
thiol



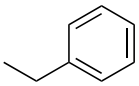
nitrile



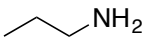
carbylic acid anhydride



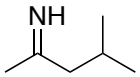
acid chloride



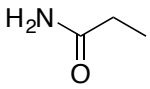
arene or phenyl



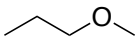
amine



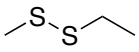
imine



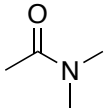
amide



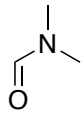
ether



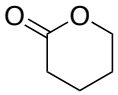
disulfide



amide

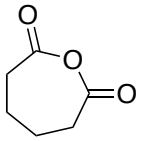


amide



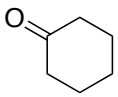
lactam

alkene



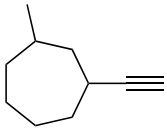
carboxylic acid anhydride

amide

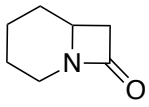


ketone

disulfide



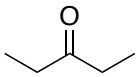
alkyne



amide or lactam

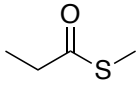
D. Abbreviated Forms Of Functional Groups

EtCOEt



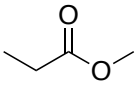
name of functional group
ketone

EtCO(SMe)



name of functional group
thioester

$EtCO_2Me$

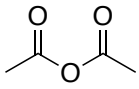


name of functional group
ester

EtCOH

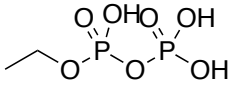
name of functional group
aldehyde

$MeCO_2COMe$



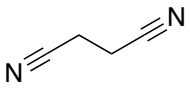
name of functional group
carboxylic acid anhydride

$EtOP(O)(OH)OP(O)(OH)_2$



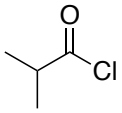
name of functional group
diphosphate

$NCCH_2CH_2CN$



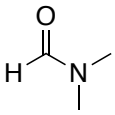
name of functional group
nitrile

$(CH_3)_2CHCOCl$



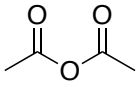
name of functional group
acid chloride

$HCONMe_2$



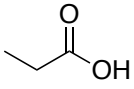
name of functional group
amide

MeCOOCOMe



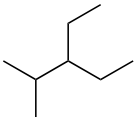
name of functional group
carboxylic acid anhydride

$CH_3CH_2CO_2H$



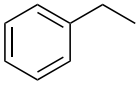
name of functional group
carboxylic acid

$(CH_3)_2CHCH(CH_2CH_3)_2$



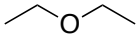
name of functional group
alkane

$C_6H_5CH_2CH_3$



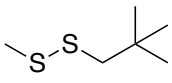
name of functional group
arene

$CH_3CH_2OCH_2CH_3$



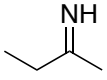
name of functional group
ether

$CH_3S_2CH_2C(CH_3)_3$



name of functional group
disulfide

$CH_3CH_2CNHCH_3$

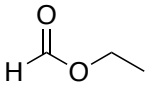


name of functional group
imine

Me_2SO

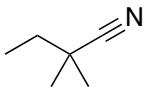
name of functional group
_____sulfoxide_____

HCO_2Et



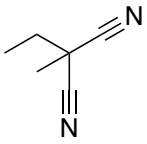
name of functional group
_____ester_____

$CH_3CH_2C(CH_3)_2CN$



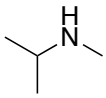
name of functional group
_____nitrile_____

$CH_3CH_2C(CN)_2CH_3$



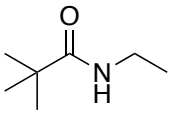
name of functional group
_____nitrile_____

$^{i}PrNHMe$



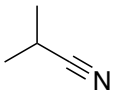
name of functional group
_____amine_____

$^{t}BuCONHEt$



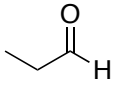
name of functional group
_____amide_____

$(CH_3)_2CN$

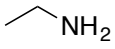


name of functional group
_____nitrile_____

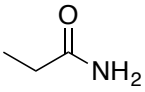
CH_3CH_2COH



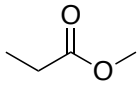
name of functional group
_____aldehyde_____



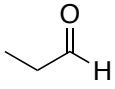
name of functional group
_____amine_____



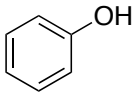
name of functional group
_____amide_____



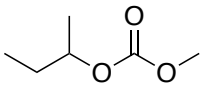
name of functional group
_____ester_____



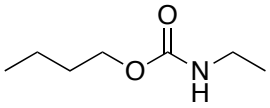
name of functional group
_____aldehyde_____



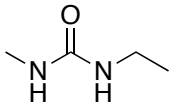
name of functional group
_____phenol_____



name of functional group
_____carbonate_____

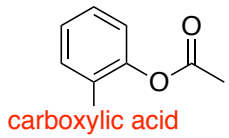


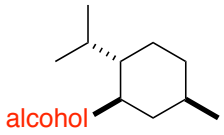
name of functional group
_____carbamate_____

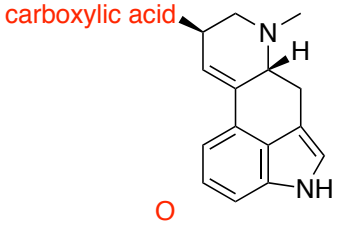


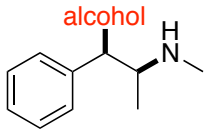
name of functional group
_____urea_____

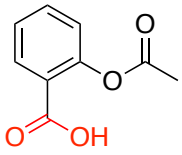
Find this question hard? Remember: go to the web and to figure out the answers for the maximum benefit (do not look at a key!).



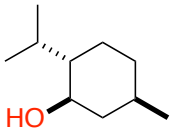




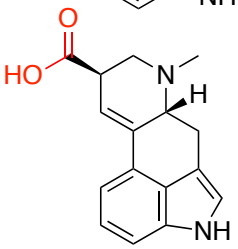




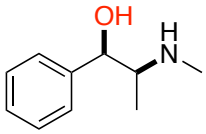
aspirin



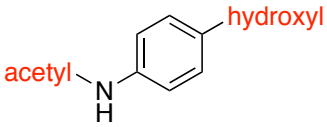
menthol

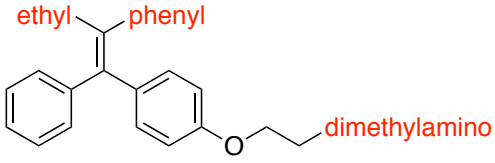


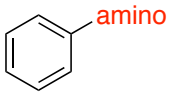
lysergic acid (LSD)

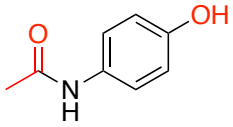


ephedrine

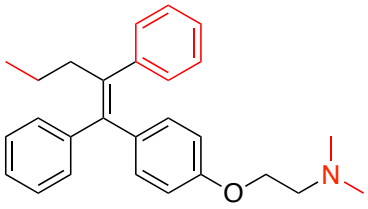




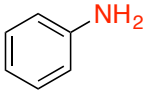




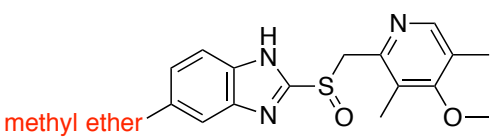
acetaminophen (tylenol)

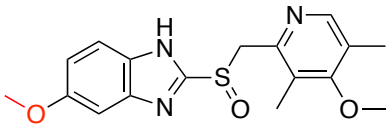


tamoxifen

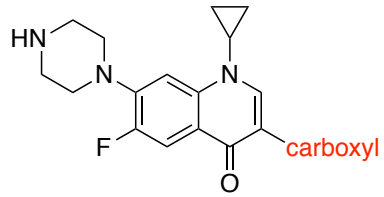


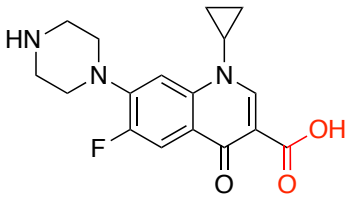
aniline



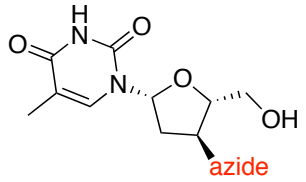


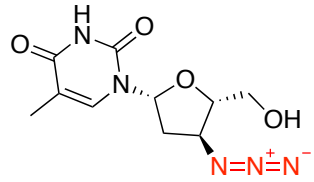
omeprazol



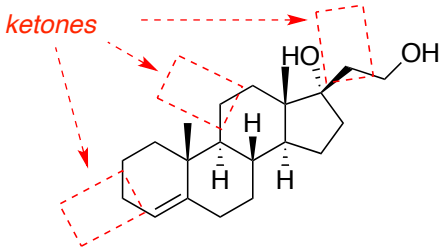


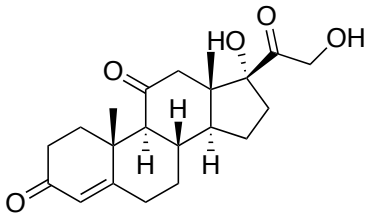
ciprofloxacin "cipro"



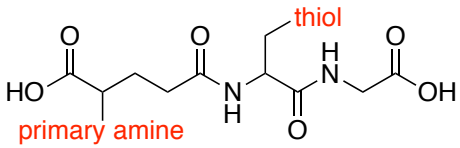


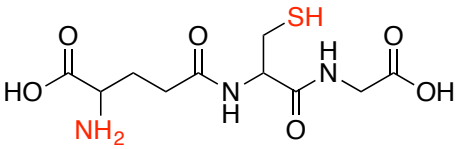
azidothymidine



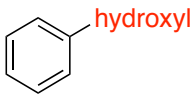


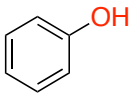
cortisone



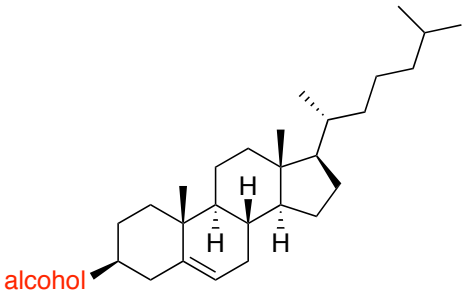


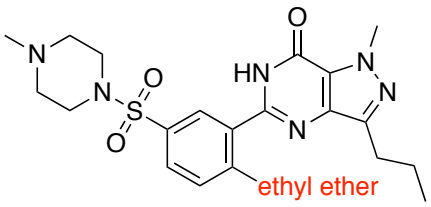
glutathione

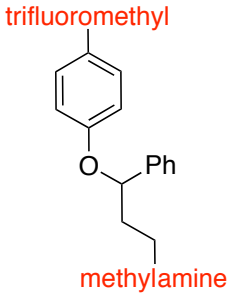




phenol



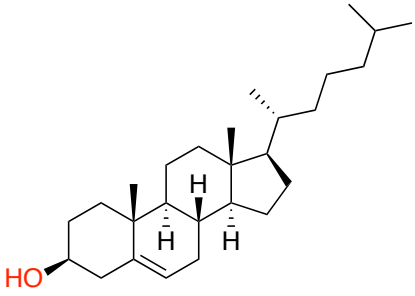


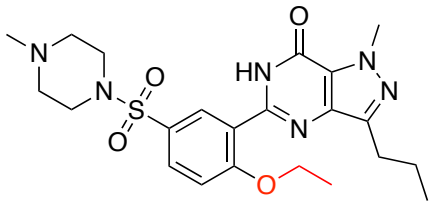


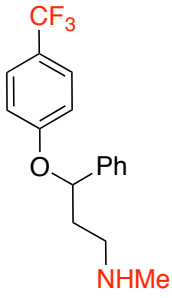
cholesterol

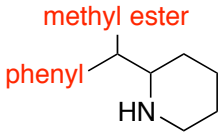
viagra

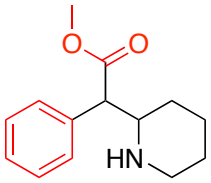
prozac











methylphenidate

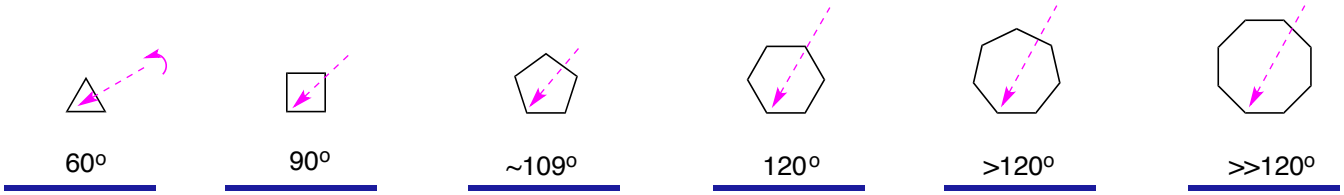
My chemistry instructor might like me to take methylphenidate (other name: retalin) to improve my *attention*.

Conformations Of Cyclic Hydrocarbons

from chapter(s) _____ in the recommended text

A. Introduction

B. Angle Strain



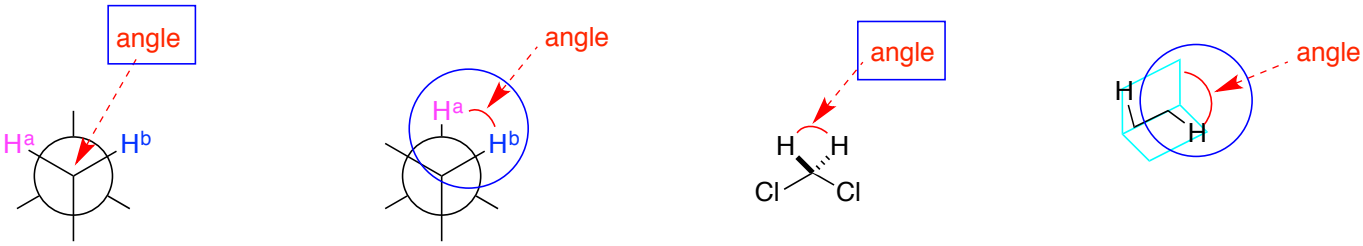
is around *109°*.
has *angle* strain.

: *cyclopropane / cyclobutane*.

cyclohexane / cycloheptane / cyclooctane.

most compressed and expanded angles are: *cyclopropane and cyclooctane*.

C. Bond Strain

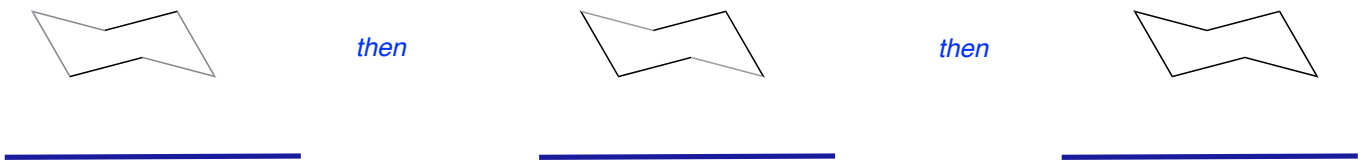


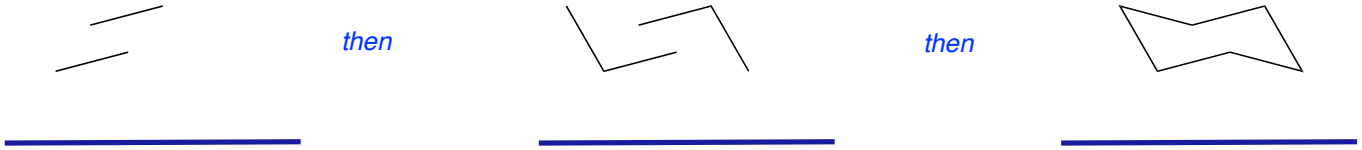
3 atoms, whereas torsional angles involve *4*.
e⁻ in bonds and is *minimized* as

high *torsional* strain.

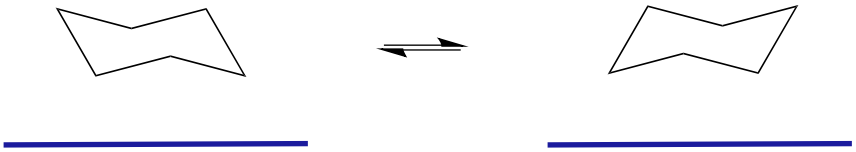
D. Cyclohexane

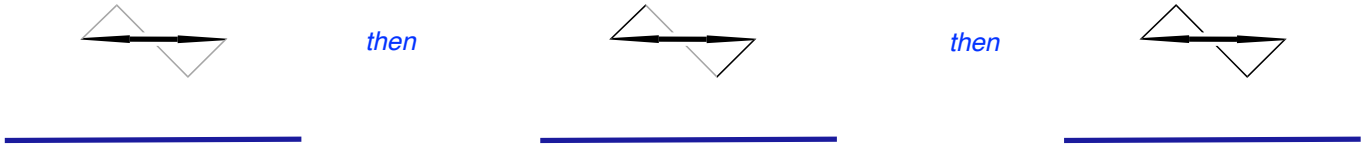
have *less* angle strain because the internal angle is *closer to* the ideal sp^3 angle.
to *torsional* strain.

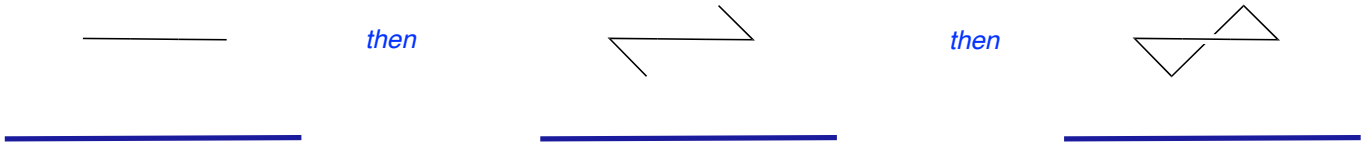




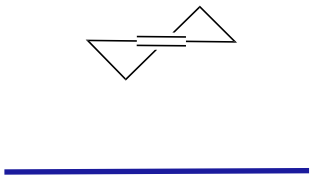
have *exactly the same* energies.

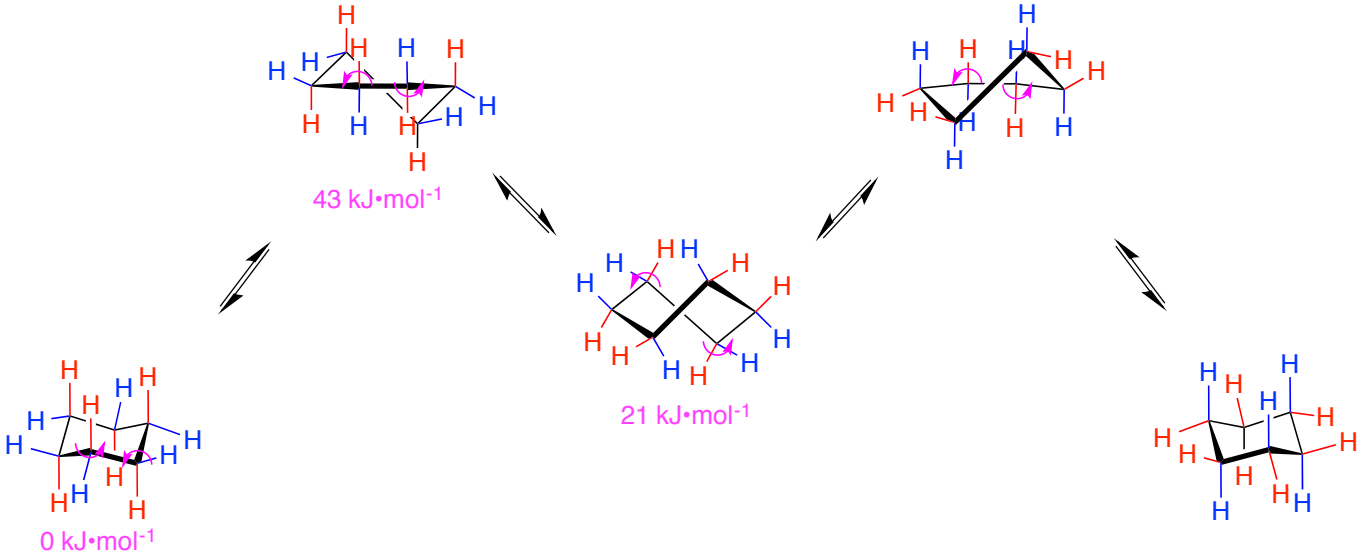


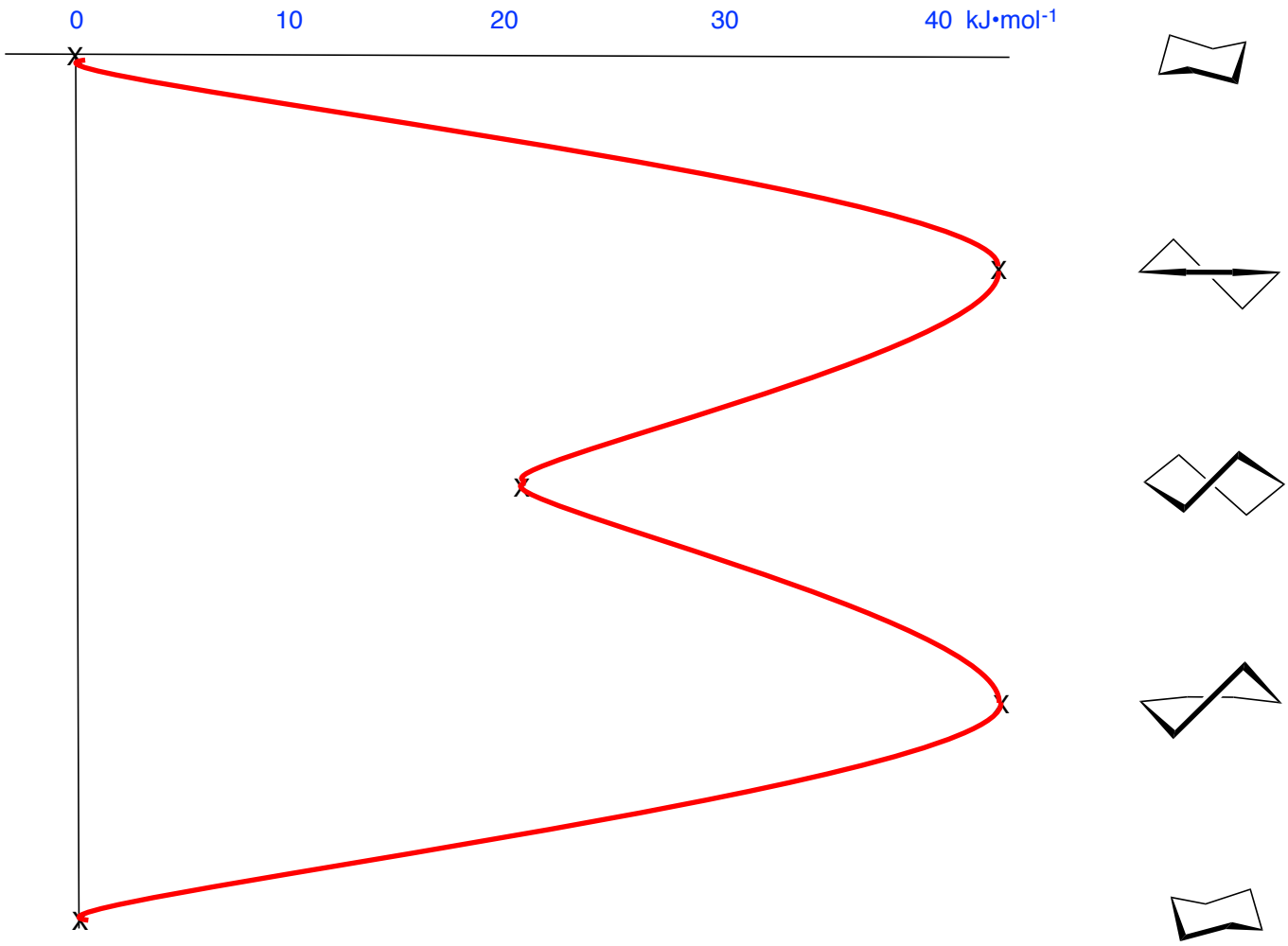




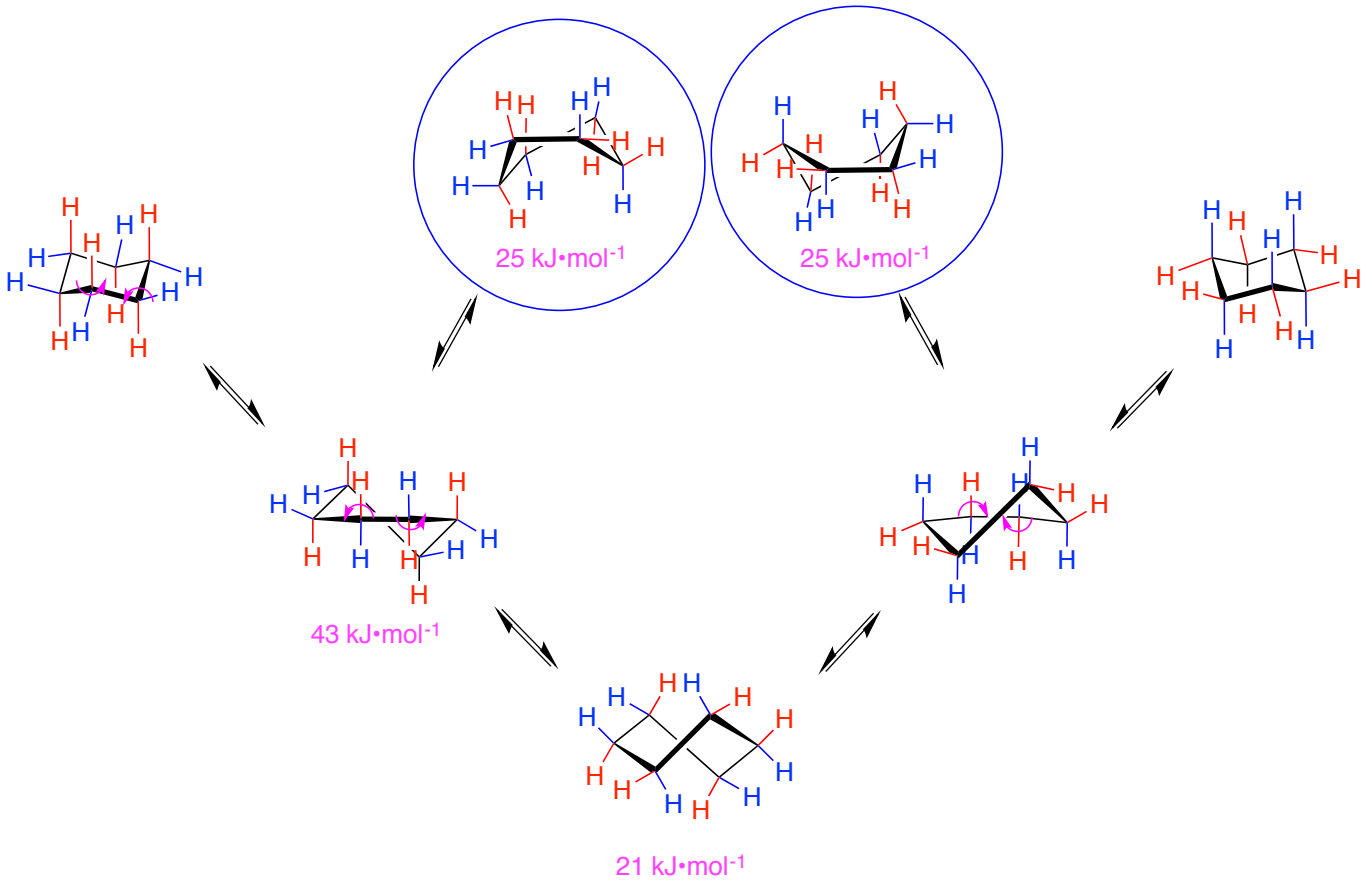
Cyclohexene



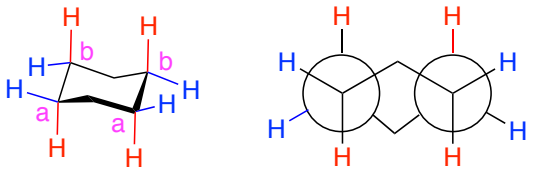

43 kJ•mol-1
21 kJ•mol-1
0 kJ•mol-1

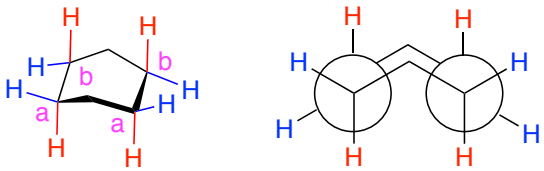

0
10
20
30
40 kJ•mol-1

Boat conformers *are not necessarily*



are *three* dimensional.

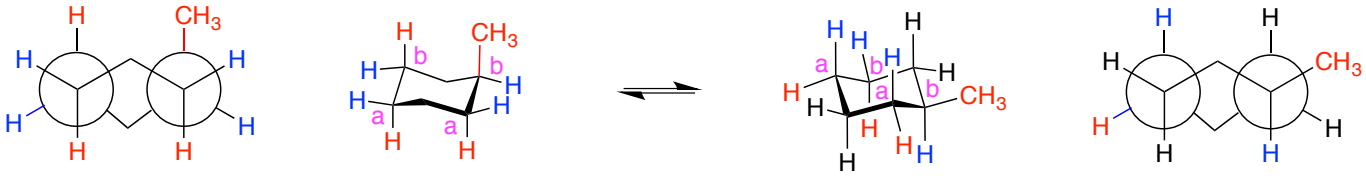




like the *antiperiplanar* conformation of butane,

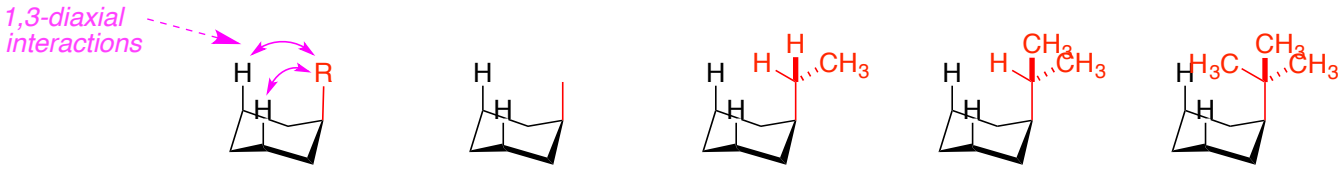
gauche conformer.

Monosubstituted Cyclohexanes



less stable *more stable*

has *1* gauche interaction,
0 such interactions



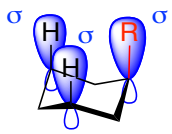
because _____ 1,3-diaxial interactions between the axial hydrogen atoms and the tert-butyl group is higher than others, because of the extra methyl.

equatorial conformer is observed.

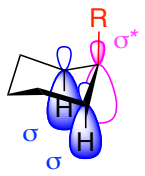
NMR *does not*

1,000 times per second.

lower σ- and σ*-orbitals

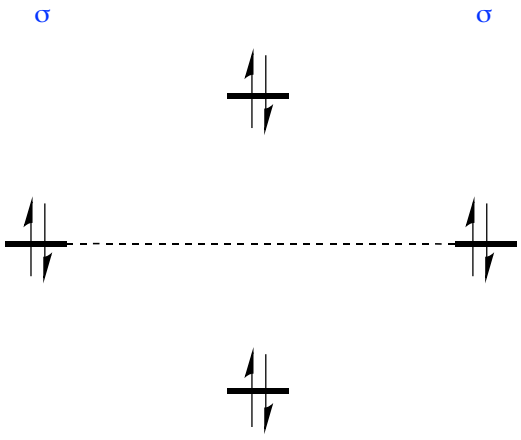


repulsive

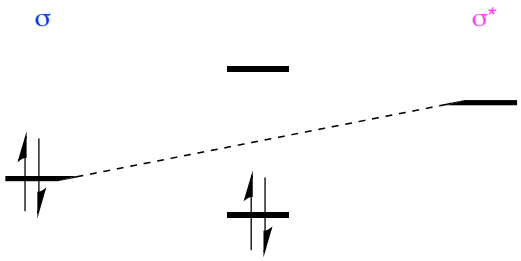


attractive

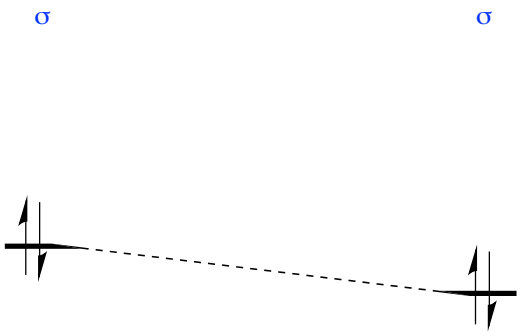
R = Me



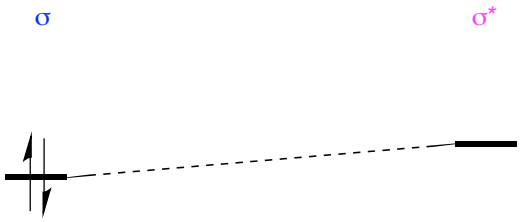
R = Me



R = OMe



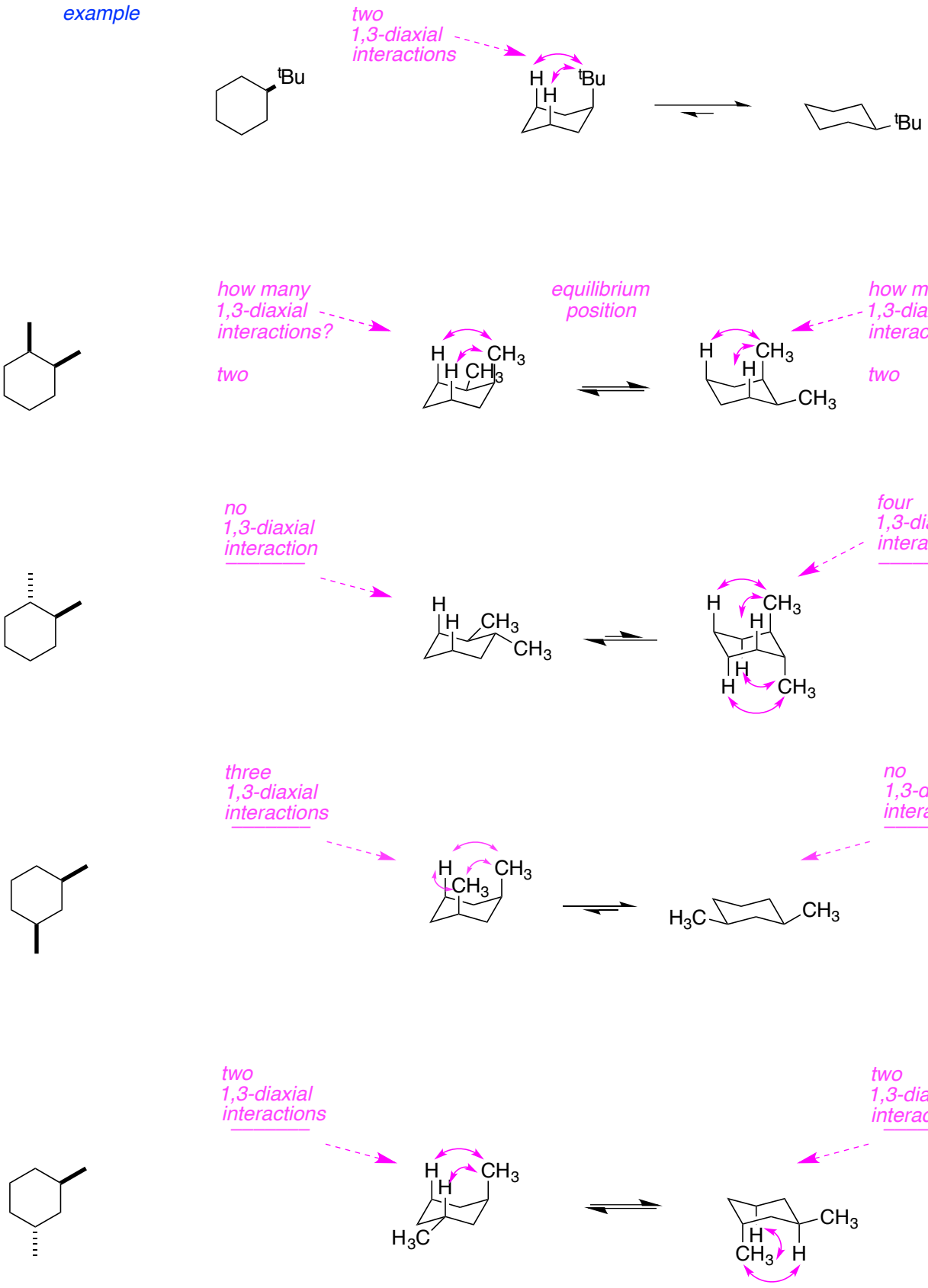
R = OMe

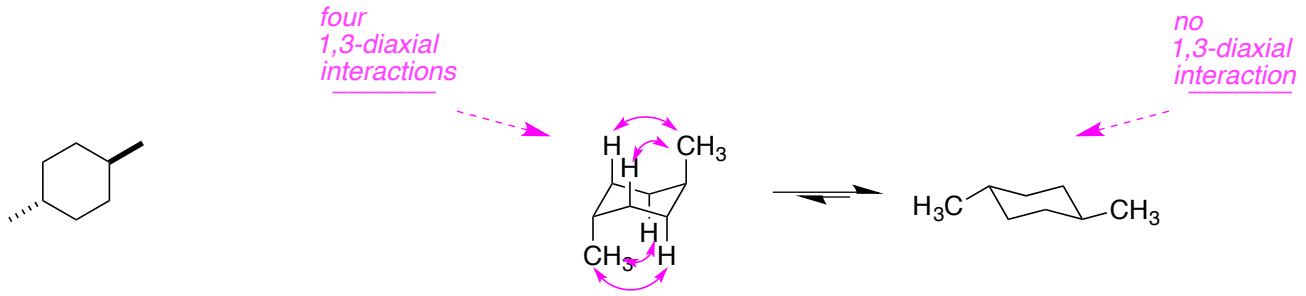


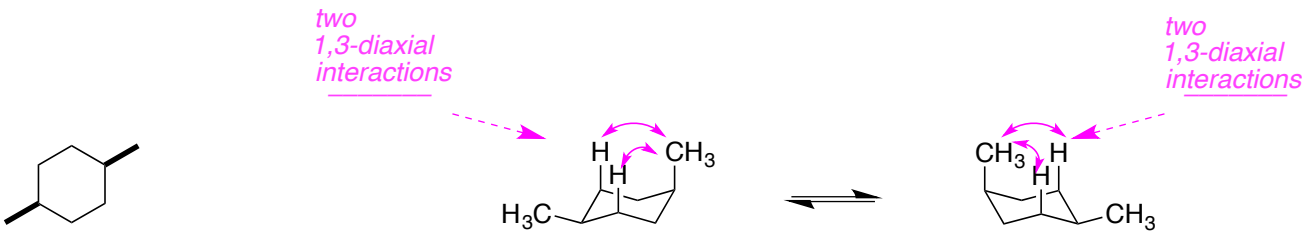
involve *less* overlap than the corresponding σ-to-σ 1,3-interactions, and, based on the orbital energy levels, the 1,2-interaction for the σ-to-σ* is *less* R = Me than it is for R = OMe.

because _____ *C – O* bonds have lower σ- and σ*-orbitals, stabilizing σ-to-σ* interaction.

Disubstituted Cyclohexanes

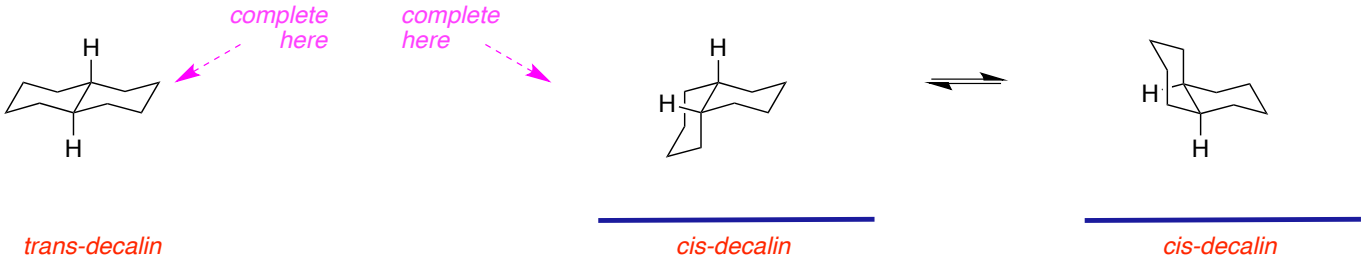


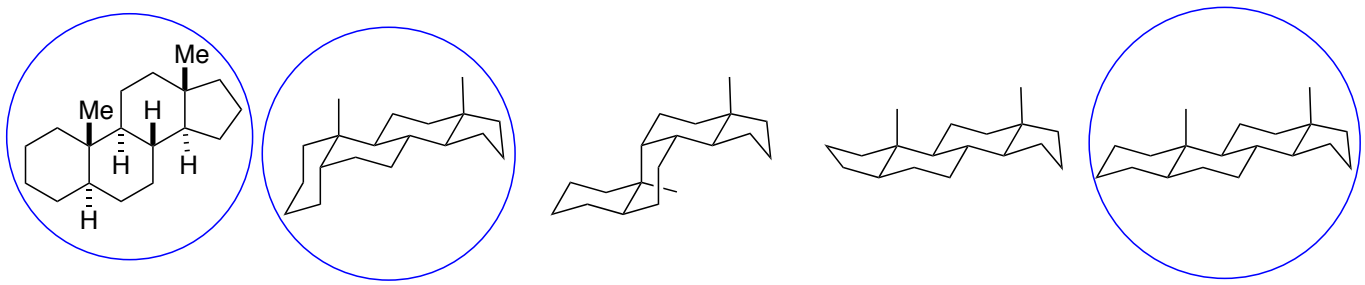




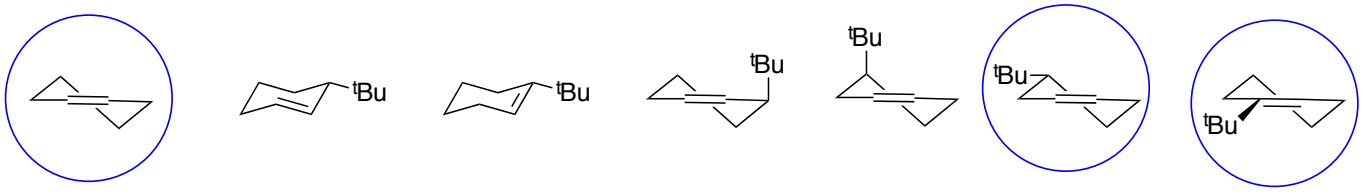
Decalins

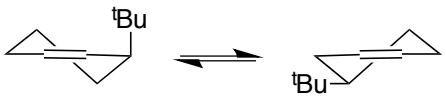
a bond; look up the structure in Wiki.

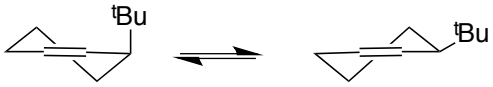


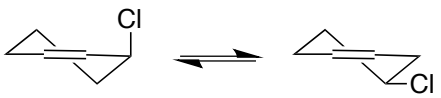


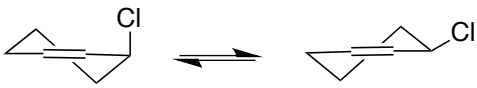
Cyclohexenes

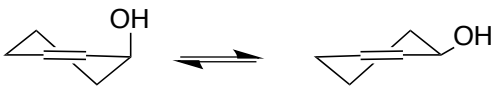


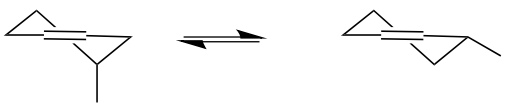


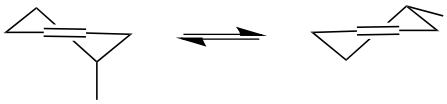




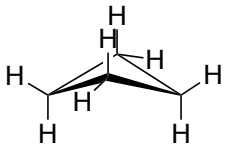




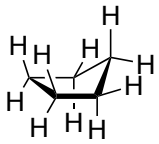




E. Other Rings



cyclobutane



cyclopentane

do rapidly interchange (on the NMR time-scale)
are *rigid and flat*.
eclipsed

Curly Arrows And Electron Flow

A. Introduction

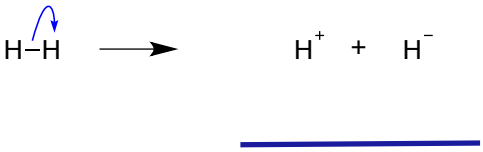
B. Electron Flow

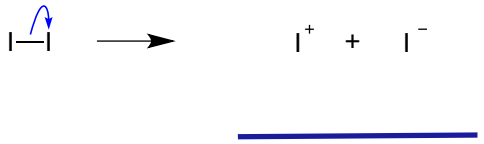
double-headed arrow.
are,
high electron density.

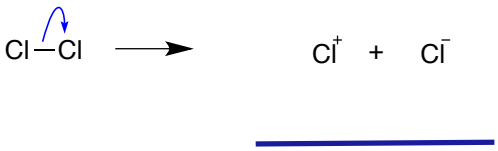
never

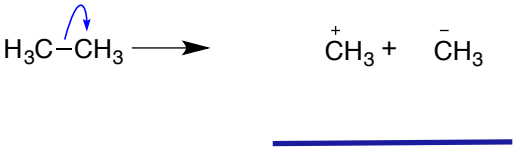
Effecting Only One Bond

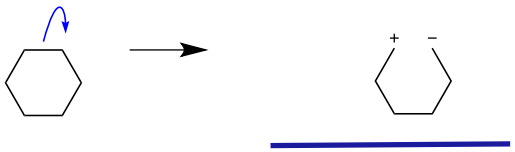
heterolytic





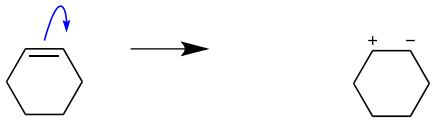






need not be
possible

does not
must equal the number of anions.
2 e; this *sometimes*



a

b

is *less*
towards Y.

pathway 1

more favorable

pathway 2

less favorable

more favorable

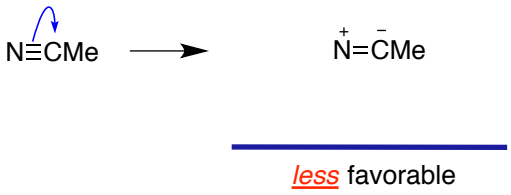
less favorable

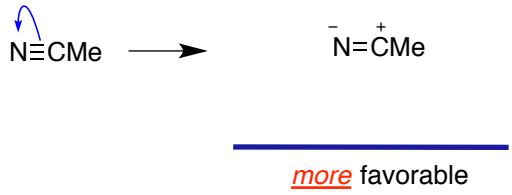
more favorable

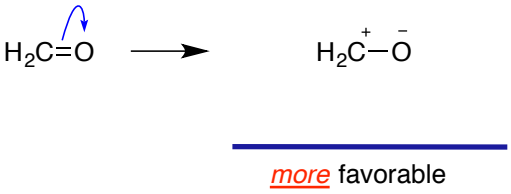
less favorable

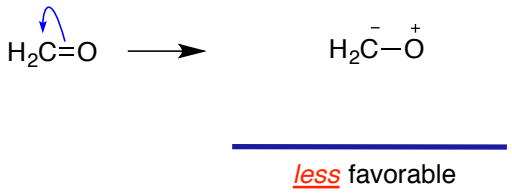
less favorable

more favorable



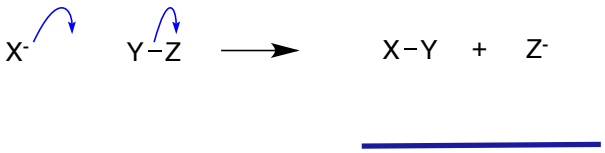






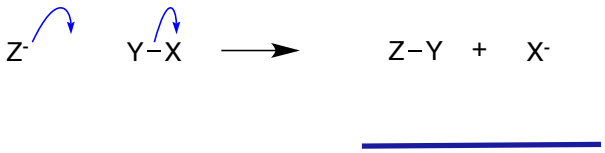
Effecting Two Bonds

a



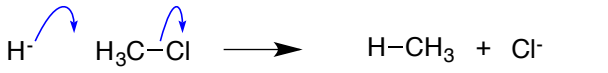
disfavored

b

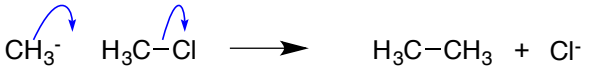


pathway 1

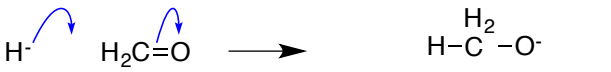
more favorable



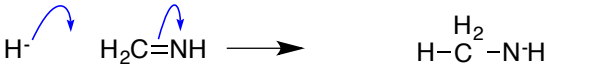
more favorable



more favorable

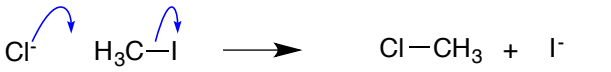


more favorable

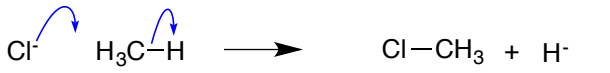


more favorable

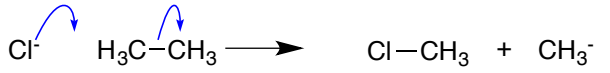
pathway 2



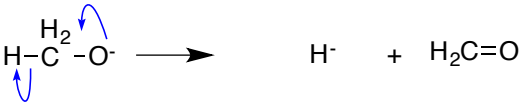
less favorable



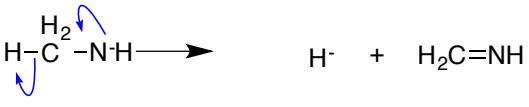
less favorable



less favorable



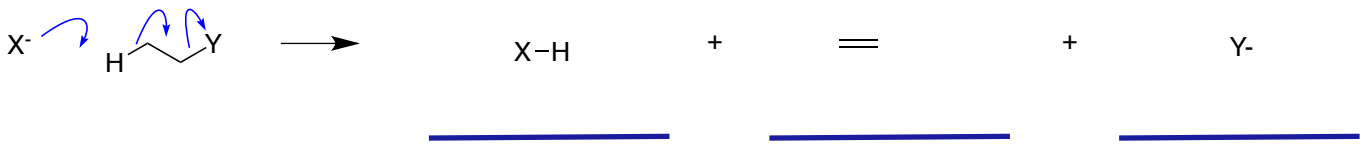
less favorable



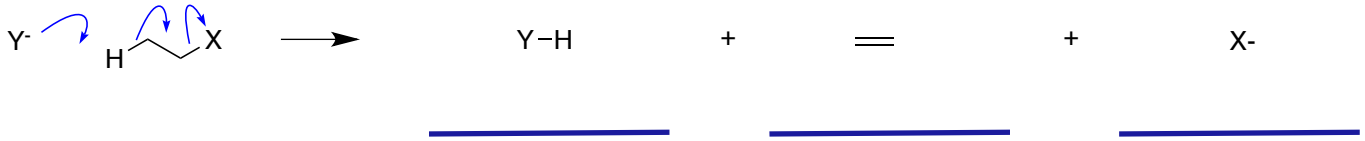
less favorable

Effecting Four Bonds

a



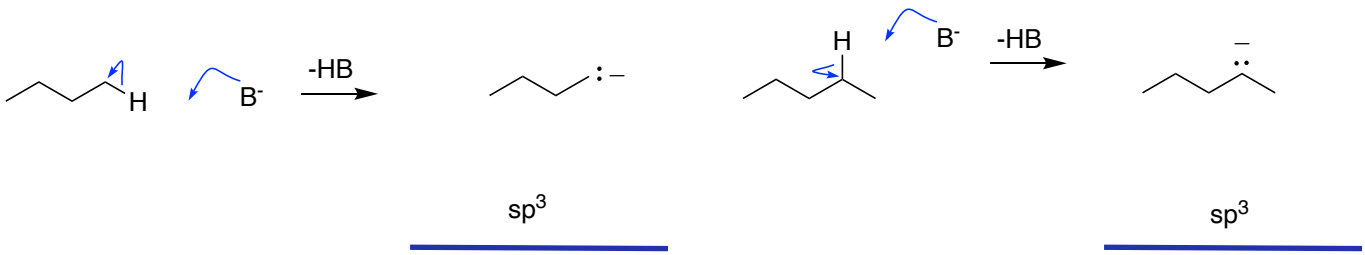
b

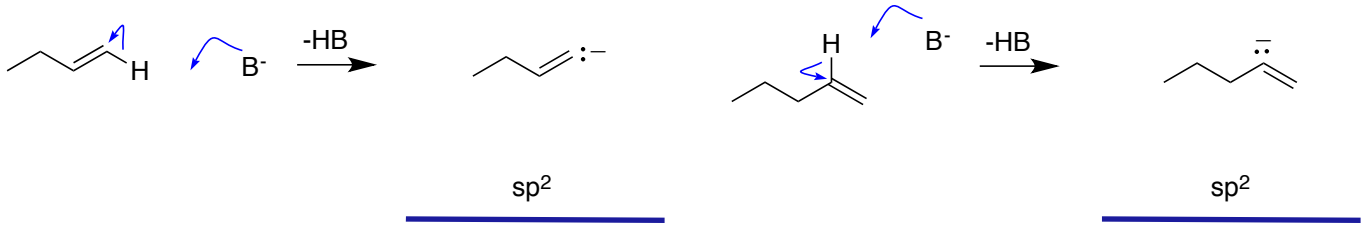


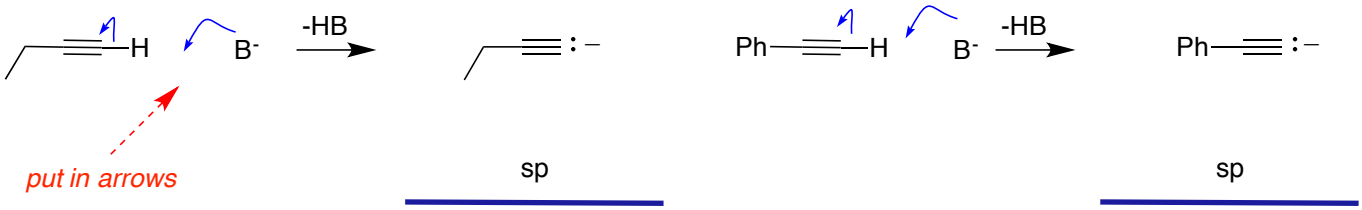
favored if X is more basic than Y

C. Representations Of Charged Hydrocarbon Scaffolds

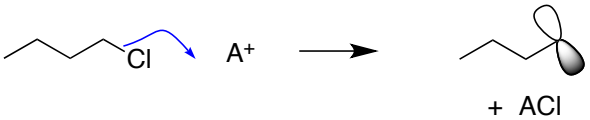
sp^3 hybridized carbon the resulting anion is *sp^3* hybridized.
electrons move *towards C* and the resulting anion is *sp^2* hybridized.
sp -Hybridized carbanions



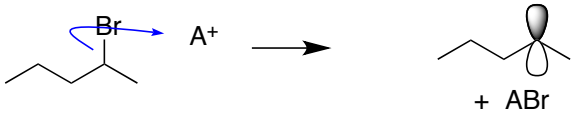




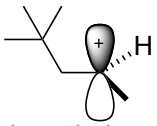
A sp^3-hybridized carbon has __4___
tend to be *sp^2* hybridized.



sp^2

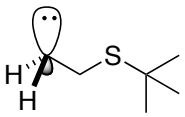


sp^2

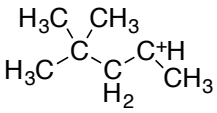


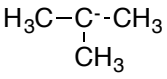
trigonal planar

pyramidal

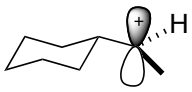


pyramidal

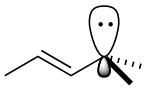




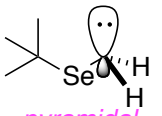
C$^-$H$_2$CH$_2$SC(Me)$_2$CH$_3$



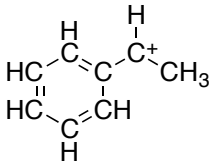
trigonal planar

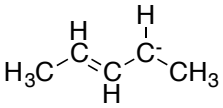


pyramidal



pyramidal



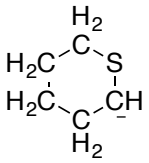


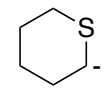
^{t}BuSeCH$_2^-$

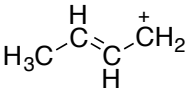
sp^2 hybridized, and carbanions C$^-$R$_3$ are *sp^3*-hybridized. Explain why this is so by considering the number of electrons around carbon in C$^+$H$_3$ and in C$^-$H$_3$.

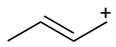
Carbon in C$^+$R$_3$ has to accommodate *three atoms* containing *six* shared electrons around it.

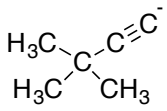
Carbon in C$^-$H$_3$ has to accommodate *three atoms and one lone pair* containing *eight* shared electrons around it.

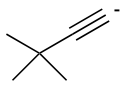


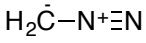


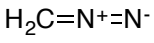


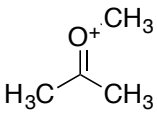




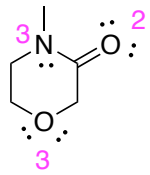


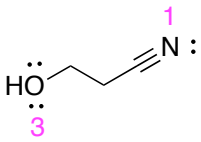


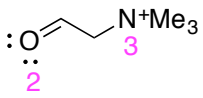


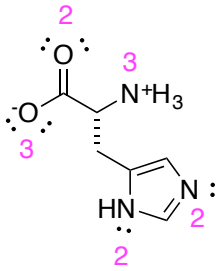


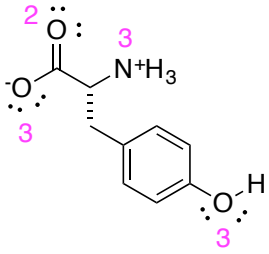
D. Heteroatoms, Lone Pairs, And Moving Electrons







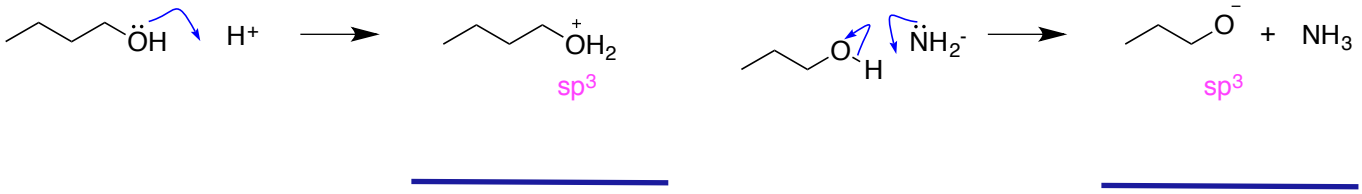


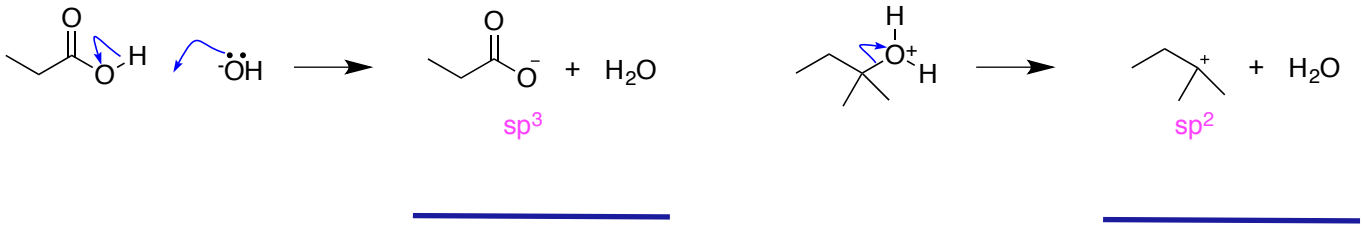


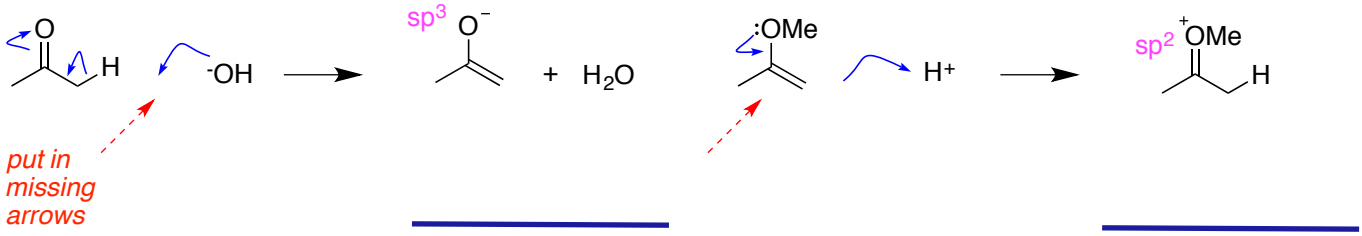
Surprise! In the answer on bottom left, *both* nitrogens are sp^2 for reasons related to aromaticity which is covered later in the book.

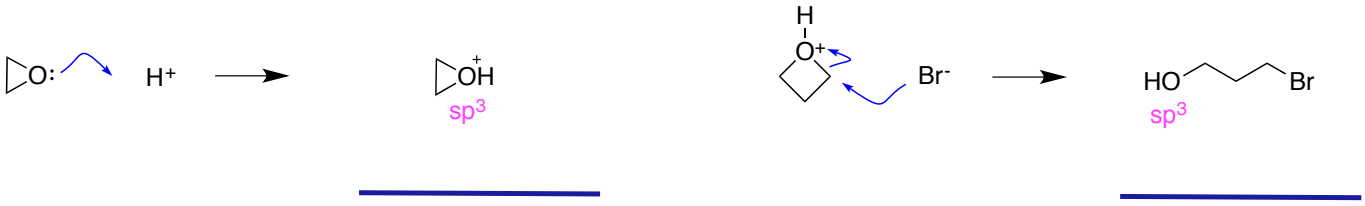
is not a change in the
gives sp^3 hybridized protonated

sp^2 hybridized protonated heteroatoms
become *sp* hybridized protonated heteroatoms.
Conversely, there *can* be

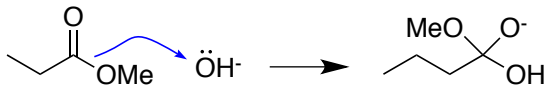


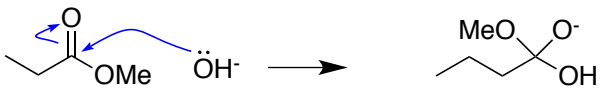


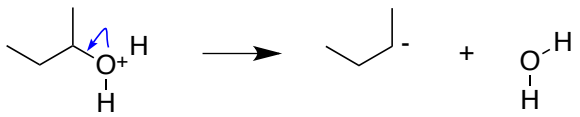


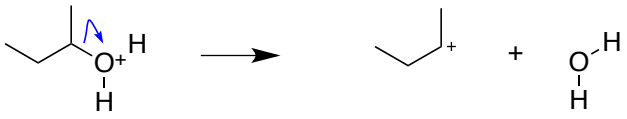


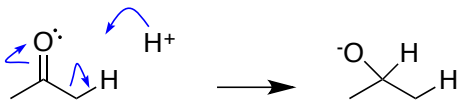
usually

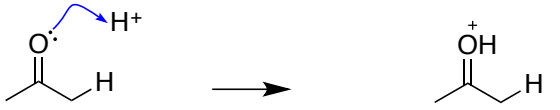

O
OMe
ÖH-
MeO
O-
OH


O
OMe
ÖH-
MeO
O-
OH

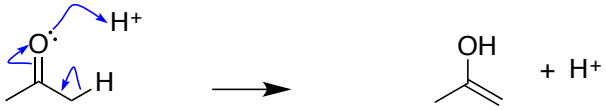

H
O+
H
-
+
O
H

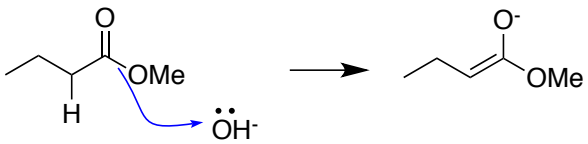

H
O+
H
+
+
O
H

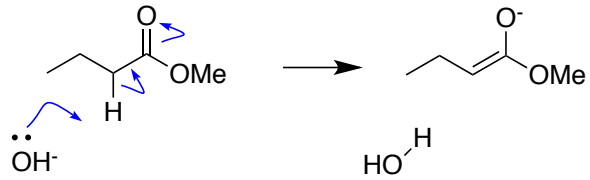

O
H+
H
-O
H
H

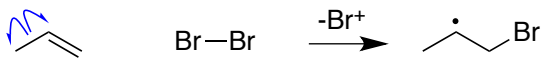

O
H+
H
+
OH
H

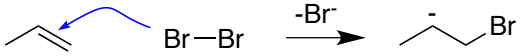
OR

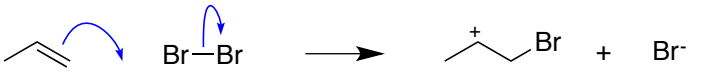

O
H+
H
OH
+ H+


O
OMe
H
ÖH-
O-
OMe

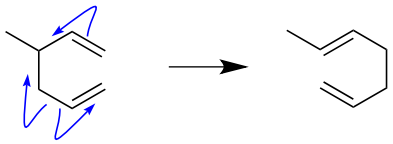

O
OMe
H
ÖH-
O-
OMe
H
HO



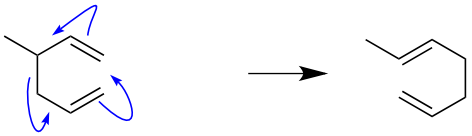




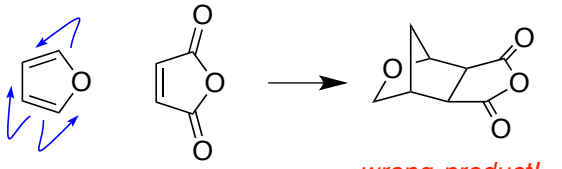
put in missing arrows



should be

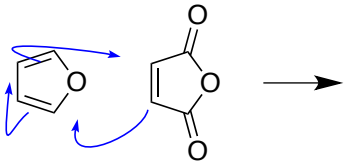


show all arrows

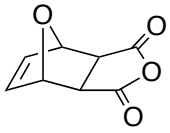


wrong product!

should be



show all arrows



Acids And Bases

A. Introduction

.

B. Log Scales To Measure Proton Dissociation From Organic Molecules

Equilibria That Generate Protons

a *constant*, because an equilibrium
variable, therefore
is not a good parameter
will not change

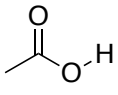
This *is* effectively the same as the statement:

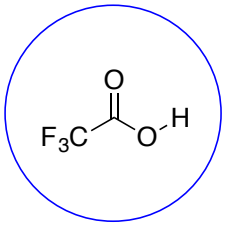
may be represented as:

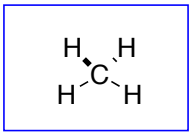
for *all* organic
a *small* fraction
a *strong* acid
is *high*.

weak acid.

therefore a significantly *stronger* acid than methane.

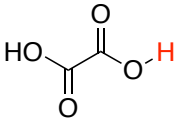






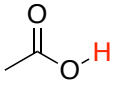
- *does*

10^{60} 10^{6} 10 (1) 10^{-6} 10^{-60}



$K_a = 5.4 \times 10^{-2}$

1



1.8×10^{-5}

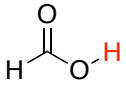
4

1.1×10^{-7}

5

1.0×10^{-14}

6



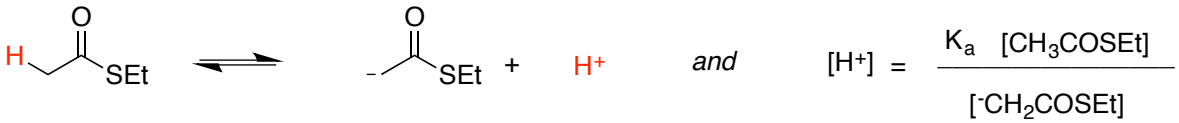
1.8×10^{-4}

3

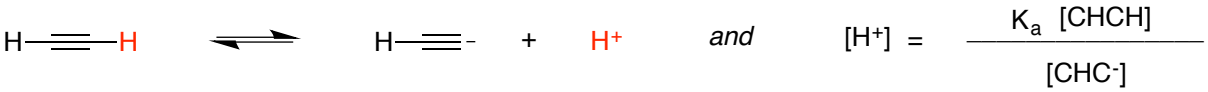
6.6×10^{-4}

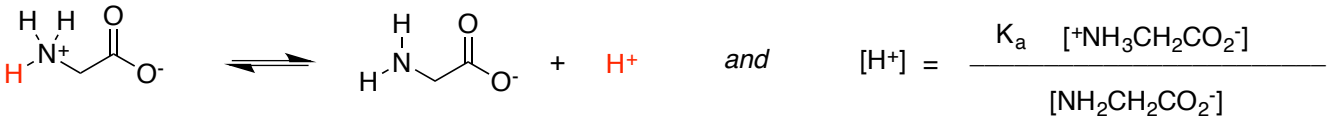
2

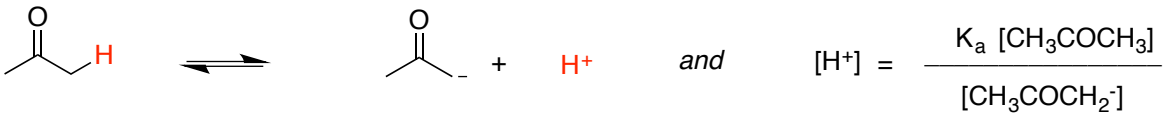
1 would be a *strong* acid.


H
O
SEt
+
H+
and
[H+] =
Ka [CH3COSEt]
[-CH2COSEt]


O
H
O
+
H+
and
[H+] =
Ka [CH3CO2H]
[CH3CO2-]

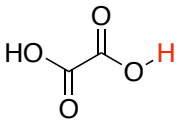

H
H
+
H+
and
[H+] =
Ka [CHCH]
[CHC-]


H
H
N+
O
O-
+
H+
and
[H+] =
Ka [+NH3CH2CO2-]
[NH2CH2CO2-]


O
H
+
H+
and
[H+] =
Ka [CH3COCH3]
[CH3COCH2-]

Simplifying The Scale: pKa

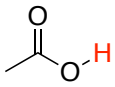
are *less* than the absolute differences



$K_a = 5.4 \times 10^{-2}$

$\log K_a = -1.27$

$-\log K_a = 1.27$



1.8×10^{-5}

$\log K_a = -4.74$

$-\log K_a = 4.74$

1.1×10^{-7}

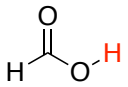
$\log K_a = -6.95$

$-\log K_a = 6.95$

1.0×10^{-14}

$\log K_a = -14$

$-\log K_a = 14$



1.8×10^{-4}

$\log K_a = -3.74$

$-\log K_a = 3.74$

6.6×10^{-4}

$\log K_a = -3.18$

$-\log K_a = 3.18$

called the *pK_a* value.

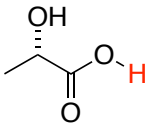
only a small amount of the compound

are *positive* for

larger K_a

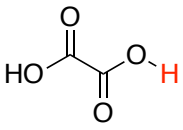
less

smaller pK_a values.



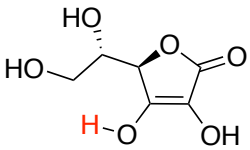
lactic acid
$pK_a = 3.86$

2



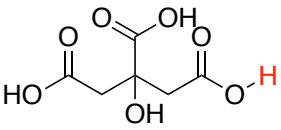
oxalic acid
4.19

4



ascorbic acid
4.10

3



citric acid
3.08

1

10 times easier

10,000,000,000 times easier to

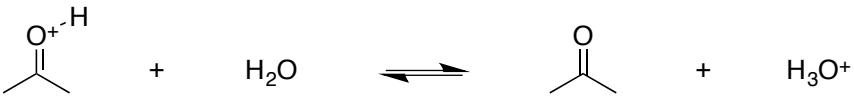
NH_4^+	NH_3	H_3O^+	H_2O
ammonium	*ammonia*	*hydroxonium*	*water*
pK_a = 9.2	*38*	*-1.7*	*14.0*
2	4	1	3

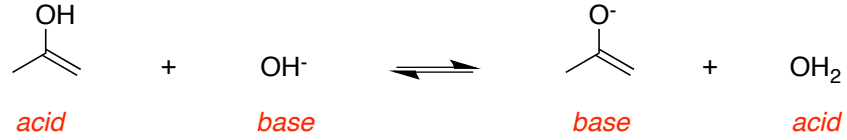
more
less likely that water will dissociate into hydroxide and a proton

C. Acid-Base Equilibria

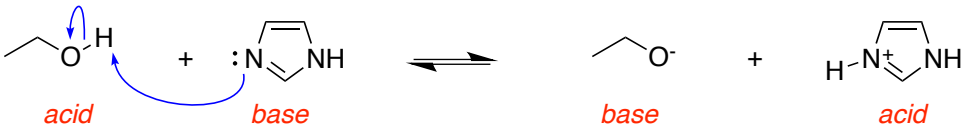
starting materials

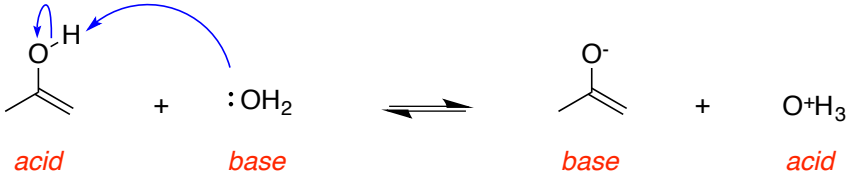
side with the *weakest* acid because
higher pK_a values

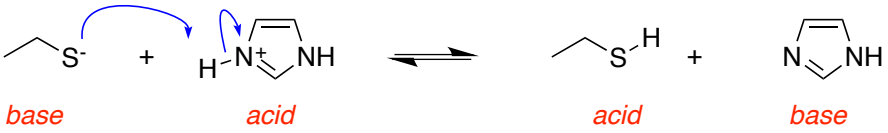


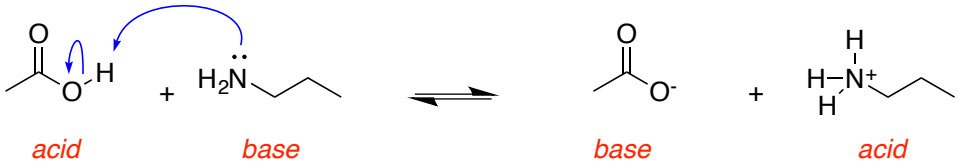


It *is* possible for

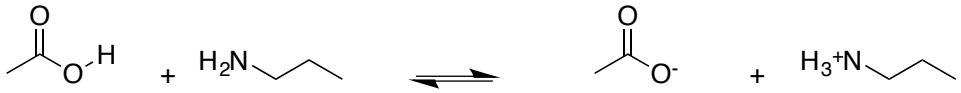








called its *conjugate base*.
formed by *protonating a base*.
acid of ammonia.
acid of water.



stronger *weaker*

favors *products*

weaker *stronger*

favors *starting materials*

stronger *weaker*

favors *products*

stronger *weaker*

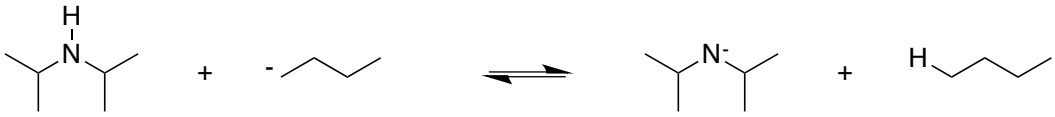
favors *products*

guanidine *stronger* *weaker*

favors *products*

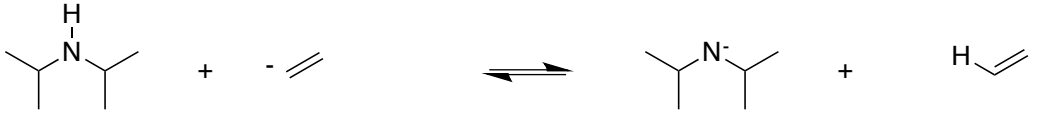
stronger *weaker*

favors *products*



stronger *weaker*

favors *products*



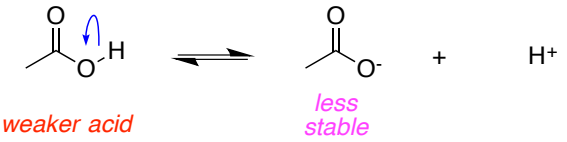
stronger *weaker*

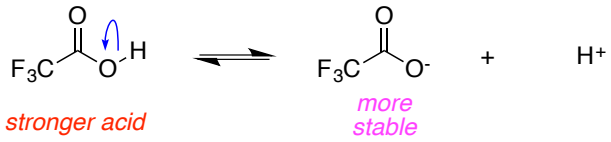
favors *products*

weaker *stronger*

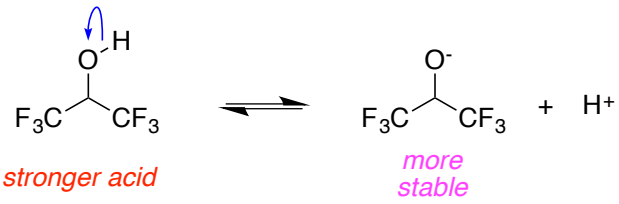
favors *starting materials*

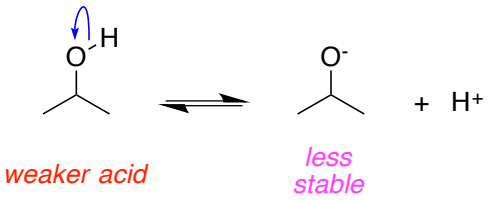
D. Predicting Relative pK_a Values





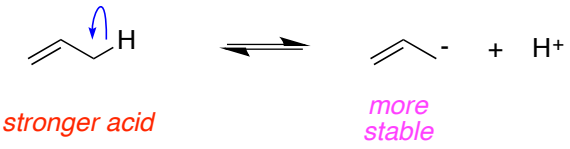
Ethanoic acid is a *weaker* stabilized by *electronegativity*

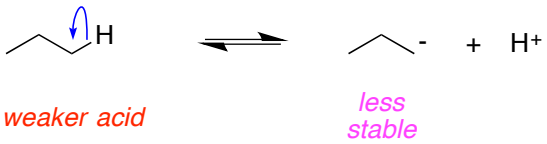




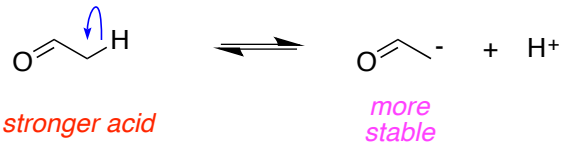
1,1,1,3,3,3-Hexafluoropropan-2-ol has a *lower* pK_a *stronger* acid.

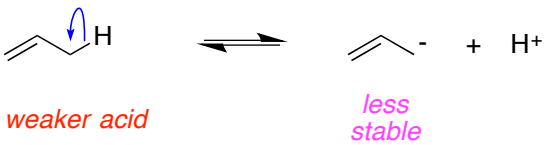
more stable than that from propan-2-ol because of *electronegativity* effects.



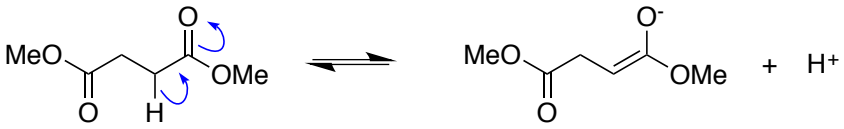


Allyl anions are *more* stable *resonance* effects, *stronger* acid than propane.

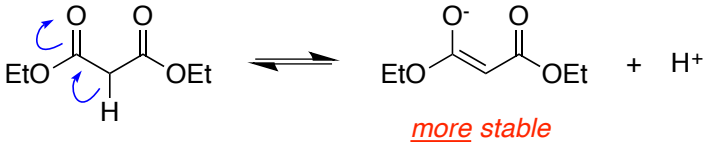




more stable than allyl anions due to *electronegativity* effects, so ethanal has a *lower* pK_a



less stable

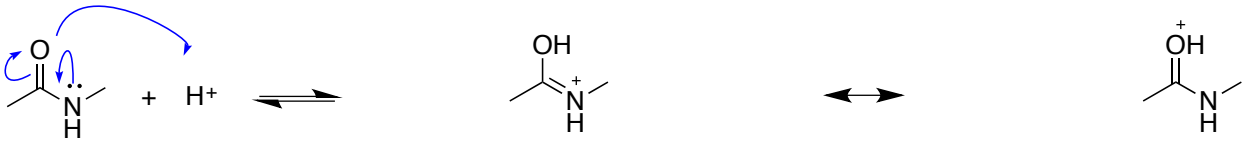


more stable

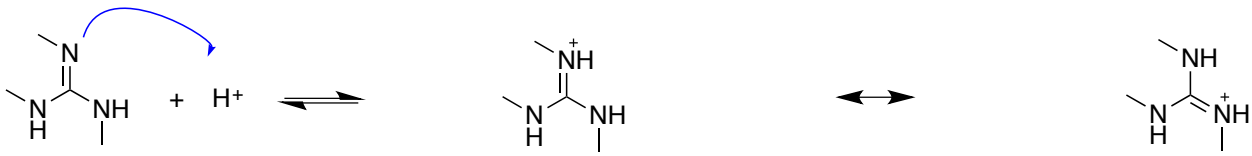
higher pK_a
resonance effects.

E. Predicting Sites Of Protonation

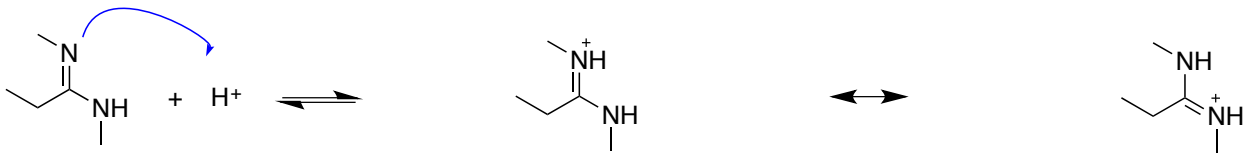
protonated form *protonated form*



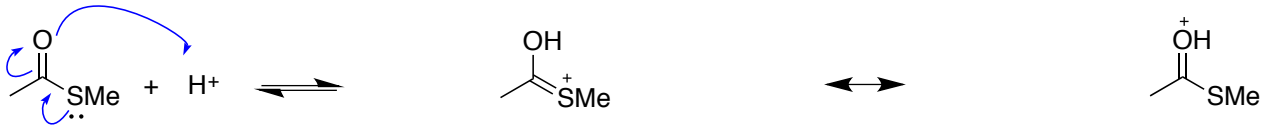
protonated form *protonated form*



protonated form *protonated form*



protonated form *protonated form*



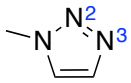
protonated form *protonated form*

protonated form *protonated form*

protonated form *protonated form*

protonated form *protonated form*

selectively at *N*[3].



explanation:

because of resonance effect, electrons can move from one *N* to another .

F. Lewis Acids And Bases

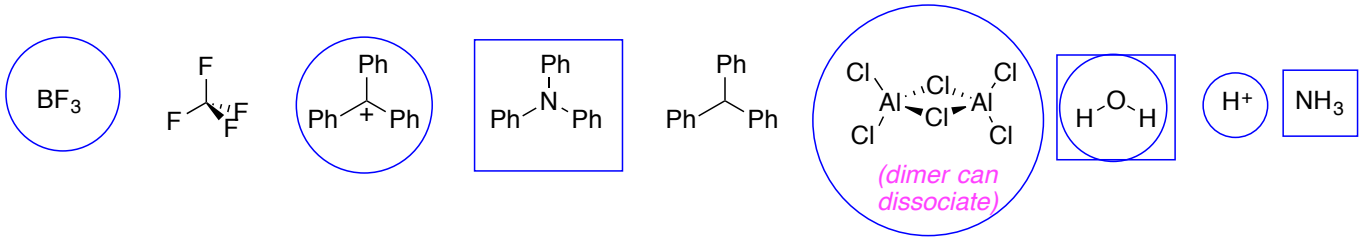
All acids *do not*
eg an empty p-orbital.

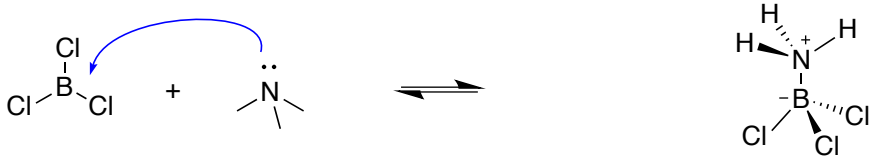
Lewis *acids*

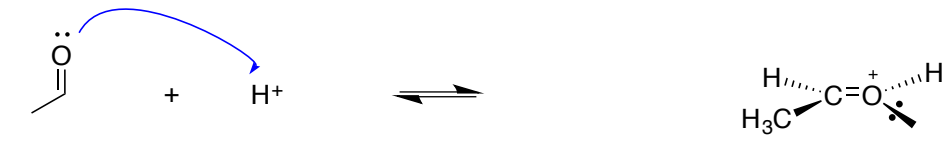
acids because they have *6* electrons in their valence shell and *an empty*

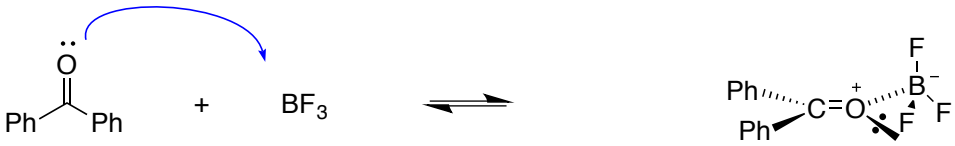
can fit the definition of a Lewis acid.

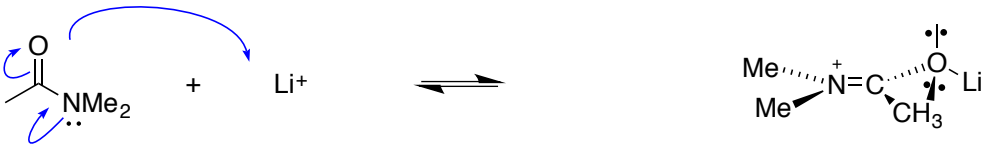
Protons *do* fit



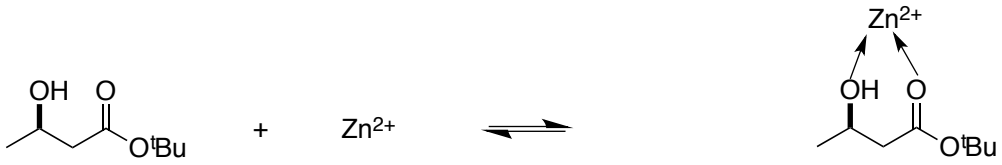



O
+
H+
H
C=O
H
H3C

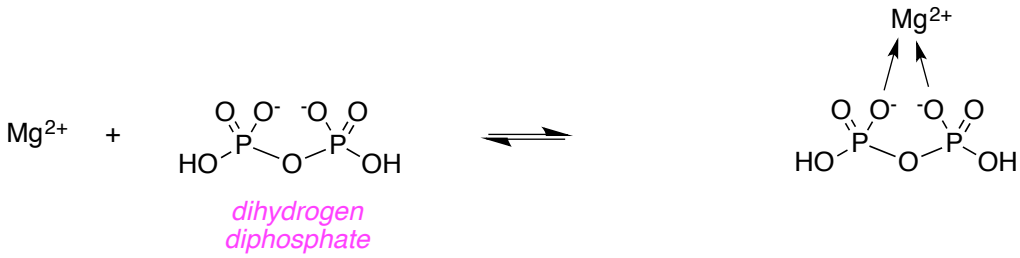

O
Ph
Ph
+
BF3
F
Ph
C=O
B
F
Ph
F
F


O
NMe2
+
Li+
Me
N=C
O
Li
Me
CH3


O
OtBu
+
Zn2+
O
Zn2+
OtBu


OH
O
OtBu
+
Zn2+
Zn2+
OH
O
OtBu

two phosphorus atoms are *sp*^{3} hybridized.



dihydrogen diphosphate

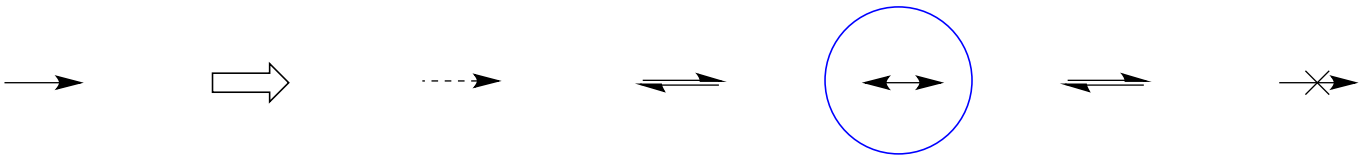
Resonance: Practicing Curly Arrows

from chapter(s) _____ in the recommended text

A. Introduction

B. Resonance

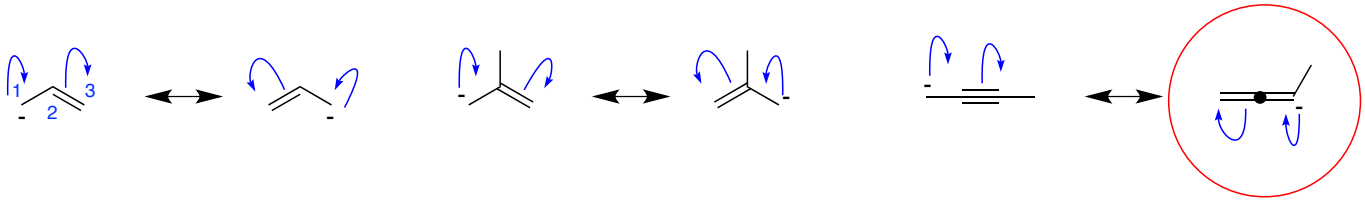
Electrons move *much faster than*



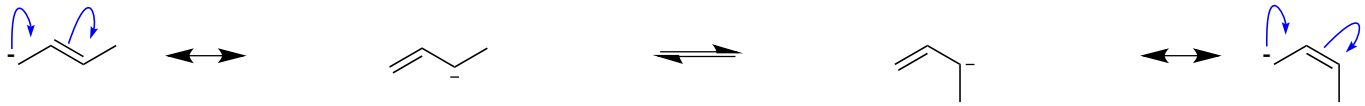
absolutely wrong to use the other descriptors shown above.

movement of *electrons*.

C. Resonance Stabilized Anions



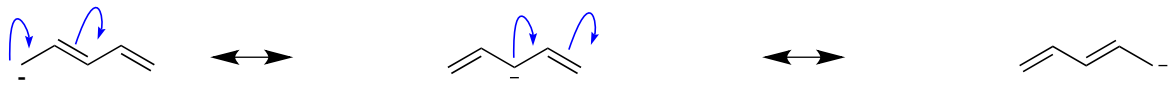
flow *does not* allow
same *is* true

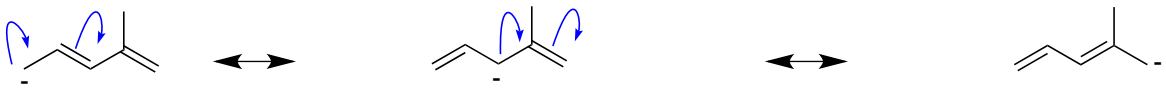


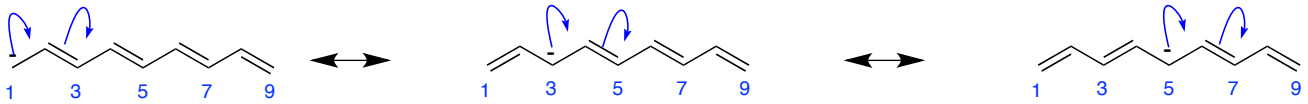
E- *Z*-

is possible for *Z*-butenyl anions to equilibrate to their more stable *E*-isomers via equilibrating conformations.

It is *possible*



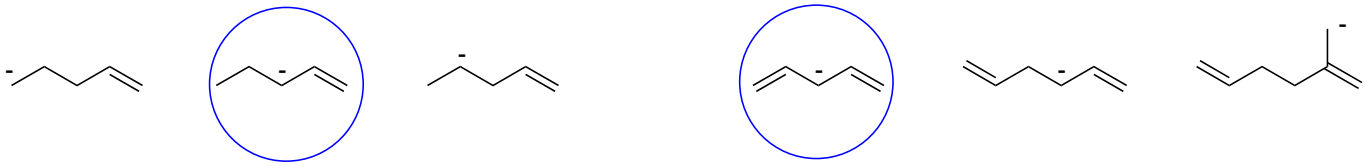




is possible for the negative charge on the nonatetraenyl anion to reside on the 1,3,5,7,9-carbon atoms. The negative charge in that anion *never*

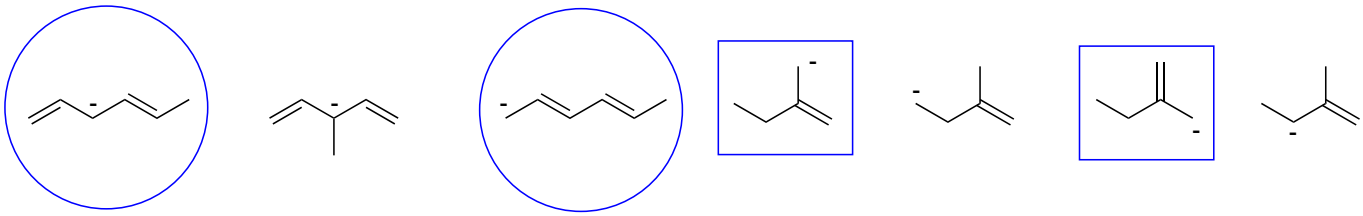
does appear

likely to be *more* stable



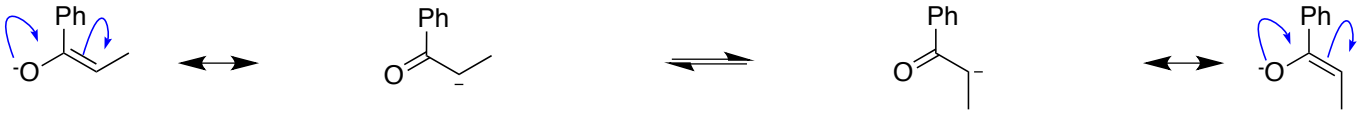
Anions that have several resonance structures are said to be *delocalized*

less stable



It *is* possible

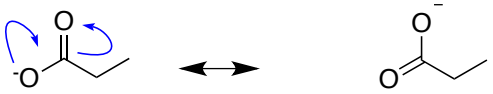
E-enolate *Z-enolate*

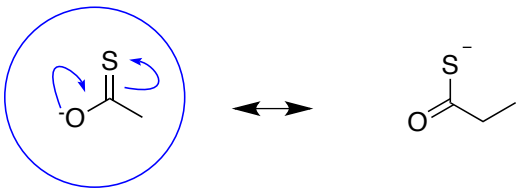


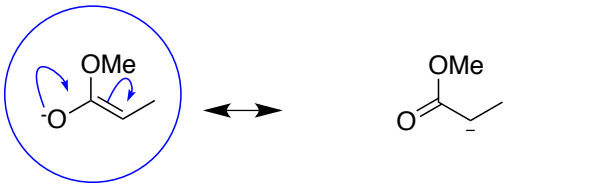
E-enolate *Z-enolate*

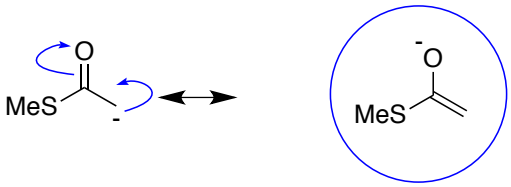
Z-enolate *E-enolate*

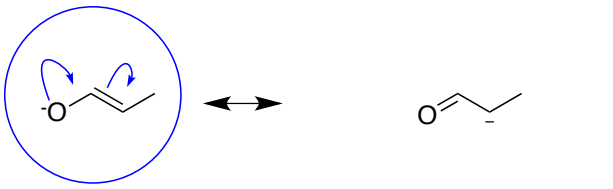
most *electronegative* atom.

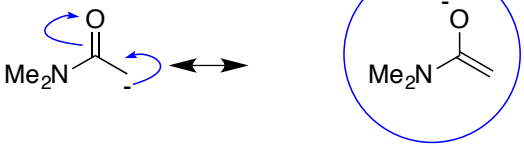


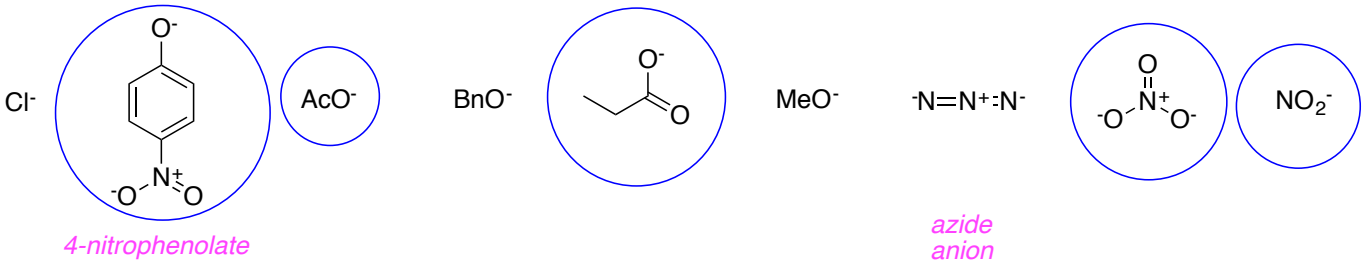












-ve charge localized on electronegative atom

many contributing resonance forms

highly localized charge

electron delocalization

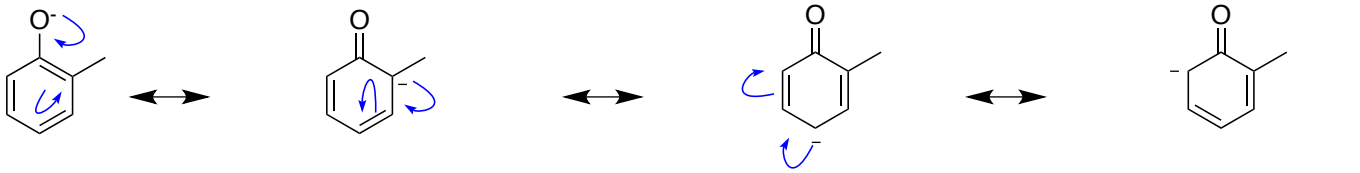
-ve charge localized on electropositive atom

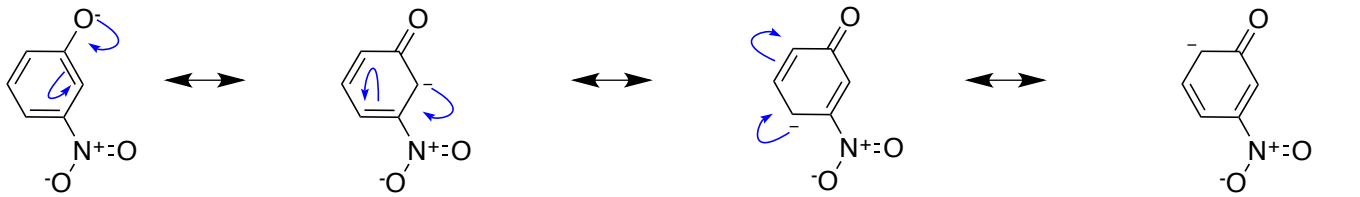
How Resonance Stabilization Of Anions Influences Acidity

product

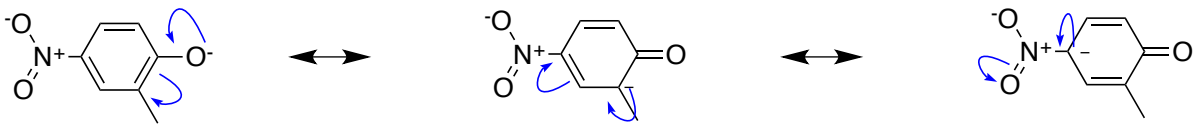
low pK_a and pH

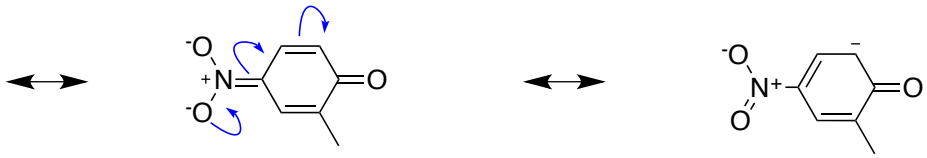
3 1 3 1



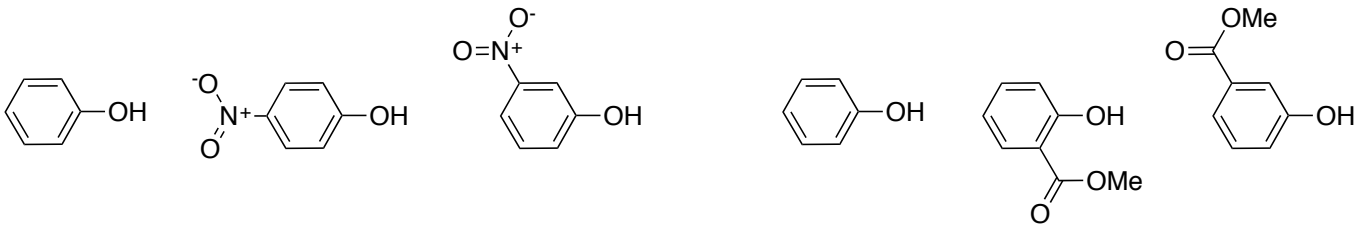


is not possible for both the *O*-atoms

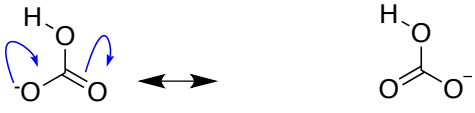




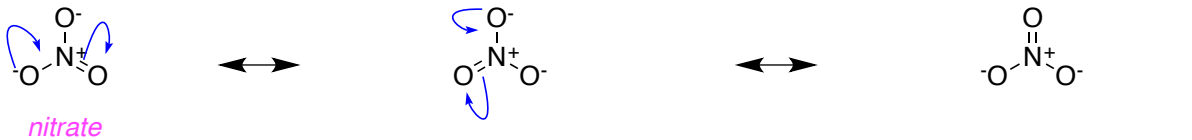
is possible for both the *O*-atoms
is possible for both the *O*-atoms of the nitro group
more stable than their 3-isomers.



nitrite



hydrogen carbonate

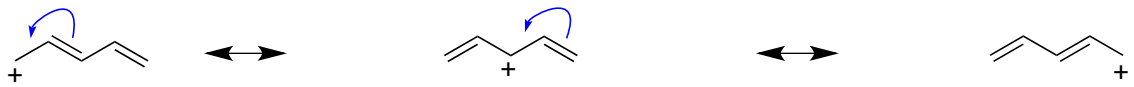


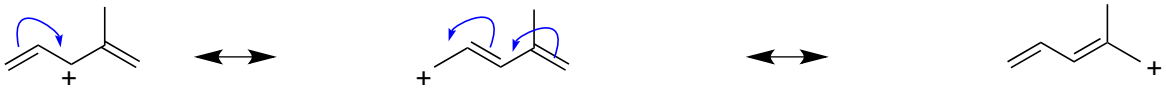
nitrate

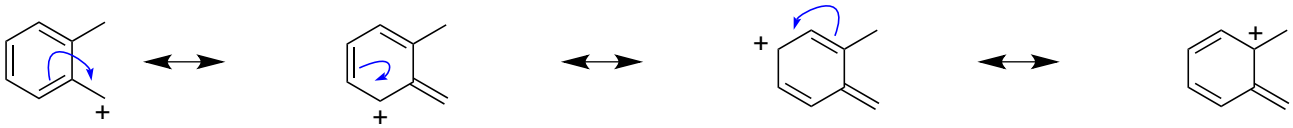
stronger acid than nitrous and carbonic acid.
in fact, HNO_3.

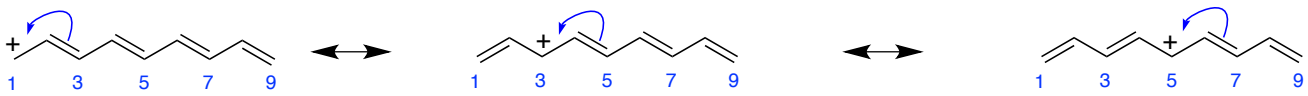
D. Resonance Stabilized Cations

towards positive charges and rarely the reverse.

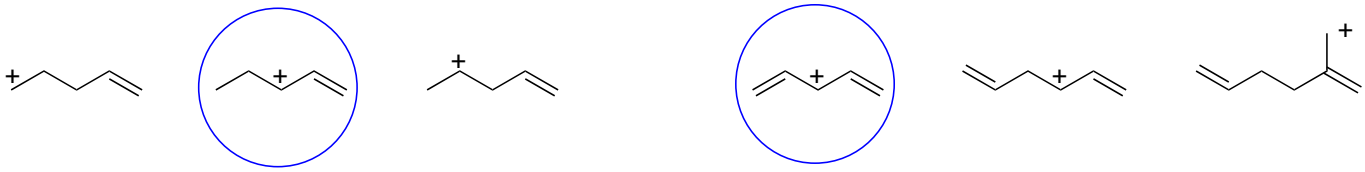




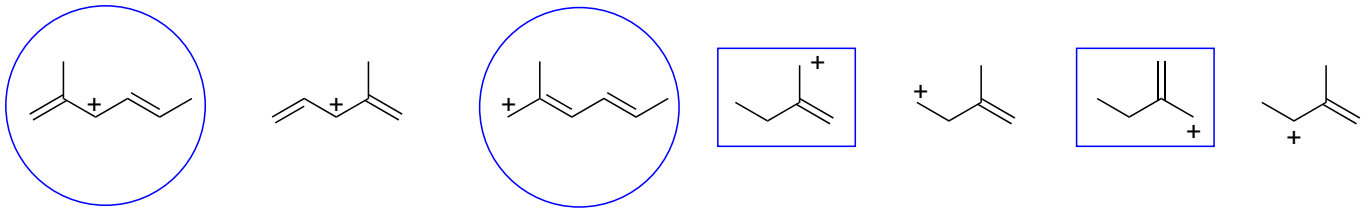




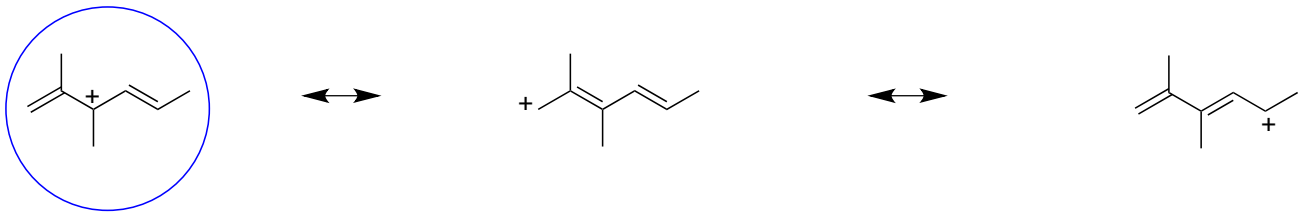
can reside on the 1,3,5,7,9-carbon atoms and it is *never does* appear

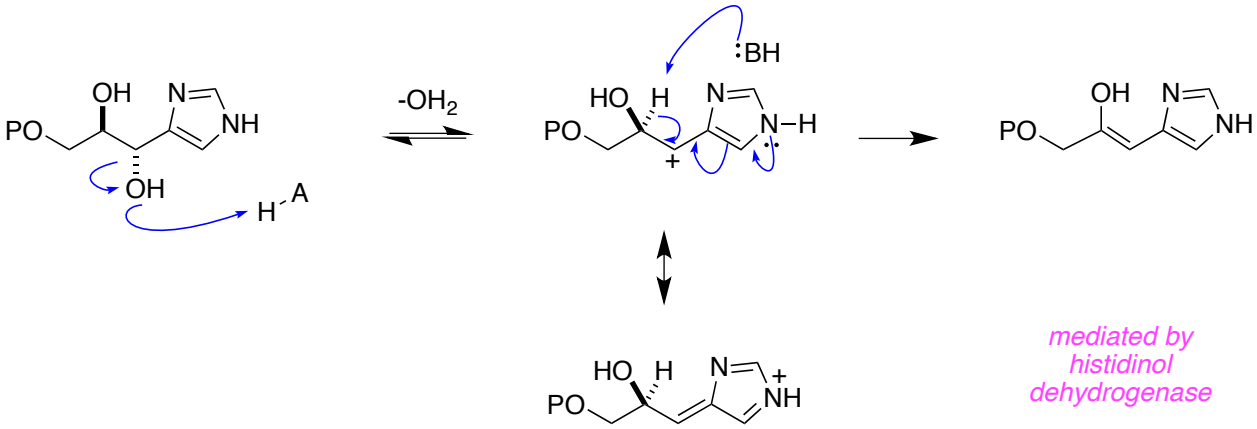


likely to be *more* stable
be *delocalized* than ones that do not.
The allyl cation is *less*



is possible for the positive charge to hop between atoms other than carbon.
most *electropositive* atom.
, *ie* *carbocations*, tend to be *more*
primary (1°).
It *is not* possible

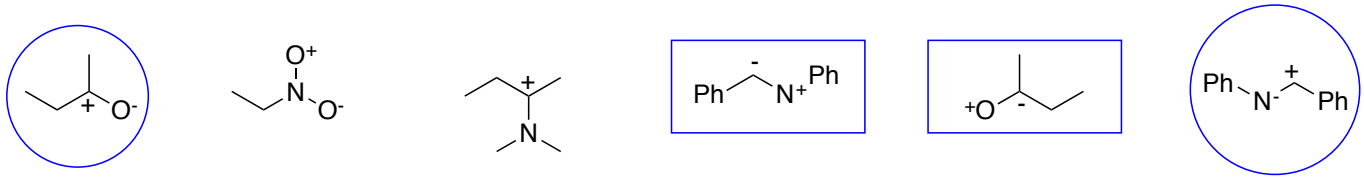




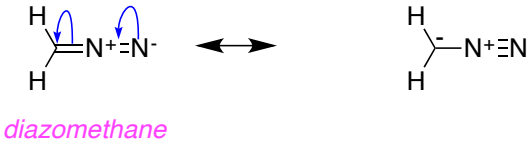
mediated by histidinol dehydrogenase

E. Resonance In Neutral Molecules

less stable

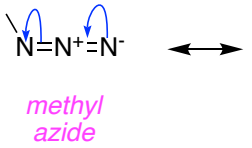


zwitterions

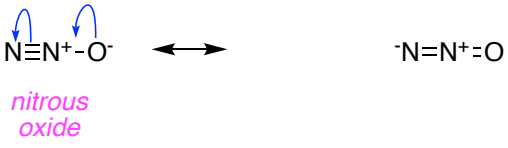


diazomethane

ozone



methyl azide



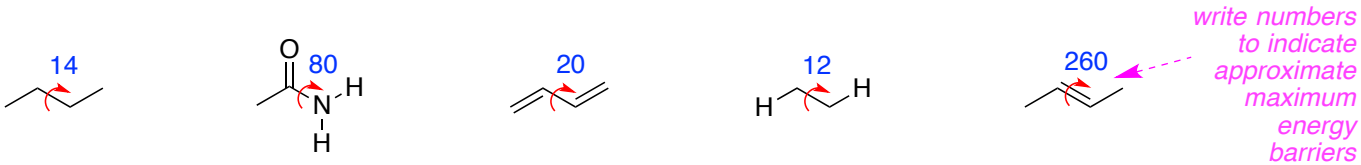
nitrous oxide

F. Resonance Stabilizes Some Conformations

charge separated form
less stable

charge separated form
more stable

The conclusion is that rotation about the σ-bond in the amide requires more energy because resonance gives that some *C* – *N* link some double bond character.



choices are: 260, 80, 20, 14, 12 kJ•mol^{-1}

Stereochemistry

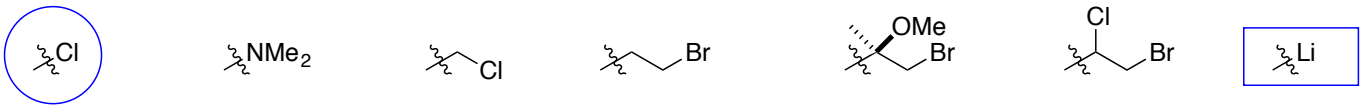
from chapter(s) _____ in the recommended text

A. Introduction

.

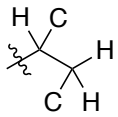
B. Priority Rules

higher atomic mass takes priority.

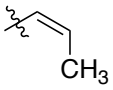


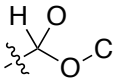
Substituents Connected Multiple Bonds

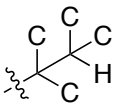
The problem is: ___the first atom of the substituents is the same for every molecule.

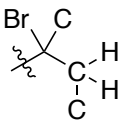
eg  *is equivalent to* 

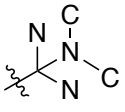
sorry, mistake in first edition

 *is equivalent to*

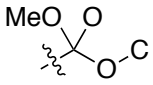
 *is equivalent to* 

 *is equivalent to* 

 *is equivalent to* 

 *is equivalent to* 

is equivalent to



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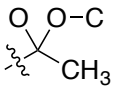

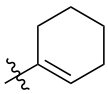

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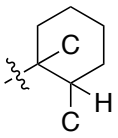

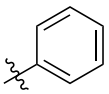

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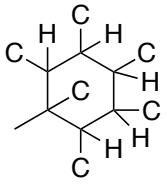

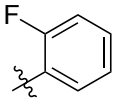

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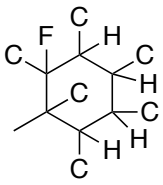
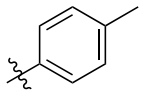
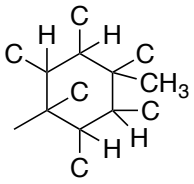
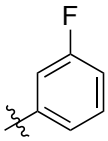


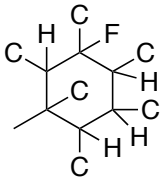


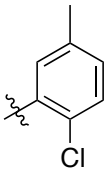
is equivalent to





is equivalent to





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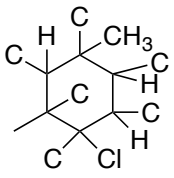

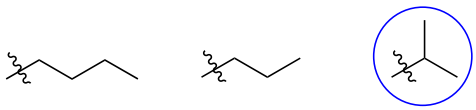

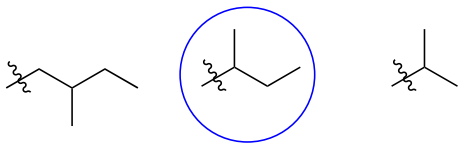

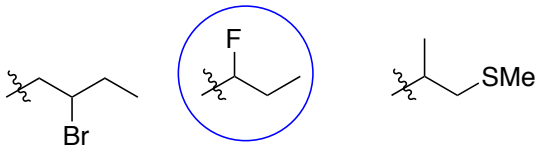
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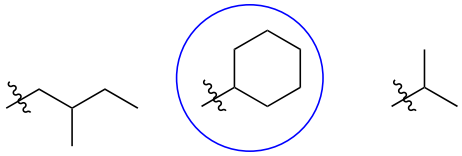

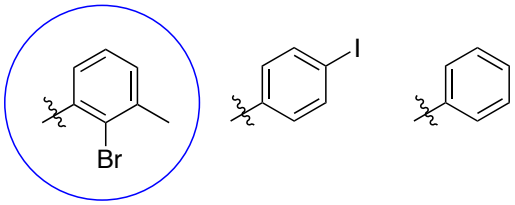
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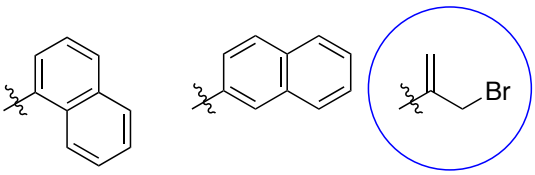
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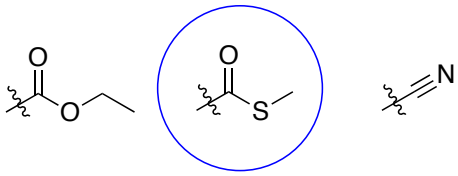
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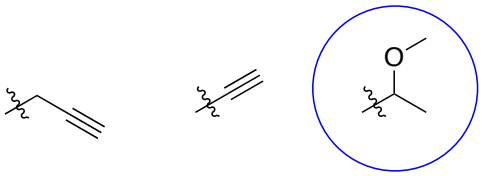
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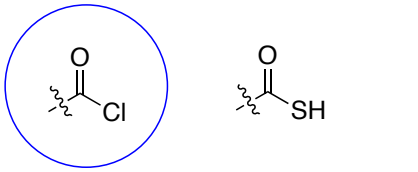
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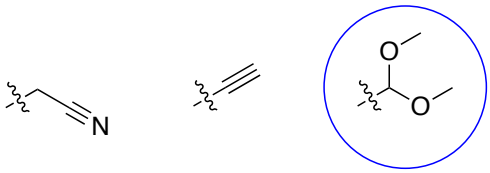
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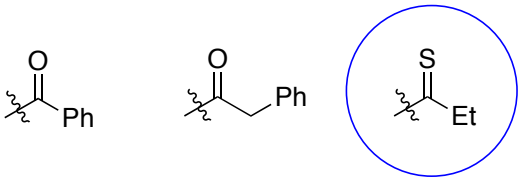
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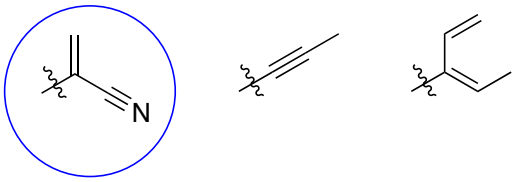
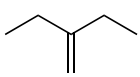

N

C. Classifying Alkene Geometries

means the same as E / Z.



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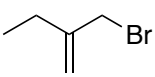

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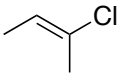
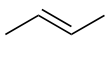


E-



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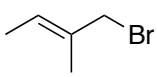

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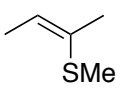
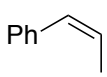


Z-



Z-

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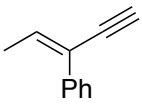
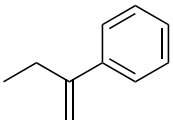


Z-



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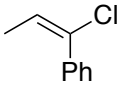

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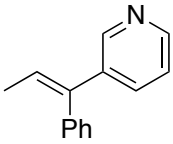

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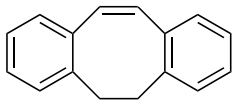

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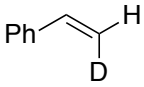
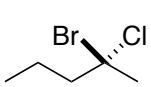
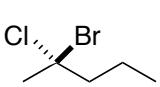


Z-

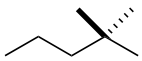
D. Chiral Centers

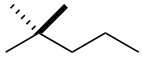
eg



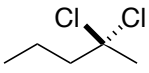


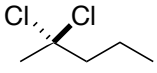
yes / no



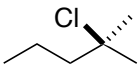


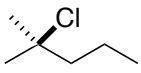
yes / no





yes / no





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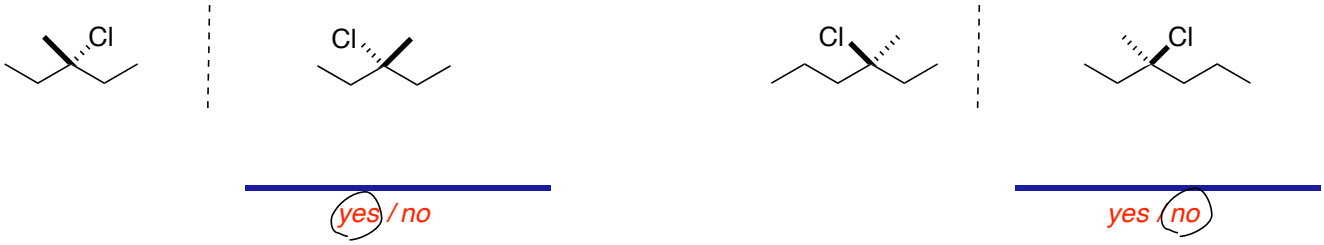
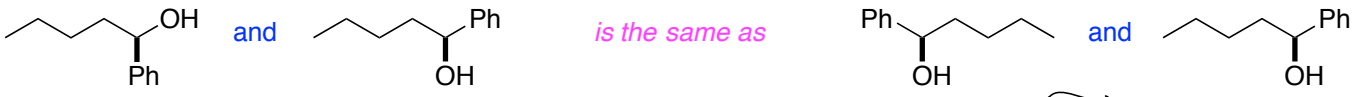


yes / no

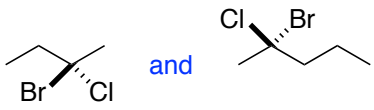
yes / no

do not absolutely (remove) require that there be four different groups on a carbon atom.
enantiomers, only if

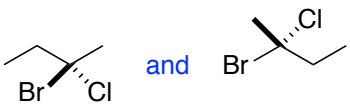
eg



yes / no



yes / no



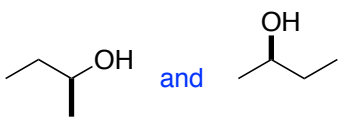
yes / no

yes / no

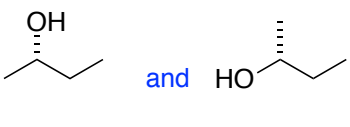
yes / no

yes / no

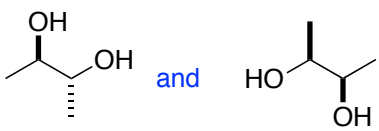
yes / no



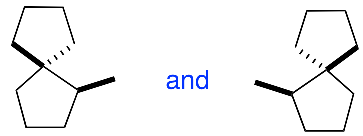
yes / no



yes / no

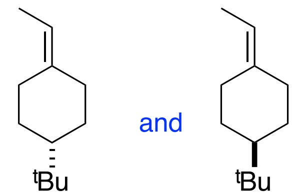


yes / no



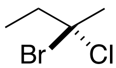
yes / no

yes / no

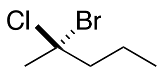


yes / no

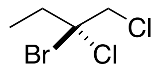
can



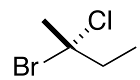
R / S



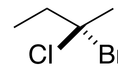
R / S



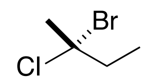
R / S



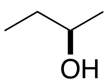
R / S



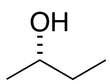
R / S



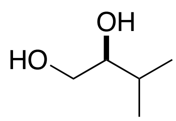
R / S



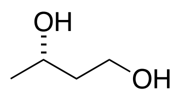
R / S



R / S

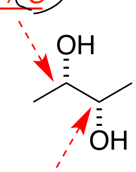


R / S



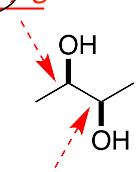
R / S

R / S



R / S

R / S



R / S

always *S-*.
always *S,S-*.
an *S,S-*configuration.

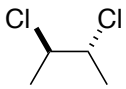
do
optical rotation,
compound concentration / temperature / wavelength of the light / solvent.

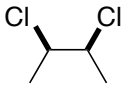
E. Combinations Of Chiral Centers

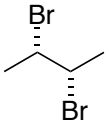
Meso-compounds *have*

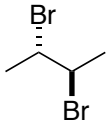
do not rotate

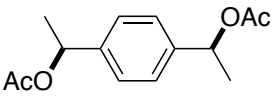
true

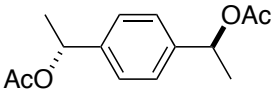


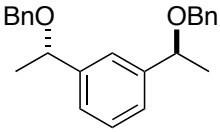


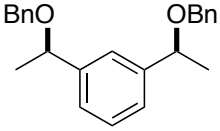


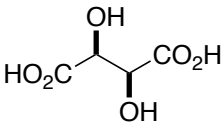




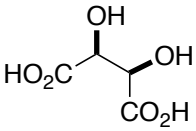




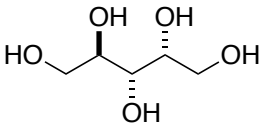




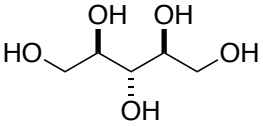
tartaric acid



should be this structure in the book



see errata there is a mistake in this structure in the first edition of the book



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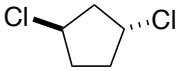

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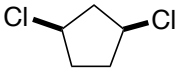
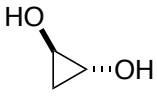


should be this structure in the book



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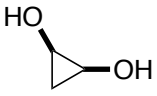
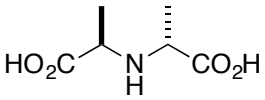
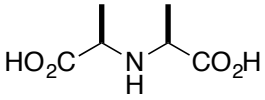
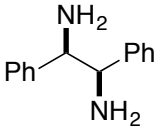
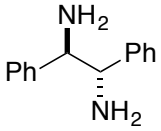
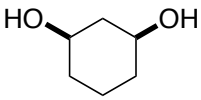


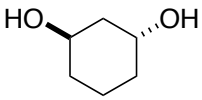

HO2C
N
H
CO2H

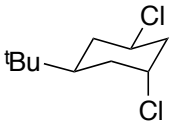

HO2C
N
H
CO2H

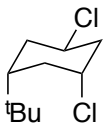

NH2
Ph
Ph
NH2

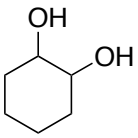

NH2
Ph
Ph
NH2

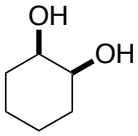

HO
OH

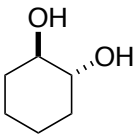

HO
OH

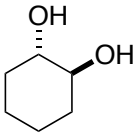

Cl
tBu
Cl

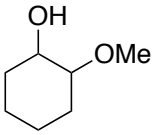

Cl
tBu
Cl

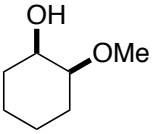

OH
OH

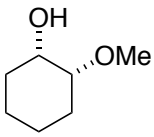

OH
OH

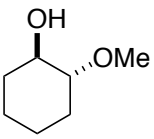

OH
OH

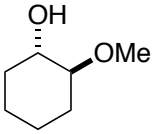

OH
OH


OH
OMe


OH
OMe


OH
OMe

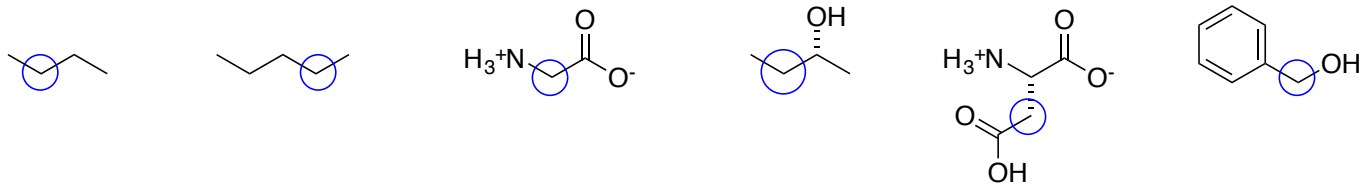

OH
OMe

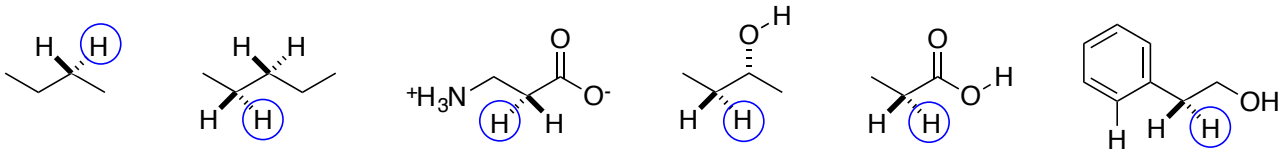

OH
OMe

F. Prochirality

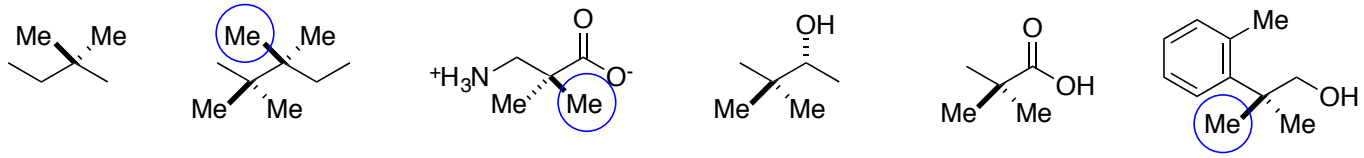
do not

true.

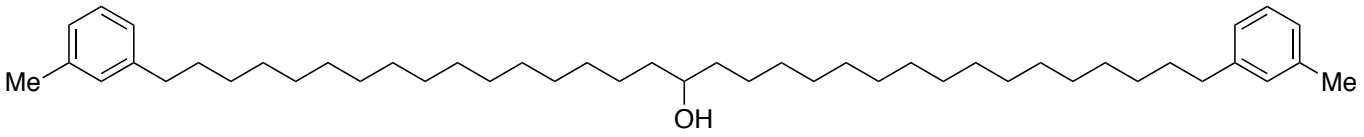




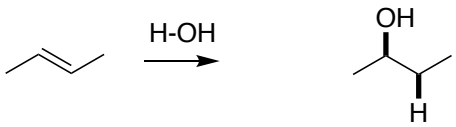
all *pro-R*.

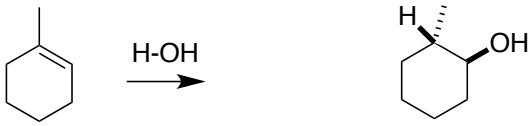


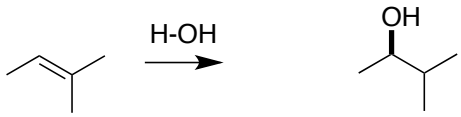
are all *pro-S*.



are prochiral.

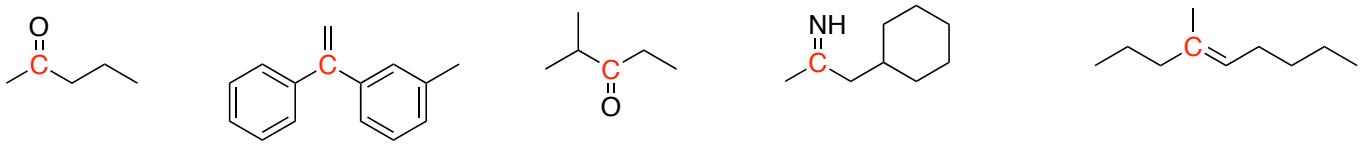


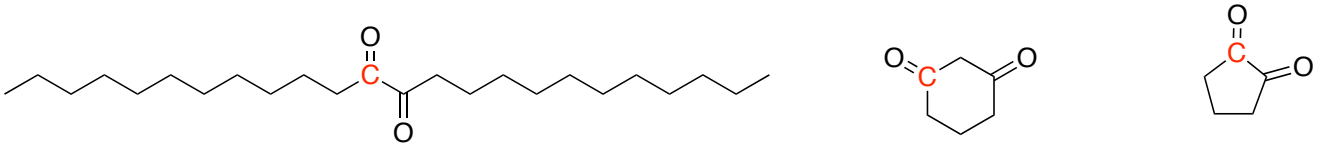




true.

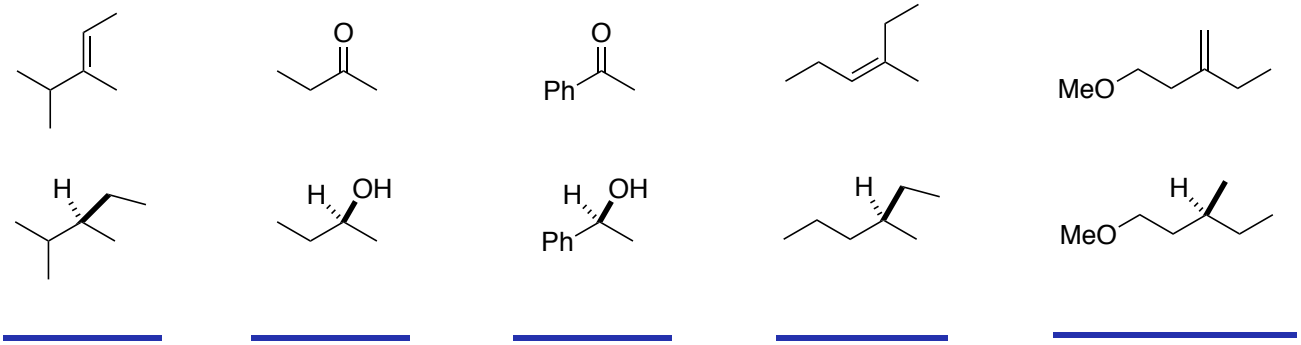
all Re-.





sorry, mistake in first edition of book

all Si-.



sometimes gives the *R*-chiral
sometimes gives the *S*-chiral centers.

S_N1 Displacement At sp^3 Centers

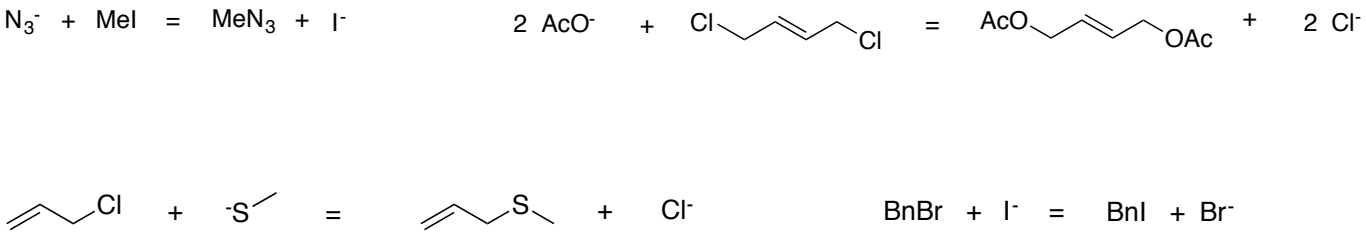
from chapter(s) _____ in the recommended text

A. Introduction

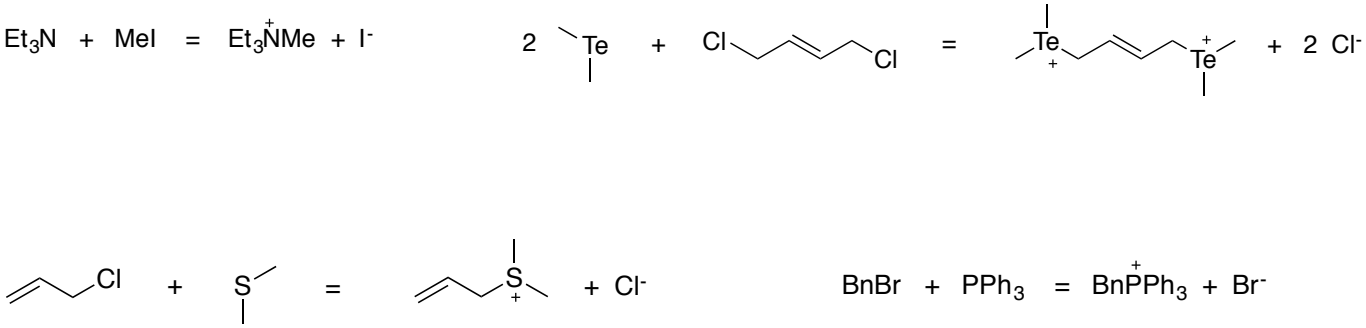
.

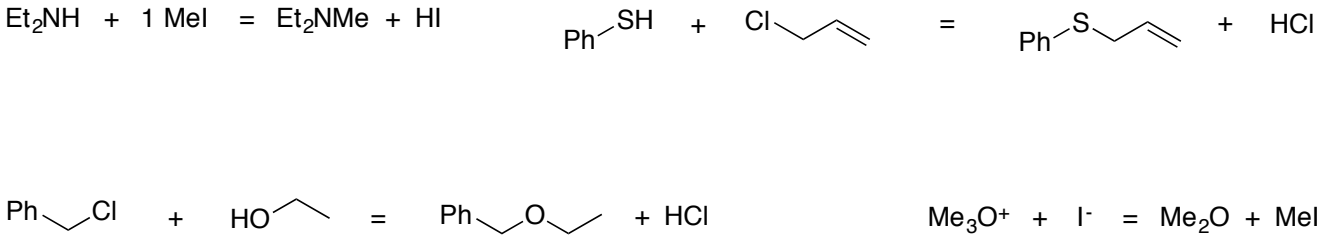
B. Types Of Nucleophilic Substitutions

Negatively Charged Nucleophiles

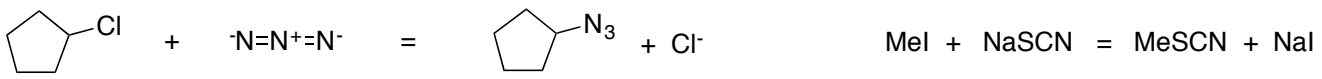


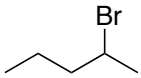
Neutral Nucleophiles

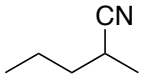




Charges On Leaving Groups

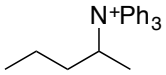


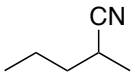


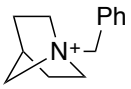
+ NC^- = 

+ Br^-

^{t}BuCl + LiI = ^{t}BuI + LiCl



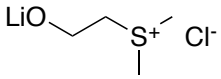
+ NC^- = 

+ NPh_3 

+ LiI = 

+ 

+ Li^+



= 

+ 

+ LiCl

(*intramolecular*)

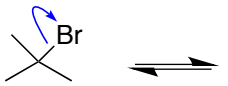
$Ph_3P^+Me\ Cl^-$ + NaSEt = PPh_3 + MeSEt + NaCl

C. S_N1

Introduction Into The Key Steps

group *replaces another*.

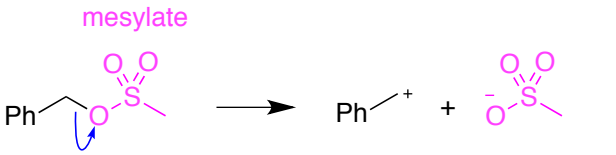
nucleophile *with first order kinetics*.



+ Br^-

+ I^-

carbocation and bromide



benzyl carbocation and $^{-}$OMs

is the rate

tosylate

allyl carbocation and O^-Ts

hydrogen phosphate

allyl carbocation and hydrogen phosphate

geraniol hydrogen phosphate

an allyl carbocation and hydrogen phosphate

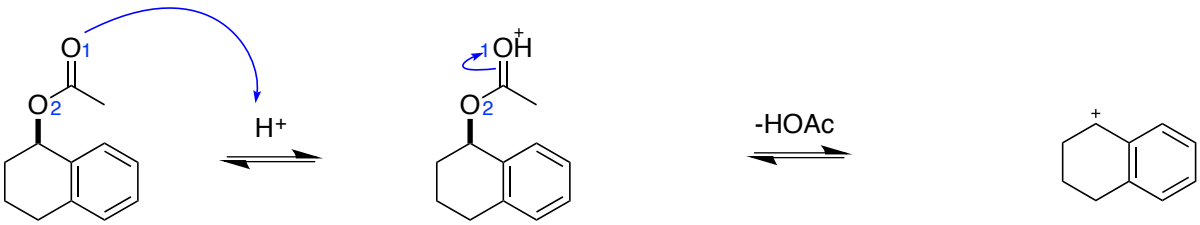
carbocation and hydroxide

carbocation and water

better
right
left
true.

protonated intermediate

carbocation intermediate

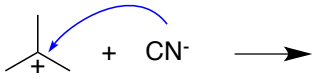


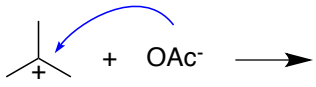
protonated intermediate

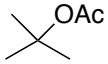
carbocation intermediate

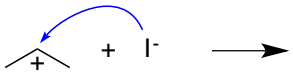
O[1] is

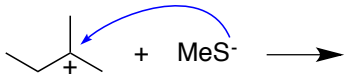
Carbocations *can*





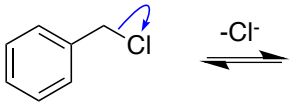


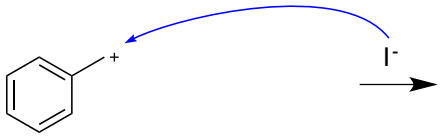


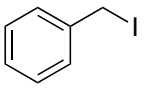


cations

racemic,
sp^2
flat and the nucleophile can

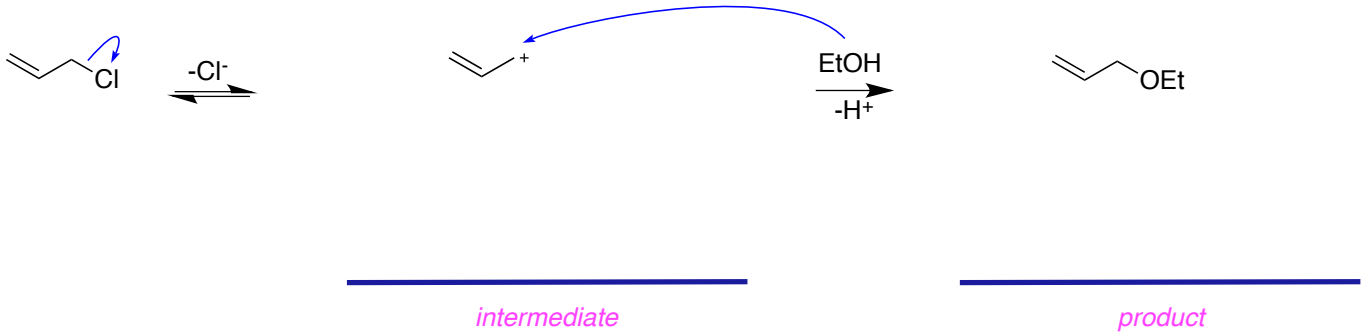


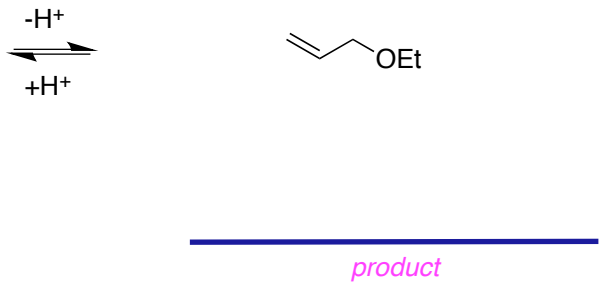




intermediate

product

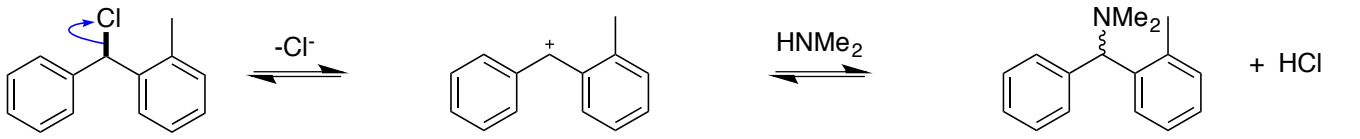




two intermediates.

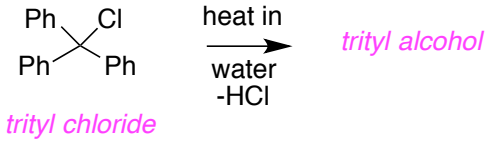
one intermediates.

S_N1 reaction of bromide with allyl chloride involves *one*

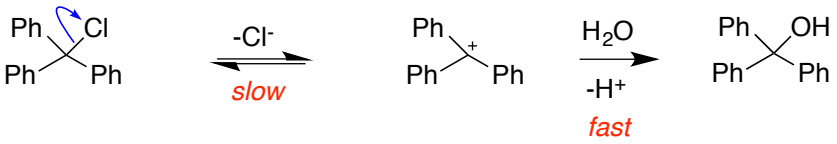


carbocation intermediate *product and HCl*

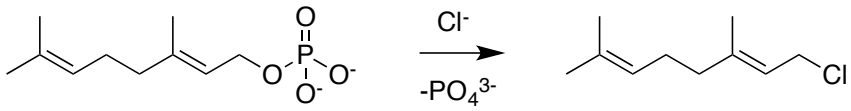
a



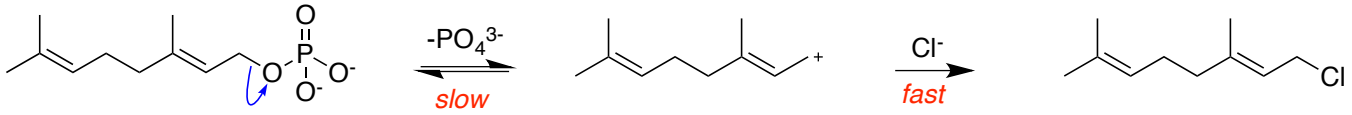
trityl chloride *trityl alcohol*

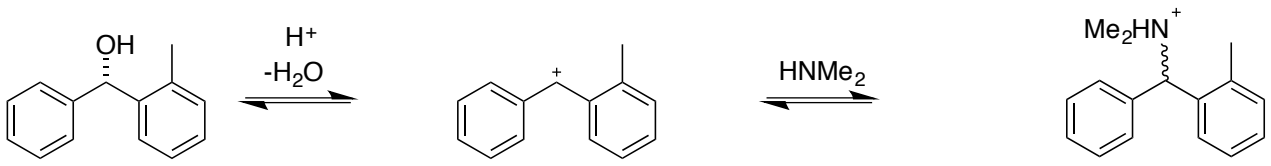


b



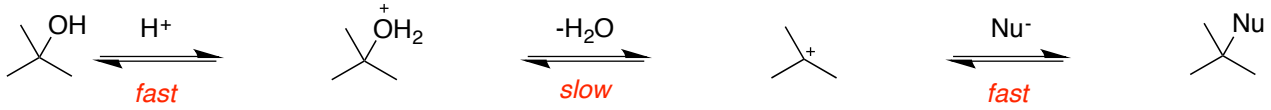
geranyl phosphate *geranyl chloride*



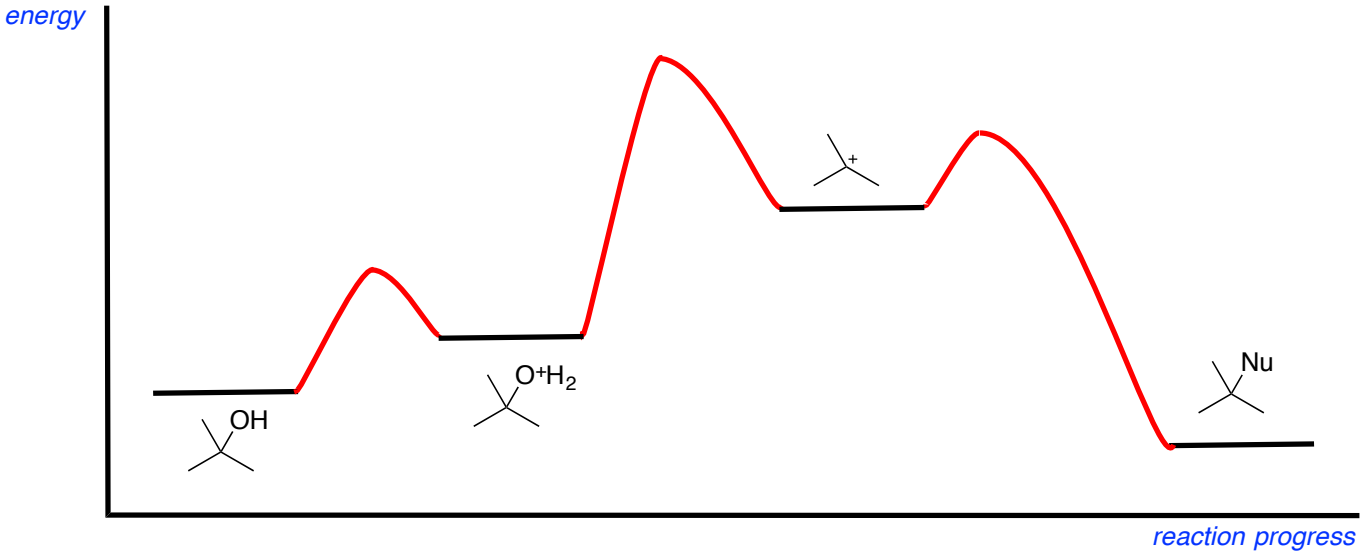


carbocation intermediate *protonated amine*

Kinetics Of S_N1



protonated intermediate *carbocation*



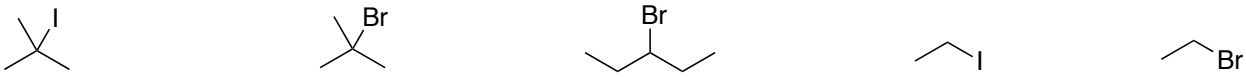
rate is proportional to [^{t}BuOH] rate = k [^{t}BuOH]

at the same rate the

Carbocation Stability

Rates of S_N1 reactions tend to *increase*

most stable *least stable*



fastest *slowest*

show 3°, 1°, 2°, Me on top of line

Me 1° 2° 3°

least stable *most stable*

0 1 2 3

on bottom of line
show number of p-to-σ interactions

*show **a** - **e** on top of line*

a methyl bromide **b** *tert*-butyl bromide

c methyl chloride **d** ethyl bromide **e** 2-bromopropane

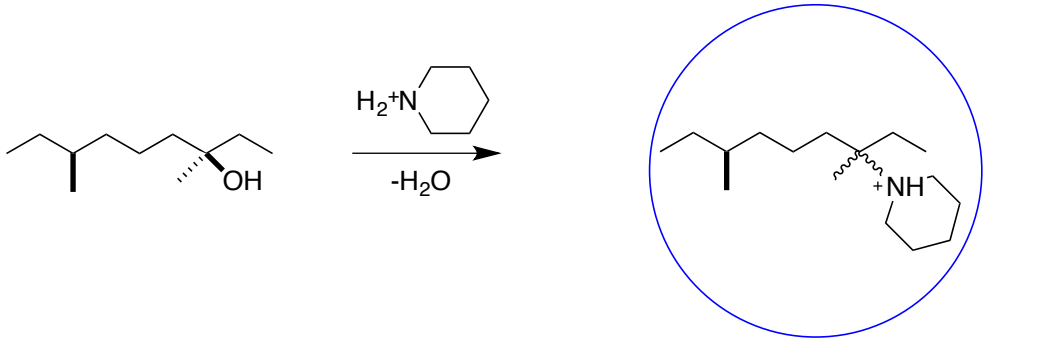
b **e** **d** **a** **c**

fastest *slowest*

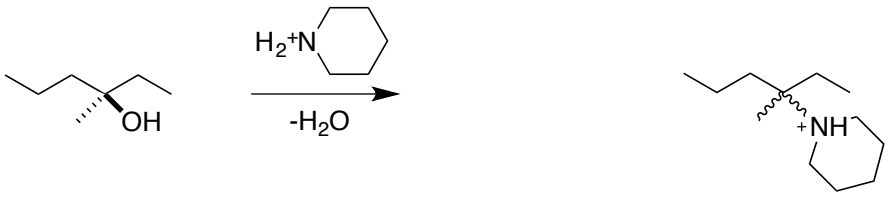
towards from the
increases the overlap

greater than that from hyperconjugation in Et^+.
more stable than many other primary carbocations.

Stereochemistry And S_N1

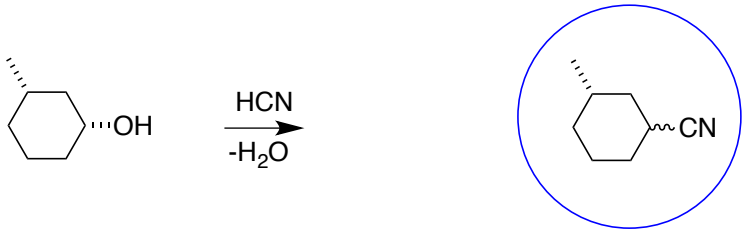


circle if optically active

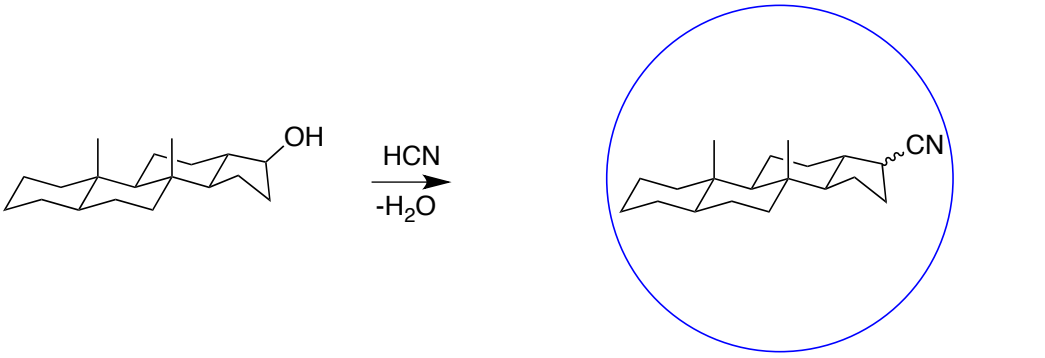


circle if optically active

circle if optically active



circle if optically active



circle if optically active

S_N2 Displacement At sp^3 Centers

from chapter(s) _____ in the recommended text

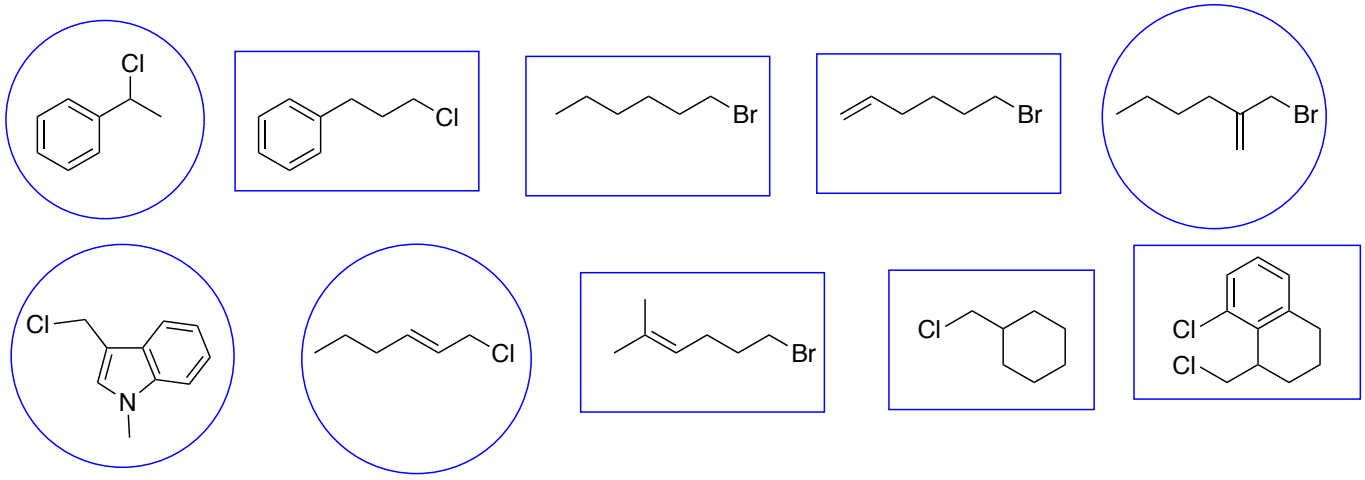
A. Introduction

.

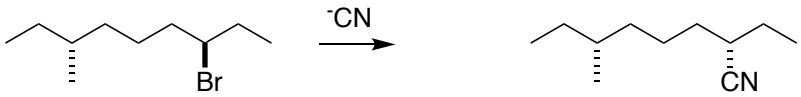
B. Differentiating S_N1 and S_N2

replaces another and *with second order kinetics*.
S_N2 processes whereas *S_N1*

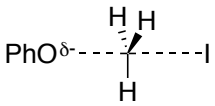
S_N2 pathways.
feature *S_N1* mechanisms.



Stereochemical Inversion In S_N2 Reactions

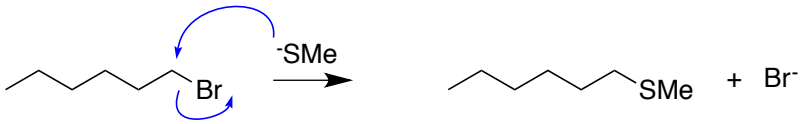


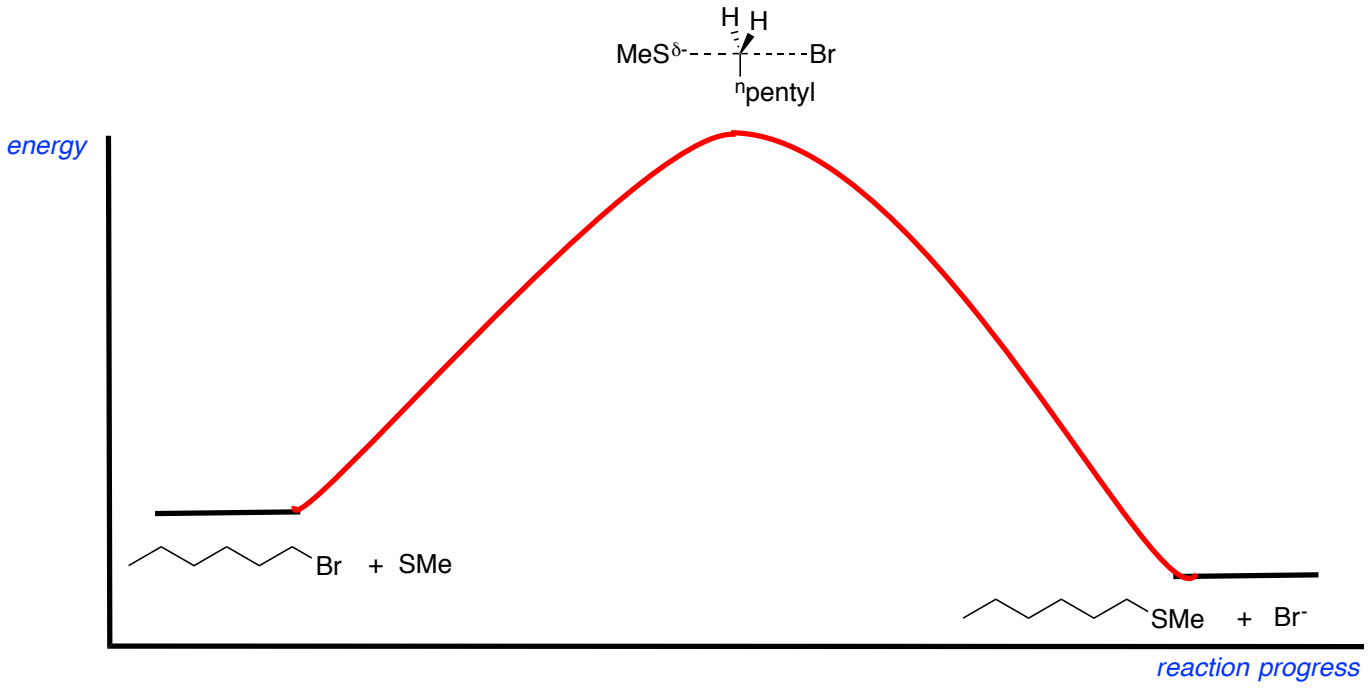
Transition states in S_N2 displacement processes have geometries that resemble *trigonal bipyramidal* shapes.



S_B2.
S_G1

Kinetics And S_N2 Pathways





doubles

accelerated

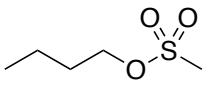
more

less.

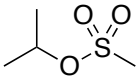
C. Interconversion Of Enantiomers And Diastereomers

Conversion Of Alcohols Into Leaving Groups

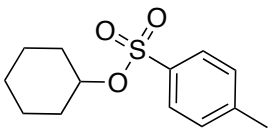
Hydroxyl groups *are not*
better



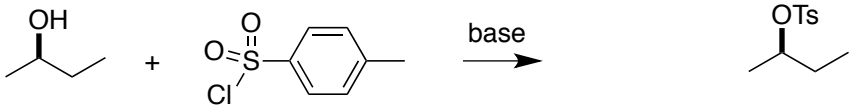
*n*butyl mesylate



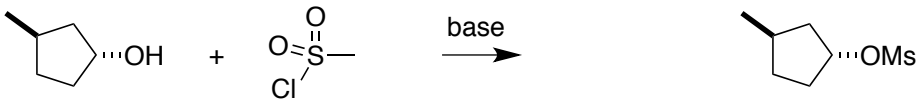
*i*propyl mesylate

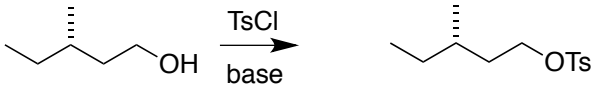


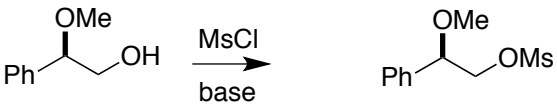
cyclohexyl tosylate

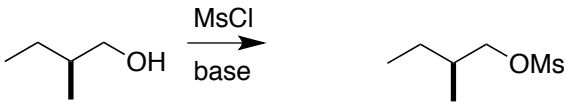


*s*butyl tosylate



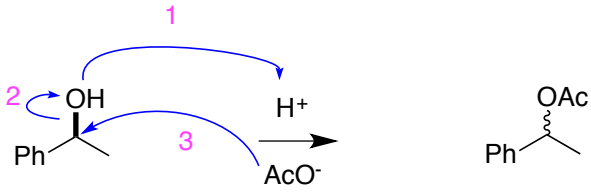






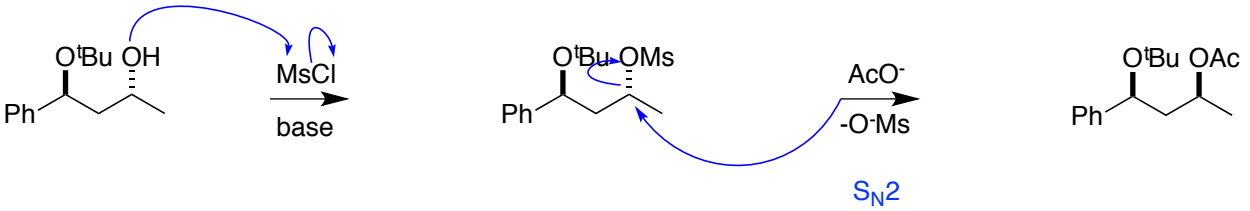
Mesylates and tosylates are *better retention* of configuration *inversion* stereochemistry.

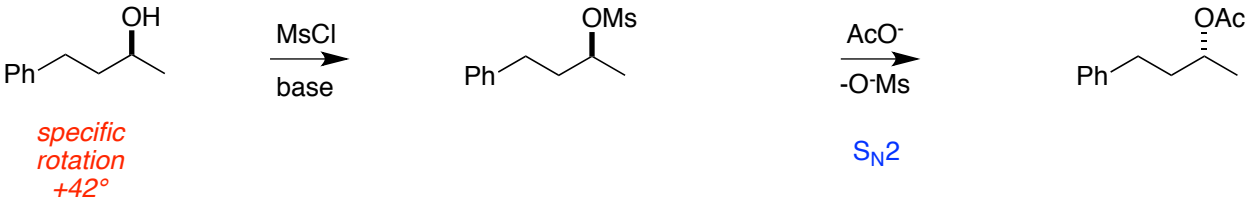
S_N1.



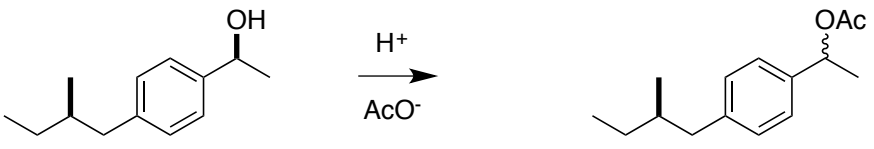
specific rotation +13°

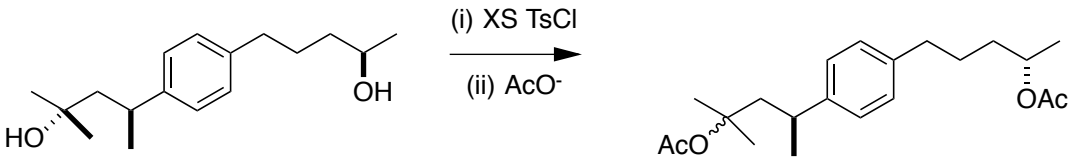
specific rotation = 0°





specific rotation = -42°



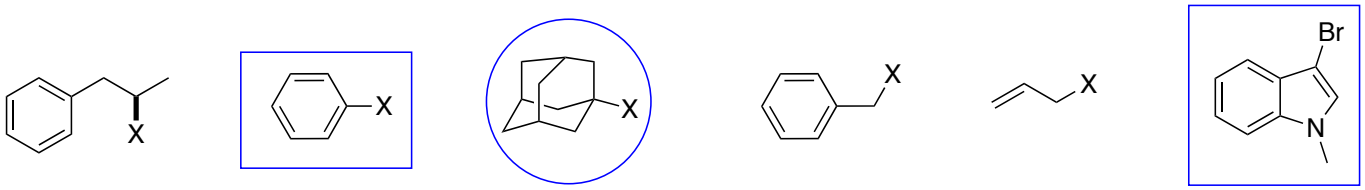


product of one S_N1 and one S_N2 reaction

Stereoelectronic Effects

S_N2 reactions

transition state



LUMO on

HOMO.

the empty p-orbital of the carbocation.

LUMO

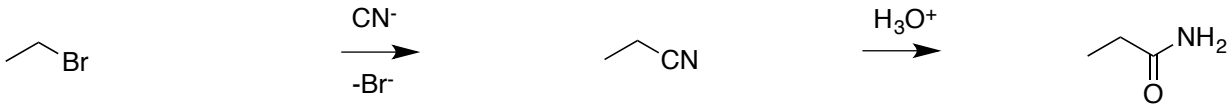
HOMO.

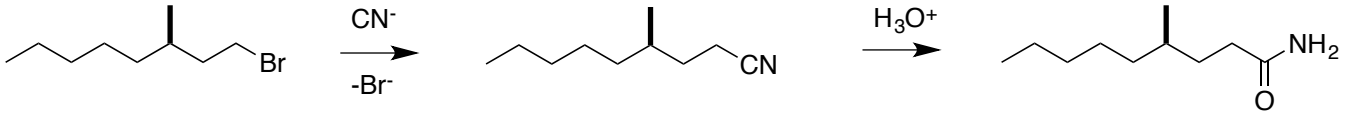
*σ** orbital.

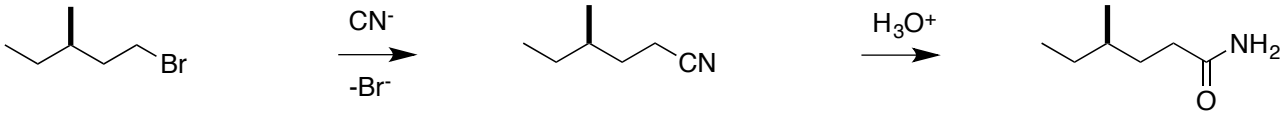
draw C - I σ-orbitals and orientation of S_N2 displacement by CN^-*

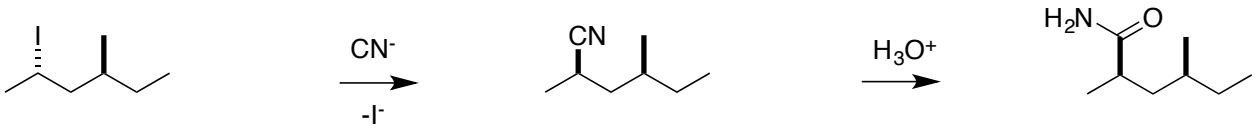
D. A Little Synthetic Chemistry For Chemistry Majors

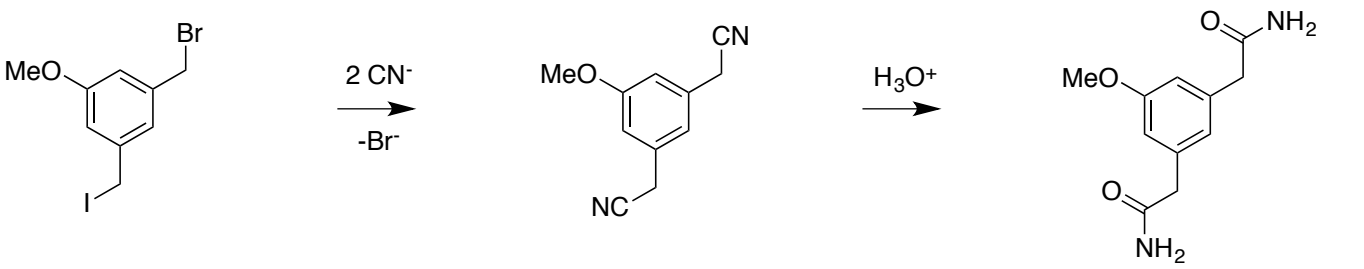
Cyanide: A Useful *C*-Nucleophile





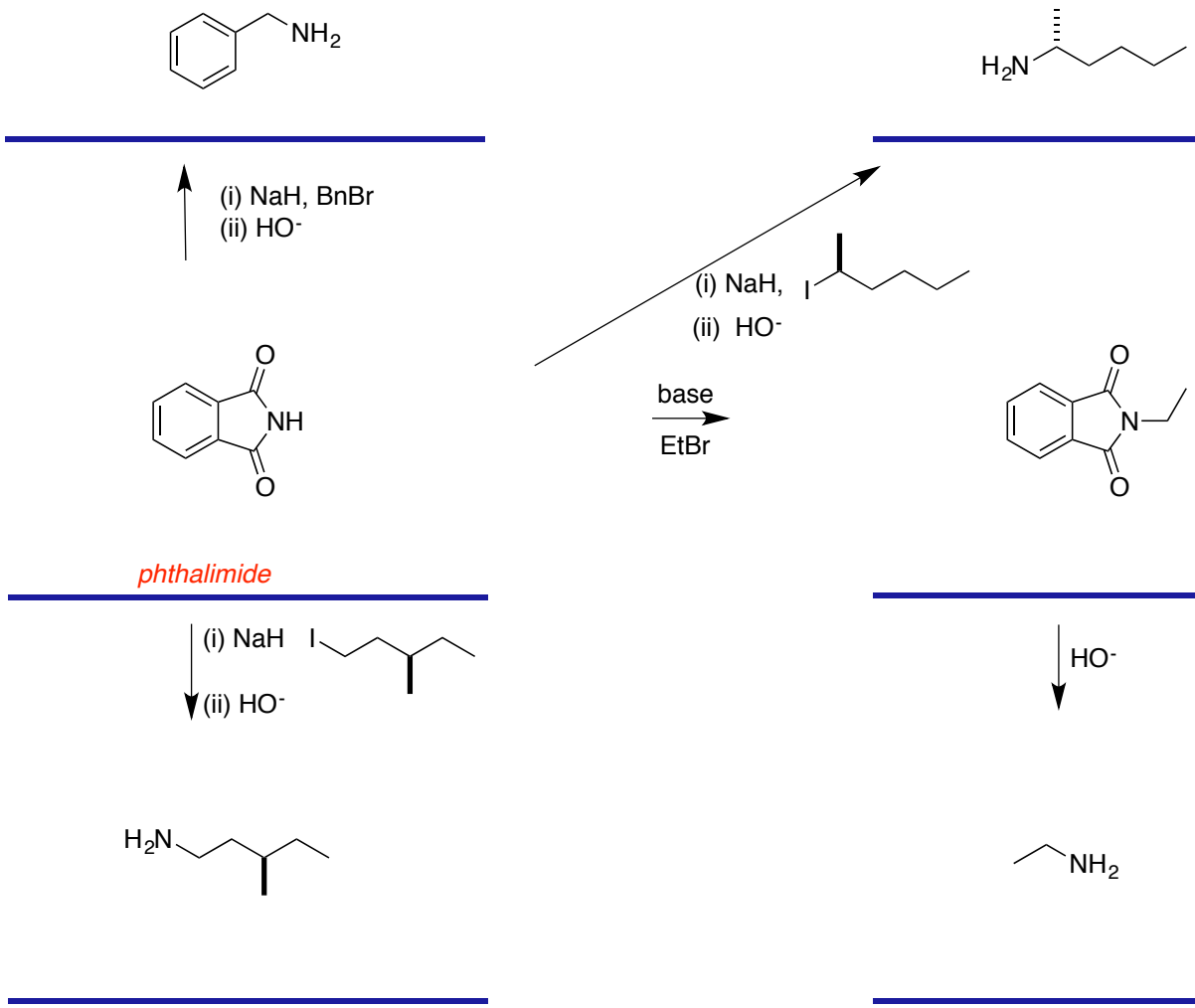






This type of transformation (nitrile displacement then hydrolysis) works for *4-MeOC$_6$H$_4$I / MeI / BnI / allyl bromide / vinyl iodide*

Phthalimide: Useful *N*-Nucleophile For Syntheses Of Primary Amines



primary amines

Gabriel synthesis is a *better*

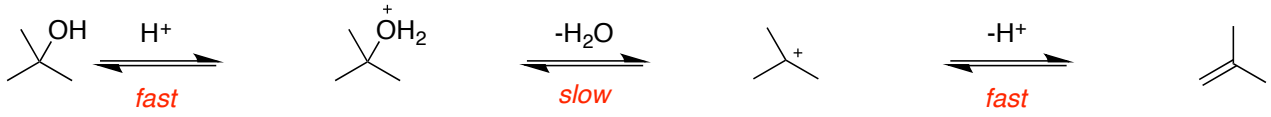
Elimination Reactions To Form Alkenes

from chapter(s) _____ in the recommended text

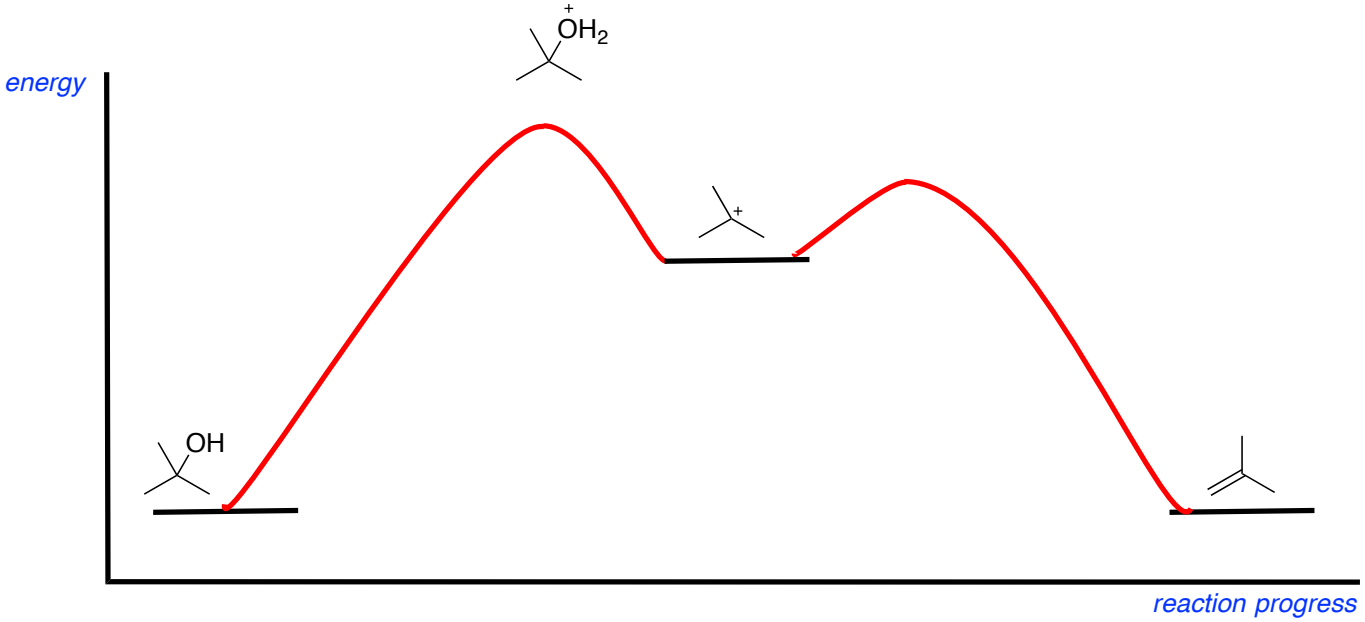
A. Introduction

.

B. E1 Mechanisms



protonated intermediate *carbocation intermediate* *alkene product*



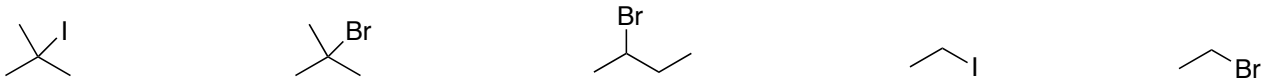
Kinetics

rate is proportional to [^{t}BuOH] rate = *k* [^{t}BuOH]

Carbocation Stability

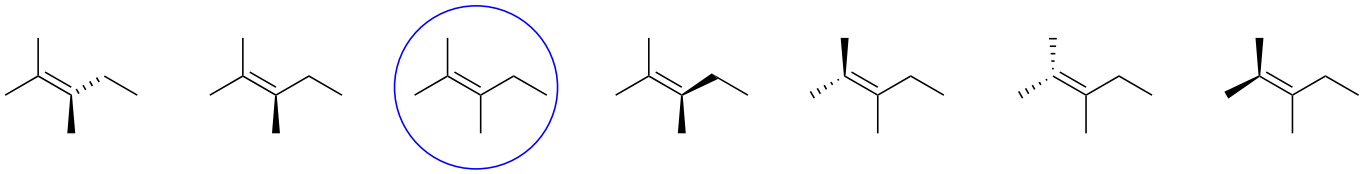
Rates of E1 reactions tend to *increase*

most stable *least stable*



fastest *slowest*

Bredt's Rule



sp^3 so it has ideal dihedral angles of about *109*

the same

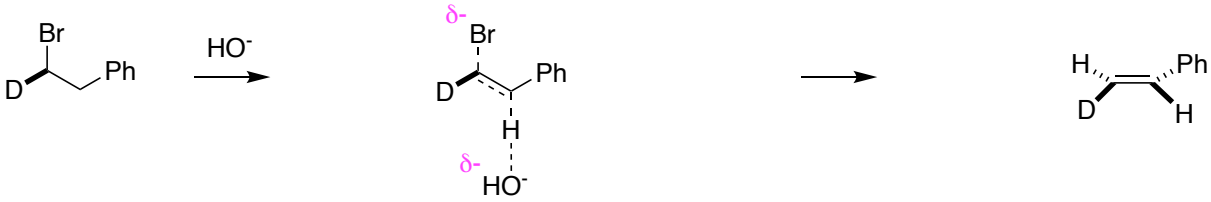
more

is not

adamantane *adamantane cation* *adamantene*

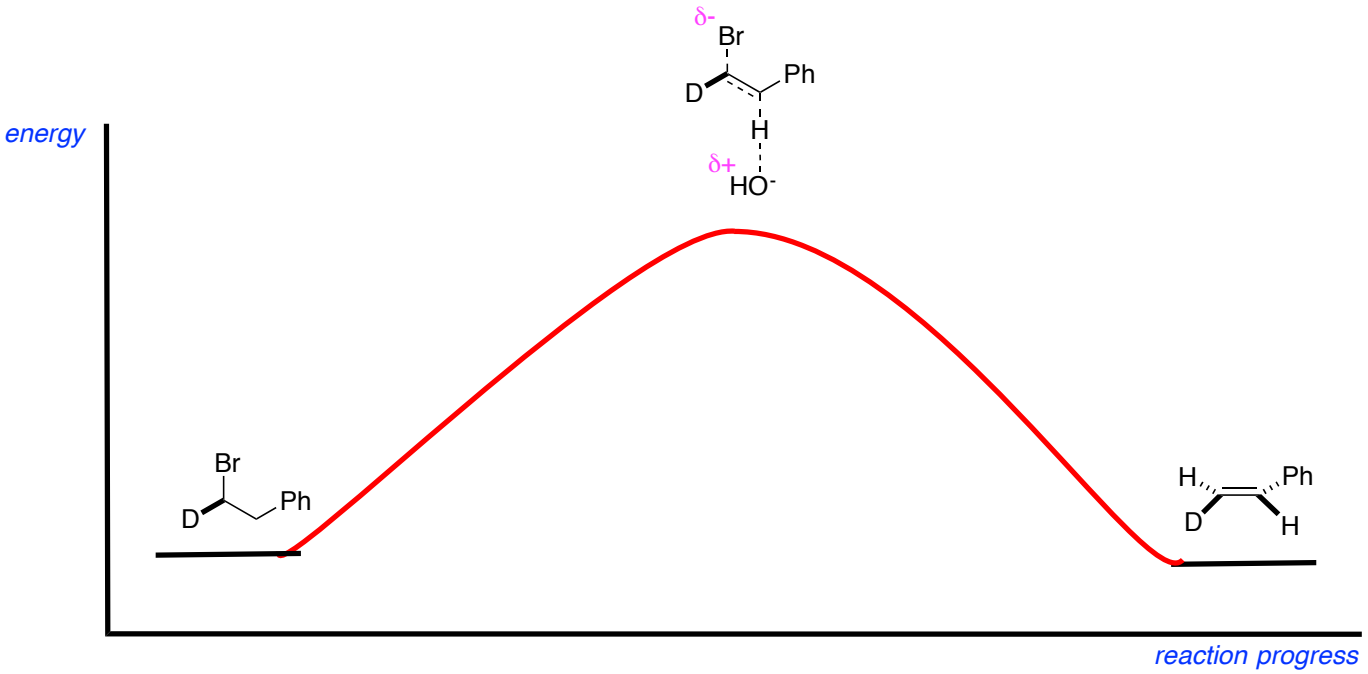
are not favorable.

C. E2 Mechanisms



transition state

product
(show stereochemistry)



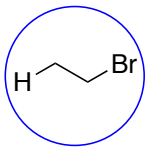
Kinetics

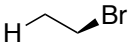
rate is proportional to [$DCHBrCH_2Ph$] [OH^-]

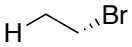
rate = k [$DCHBrCH_2Ph$] [OH^-]

doubles

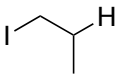
Stereoselectivity
different
perpendicular.



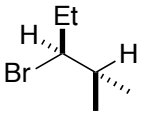




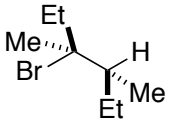
syn-periplanar EtCl



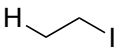
anti-periplanar 1-iodopropane



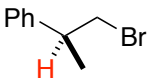
anti-periplanar EtBrHCCHMe$_2$



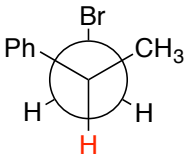
anti-periplanar EtMeHCCBrMeEt



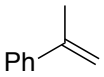
anti-periplanar ethyl iodide



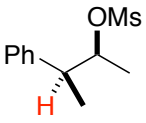
..... can be represented as



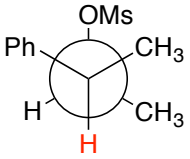
complete Newman projection

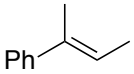


show alkene product



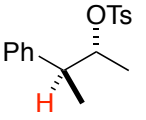
..... can be represented as



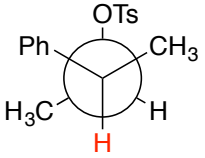


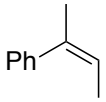
complete Newman projection

show alkene product



..... can be represented as

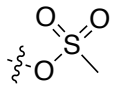




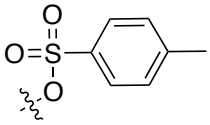
complete Newman projection

show alkene product

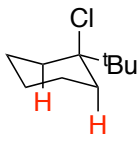
Show structures for:

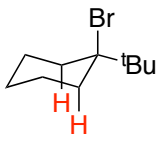


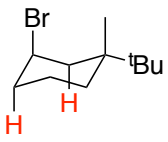
mesyl group, -OMs

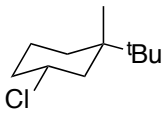


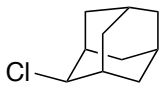
tosyl group, -OTs

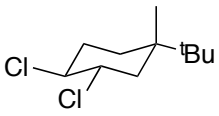


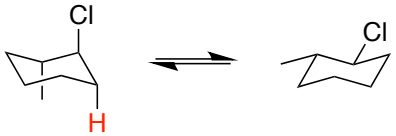


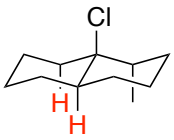


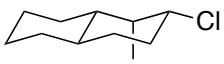


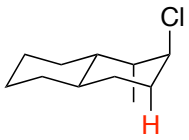


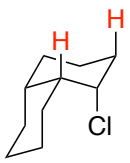


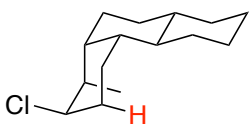


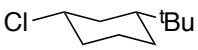


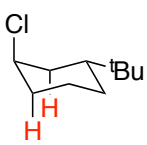


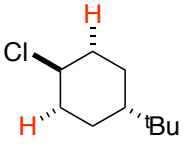




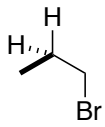


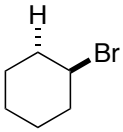


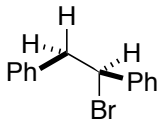


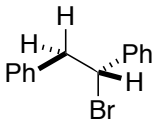


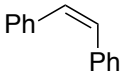
anti-periplanar.

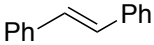


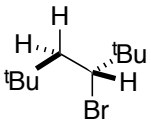


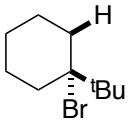


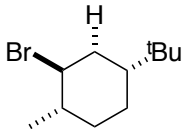


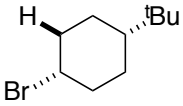


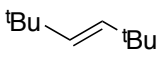


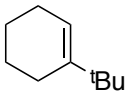


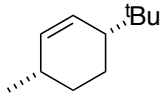


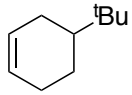


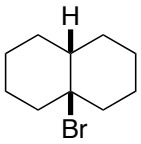


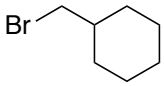


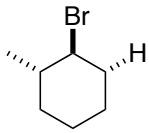


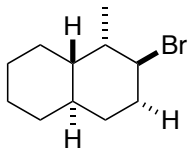


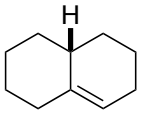


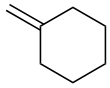


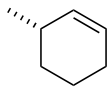


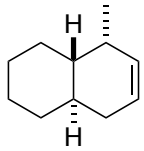


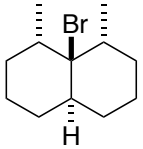


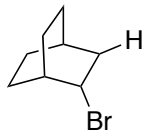


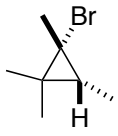


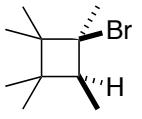


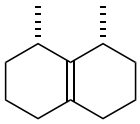


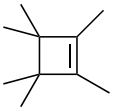












D. Factors That Favor E1, E2, S_N1, or S_N2

Basicity *vs* Nucleophilicity

(i) *E2 relative to E1* reactions and it will tend to favor *E2*

(ii) *E2 relative to E1* *favor E1*

(iii) *will not* *will not*

(iv) *S_N2 relative to S_N1* *S_N2*

increases

Nucleophilicity

(i) *S_N1* relative to *S_N2* reactions; and,

(ii) *E1* over *E2*

(i) *S_N2* relative to *S_N1* reactions;

(ii) *E2* over *E1* reactions.

The following order is approximate. It varies with the HOMO/LUMO match of the nucleophile with the electrophile.

N_3^-	CN^-	I^-	MeO^-	NH_3	H_2O	Cl^-

most nucleophilc *least nucleophilic*

NH_2^-	HO^-	PhO^-	NH_3	H_2O	Cl^-

most basic *least basic*

because HCl the strongest acid, then H_3O^+ then NH_4^+ then PhOH (marginally) then H_2O then NH_3

Temperature (and Entropy)

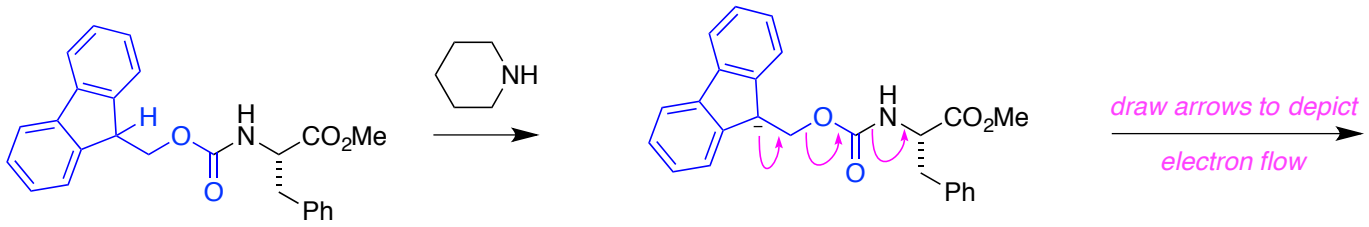
E2 and S_N2 over *E1* and S_N1.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

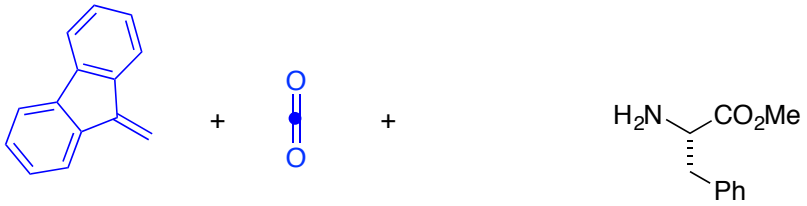
E2 and S_N2 over *E1* and S_N1 reactions.
E1 and S_N1 over *E2* and S_N2 reactions.

E. E1cB

FMOC
carbamates.



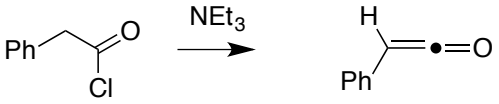
anionic intermediate



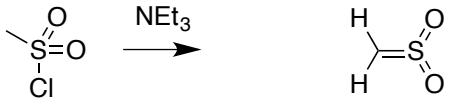
product (methyl phenylalanine)

14 πe,
aromatic.

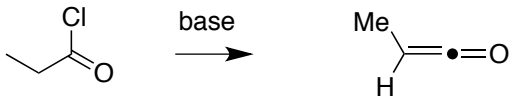
F. Eliminations To Give Allenes, Alkynes, Ketenes And Sulfenes



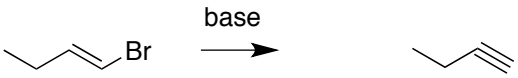
ketene



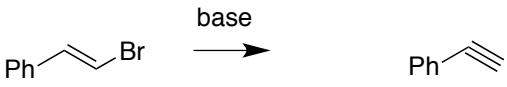
sulfene



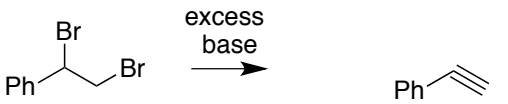
ketene



alkyne



alkyne



alkyne

Reactions Of Alkenes Via Protonation

from chapter(s) _____ in the recommended text

A. Introduction

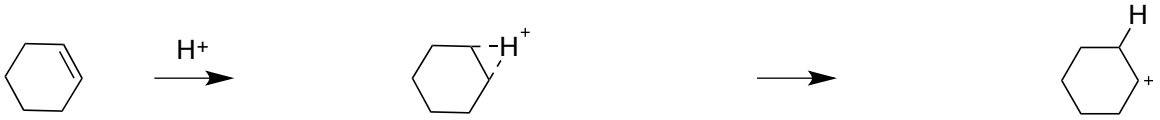
B. Protonation Of Alkenes

Generation Of Carbocations Via Protonation

simplest
sp^3 hybridized carbon and a sp^2
transition
intermediate.

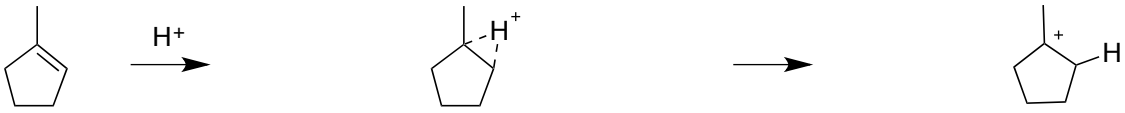
protonated alkene
transition state

carbonium ion
intermediate



protonated alkene
transition state

carbonium ion
intermediate



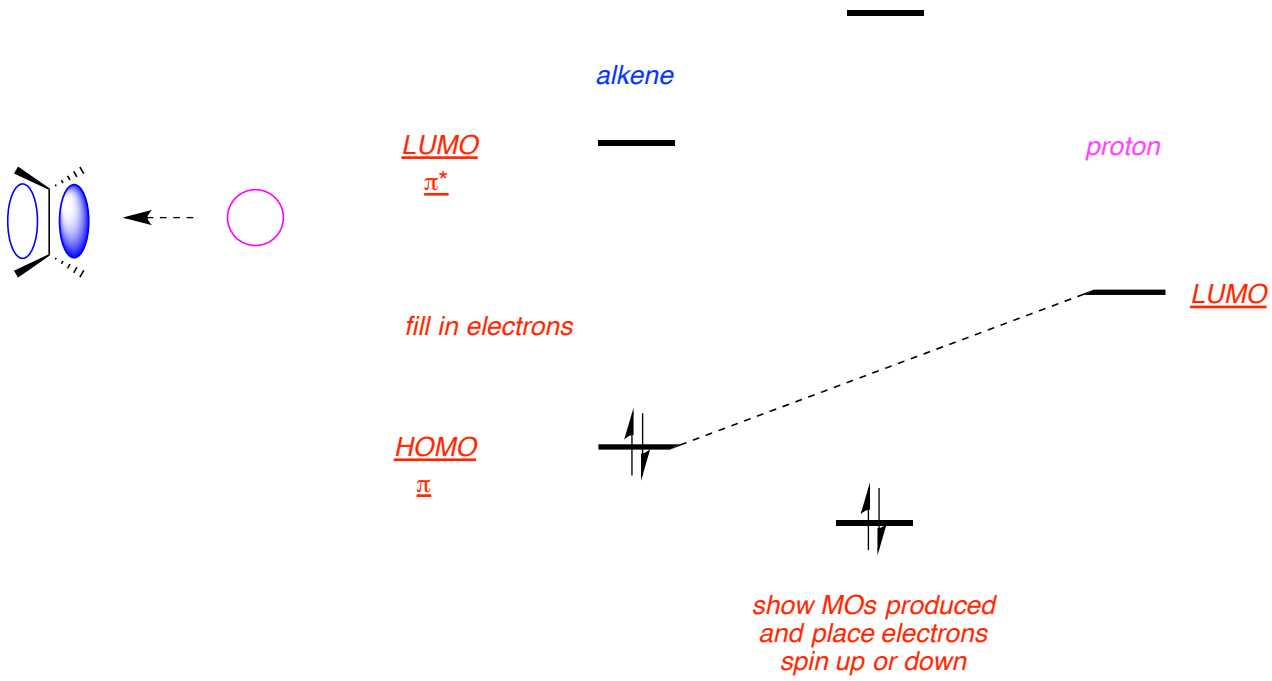
protonated alkene
transition state

carbonium ion
intermediate

sp^3 hybridized carbon and sp^2

A Molecular Orbital Picture Of Alkene Protonation

more
does not
LUMO
LUMO
HOMO



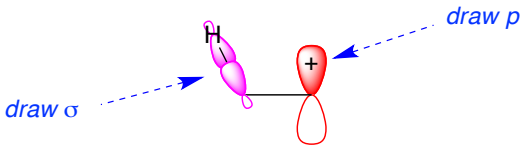
stabilizing.

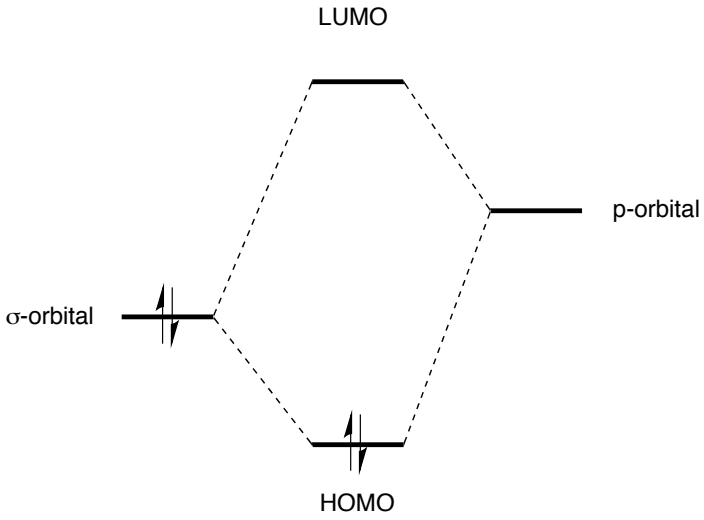
C. Carbocation Stabilities

alternative theories to explain bonding in general.

(*LUMO*)

methyl (*HOMO*





2 electrons into the interaction, whereas the p-orbital bears *0*

2_

are in the same plane.

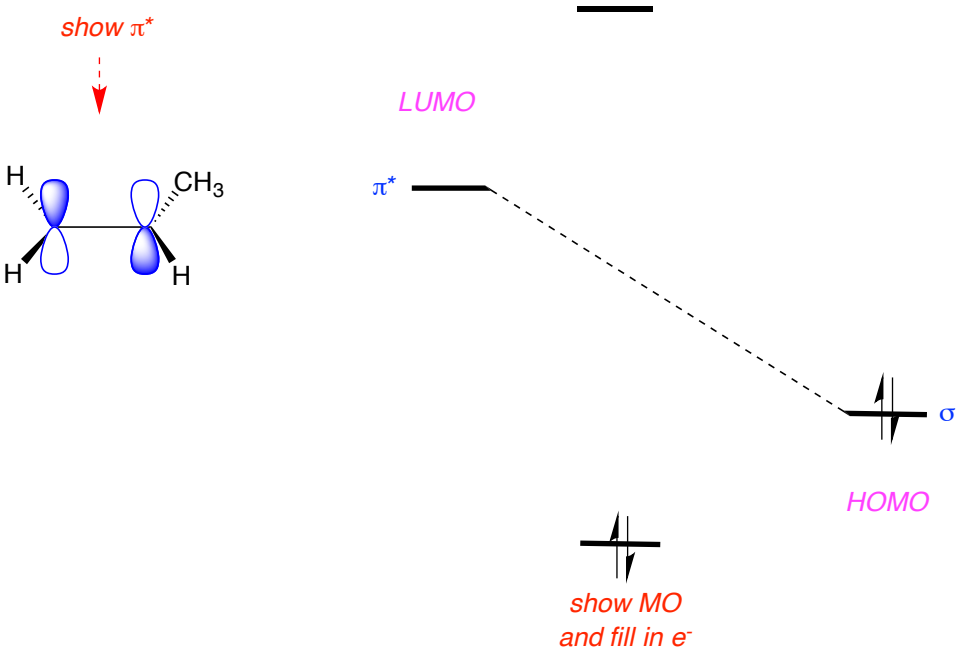
cannot achieve significant orbital overlap.

2 adjacent methyl groups, and therefore *2* *more*

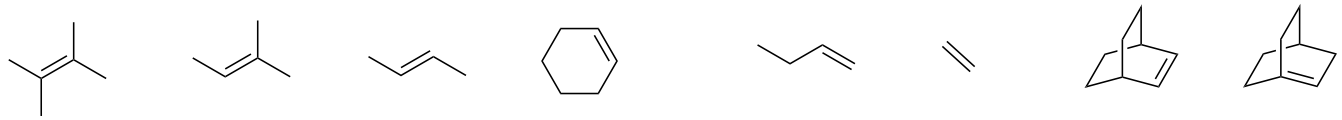
3 adjacent methyl groups, and therefore *3* *more*

D. Alkenes Stabilities

increase with



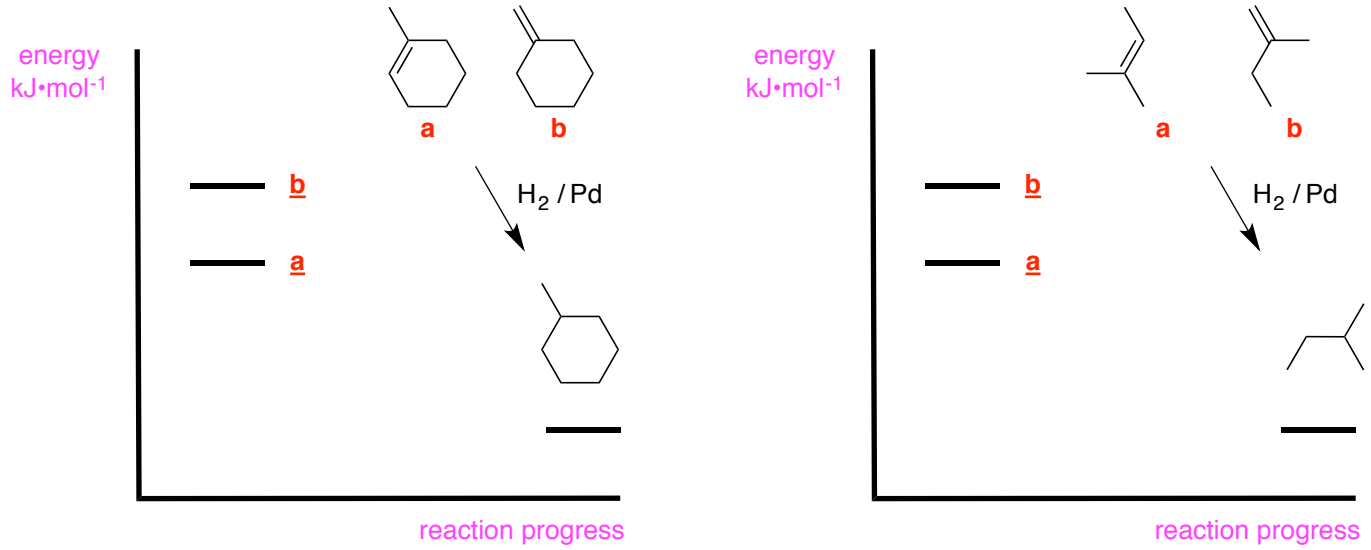
stabilizing
enhanced



most stable *least stable*

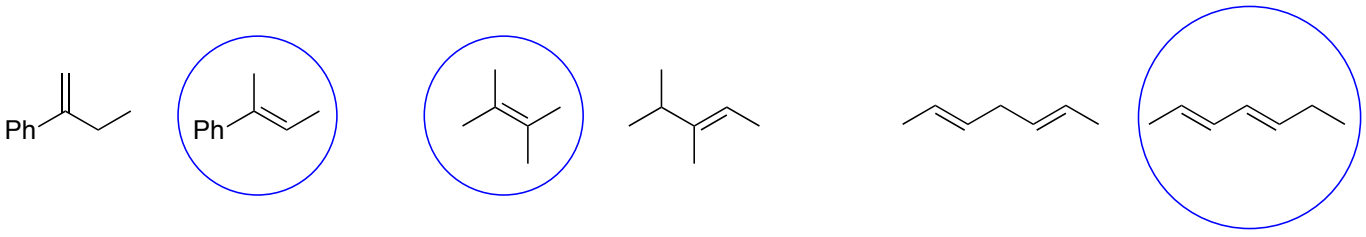
Heats Of Hydrogenation

Energy is *liberated*
lower
can
hydrogenation.

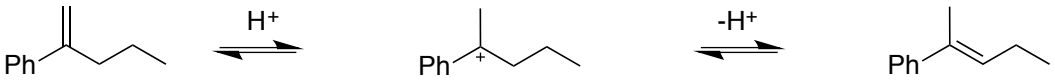


b
the right it is *b*.

E. Acid-mediated Alkene Isomerization

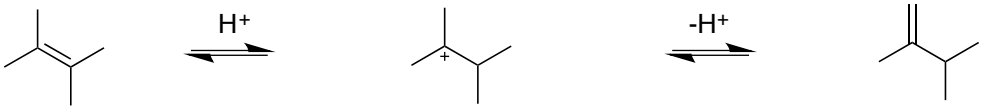


is an isomer of the first.
thermodynamics.



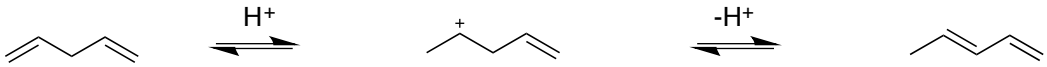
K = ≥1

carbocation alkene



K = ≤1

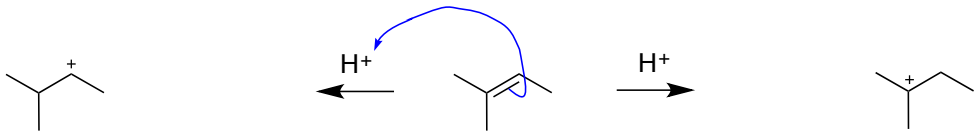
carbocation alkene



K = ≥1

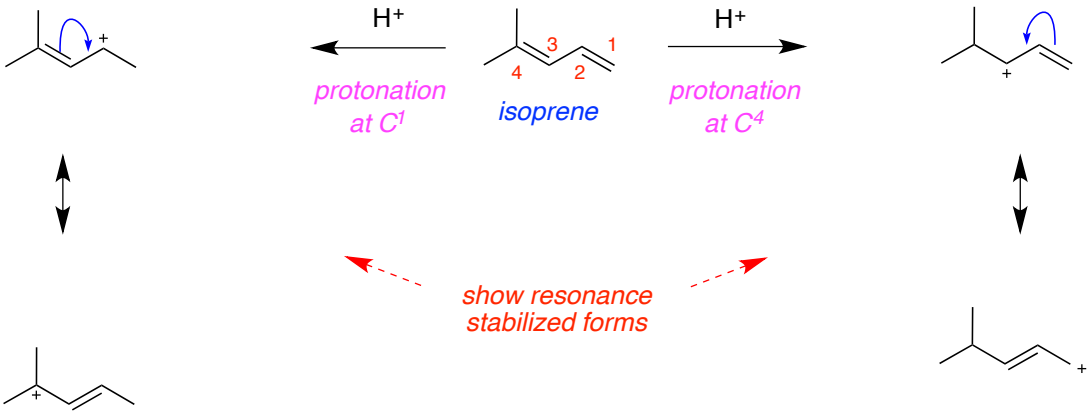
carbocation alkene

It is *conceivable*



least favorable
2° carbonium ion

most favorable
3° carbonium ion



protonation at C¹

isoprene

protonation at C⁴

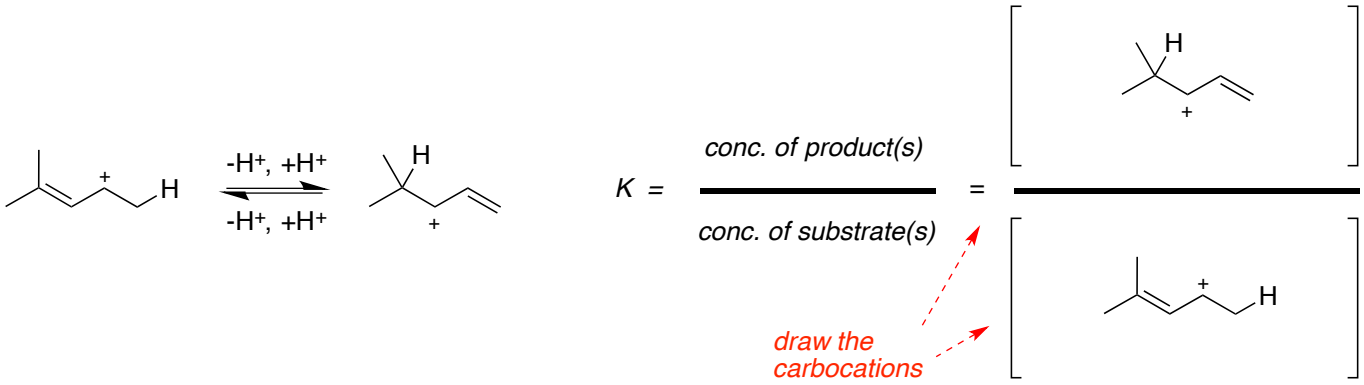
show resonance stabilized forms

most favorable
3° carbonium ion

least favorable
1° carbonium ion

gives
does not.

small
equals



less than one.

F. Carbocation Rearrangements

Hydride Shifts

hydride

hydride anion.

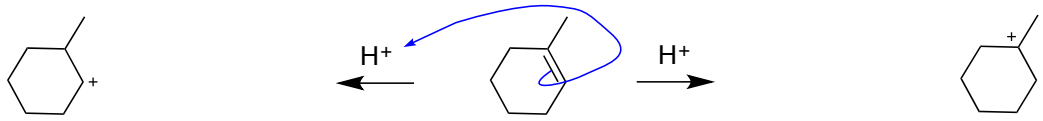
: true.

1,2-hydride

may

most

intermediates



least favorable
2° carbonium ion

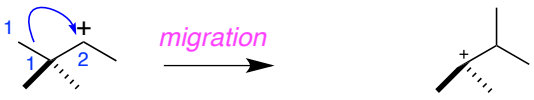
most favorable
3° carbonium ion

Alkyl Shifts

opposite
more
secondary / tertiary
tertiary

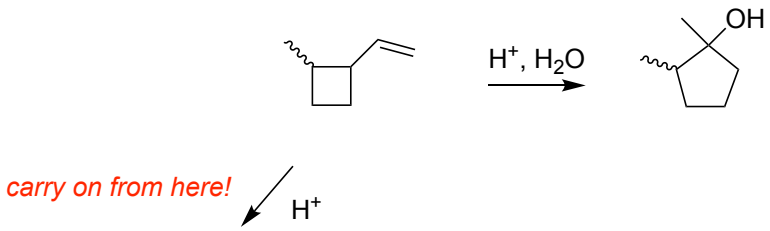
1,2-

draw curly arrows



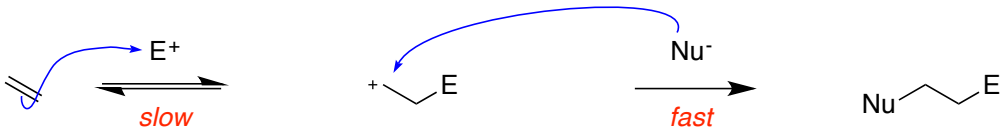
draw curly arrows
and product

alkyl shift
most able
less stable than Et^+.



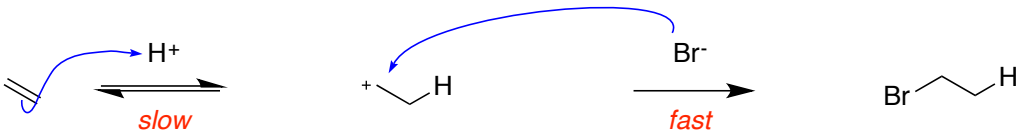
see: https://youtu.be/FsQb6o510EY

G. Electrophilic Addition Mechanisms



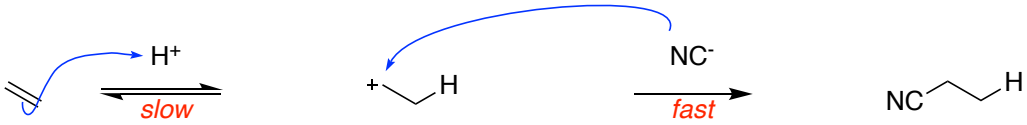
carbocation intermediate *addition product*

slow



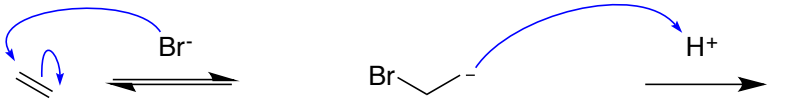
carbocation intermediate

addition product



carbocation intermediate

addition product



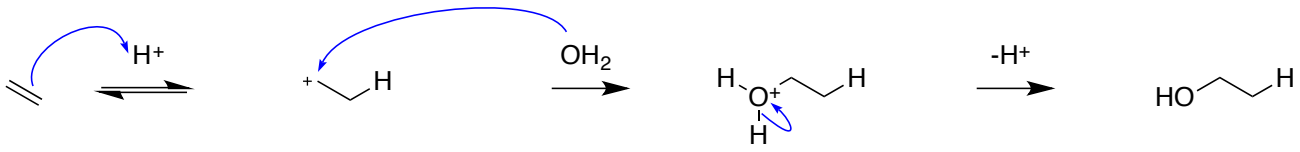
carbanion intermediate

addition product

does not proceed

- bromide, being negatively charged, is repelled by electrons in the alkene π-bond

proton,



carbocation intermediate | *protonated addition product* | *hydration product*

H. Acid-mediated Hydration Of Alkenes

1°.

two

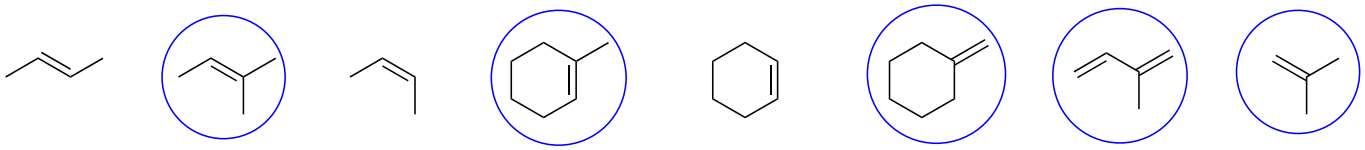
ie *regioisomers*;

2-propanol | *1-propanol*

regioselective.

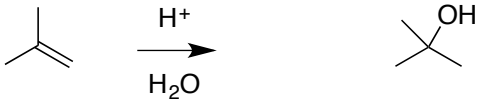
, reactions that involve reaction of one chemical functional group in preference to others are called *chemoselective*.

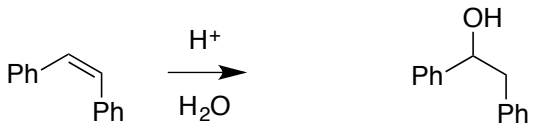
enantioselective and *diastereoselective*

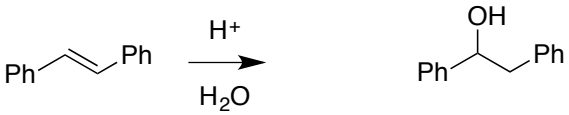


gives 2-propanol
more stable

gives 1-propanol
less stable

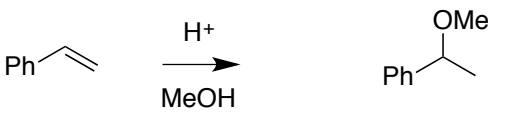


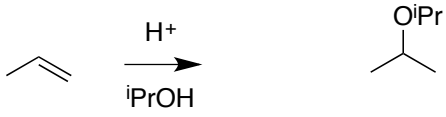


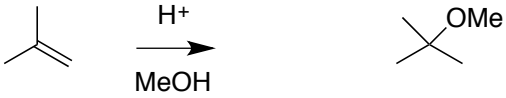


E1 pathway.

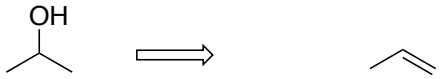
ethers.

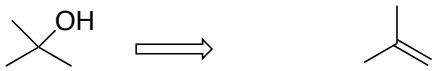


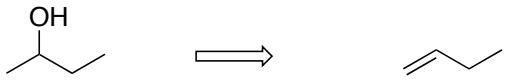


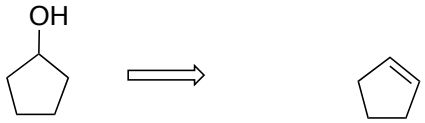


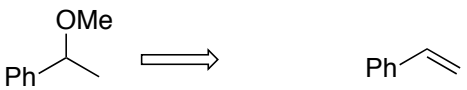
are not

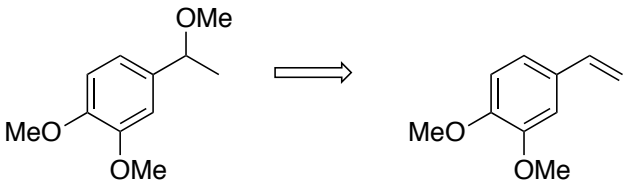

OH

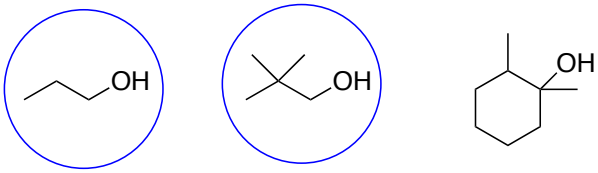

OH


OH


OH


OMe
Ph
Ph


OMe
MeO
OMe
MeO
OMe


OH
OH
OH
OH
OH
OMe

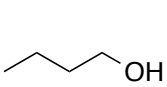
Oxidation States, Hydrogenation, And Hydrogenolysis

from chapter(s) _____ in the recommended text

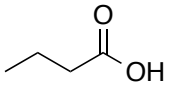
A. Introduction

B. Oxidation States In Organic Chemistry

addition
loss
addition
loss
more *less* *C-O*,
less *C-H* bonds
more *C-O*,



a



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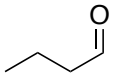
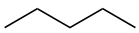


c



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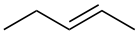
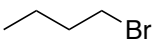
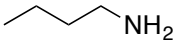


e

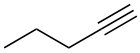


f

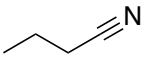
g



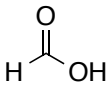
h



i



j



k

l

m

n

o

lowest oxidation state **d**

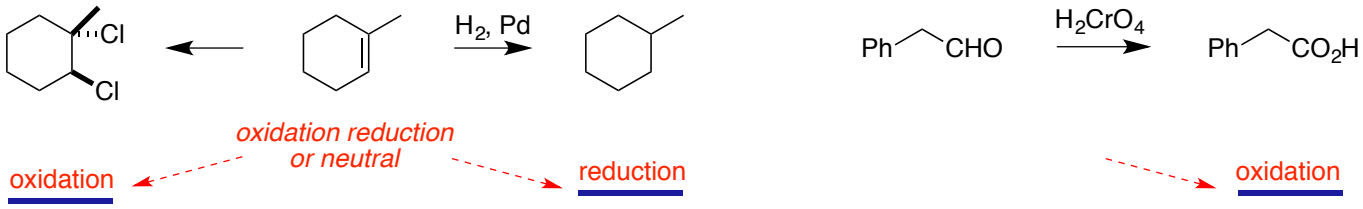
one level higher **a, e, f, h**

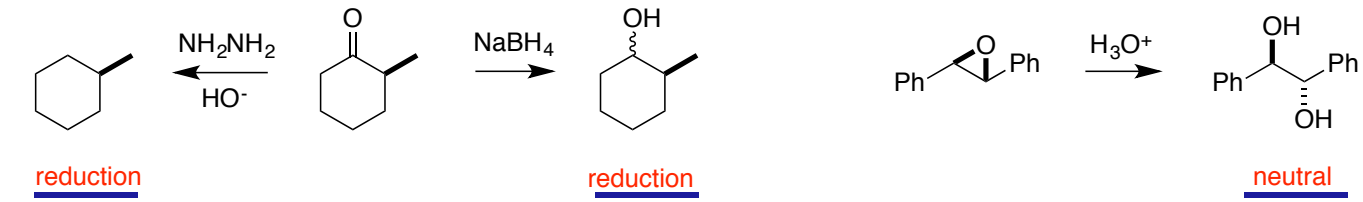
one more level higher **c, i, l, o**

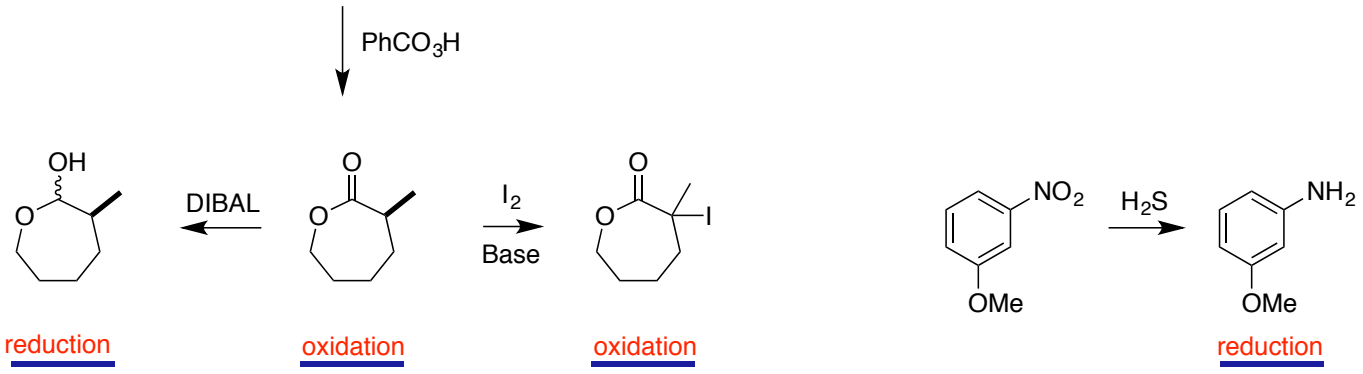
still another level higher **b, j, k, n**

highest oxidation state **g, m**

Cyclohexane is at a *higher*



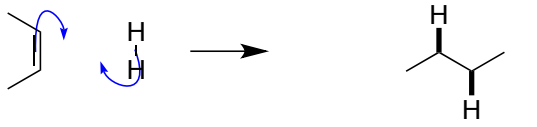


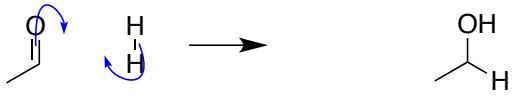


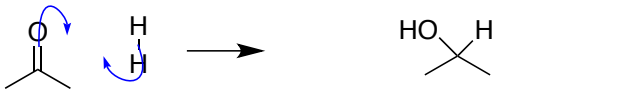
C. Addition Of H_2

Hydrogenation And Hydrogenolysis

Hydrogenation reactions
hydrogenolysis involve
homolytic
radical mechanism, than a *ionic*

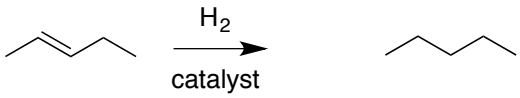


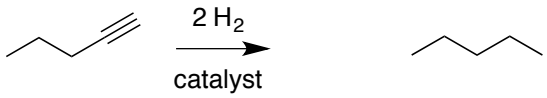


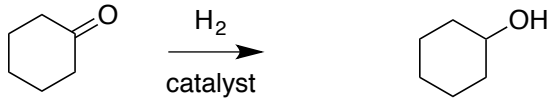


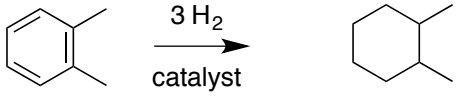
stabilize
benzyl
more
.

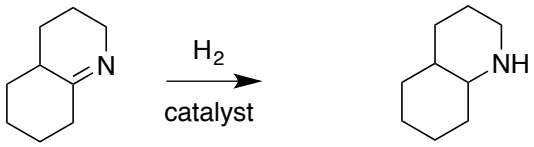
D. Hydrogenation



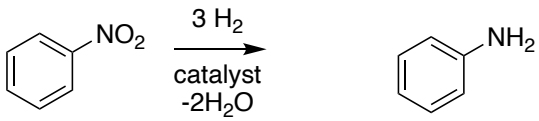


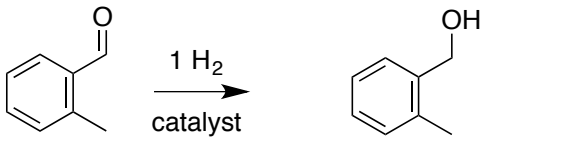


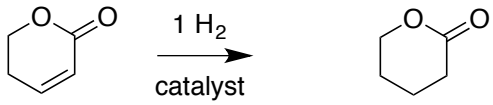

3 H2
catalyst


N
H2
catalyst
NH

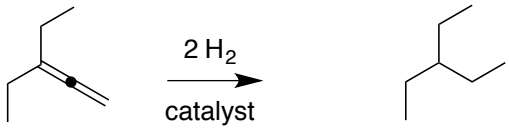

N
2 H2
catalyst
H2N

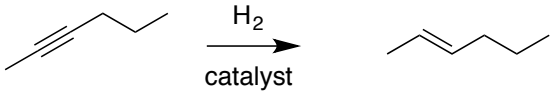

NO2
3 H2
catalyst
-2H2O
NH2

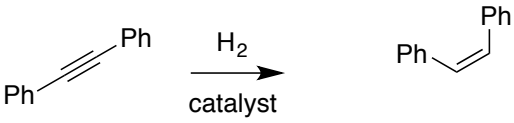

O
1 H2
catalyst
OH


O
O
1 H2
catalyst
O
O


2 H2
catalyst

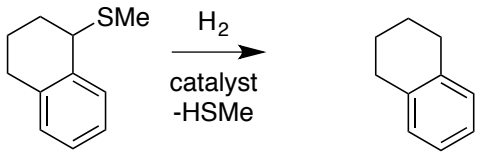

2 H2
catalyst

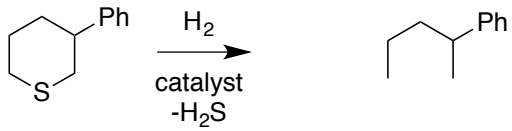

H2
catalyst

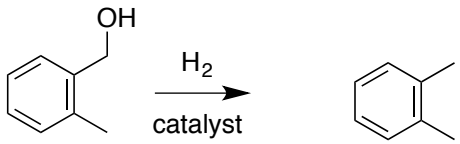

Ph
Ph
H2
catalyst
Ph
Ph

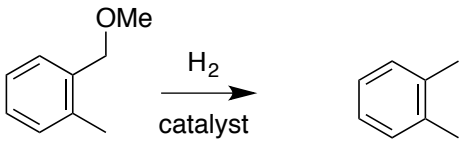
E. Hydrogenolysis

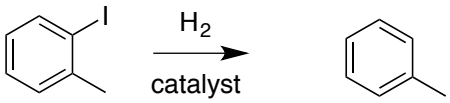
single

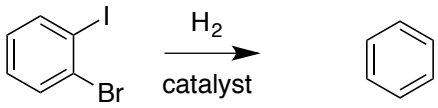


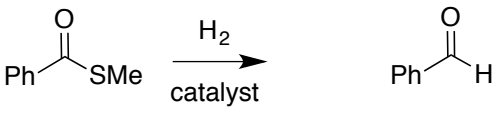


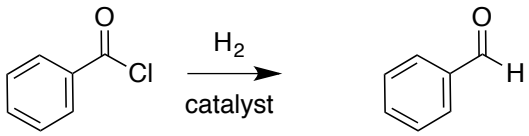




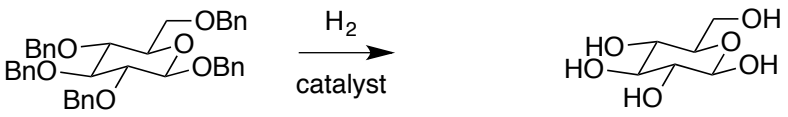


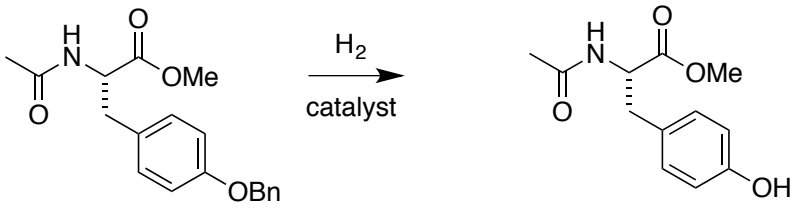


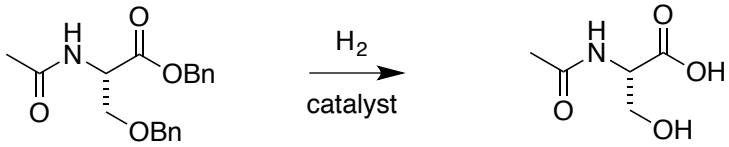


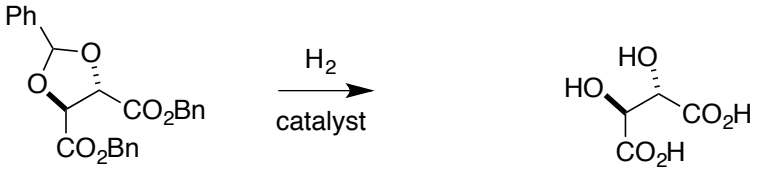


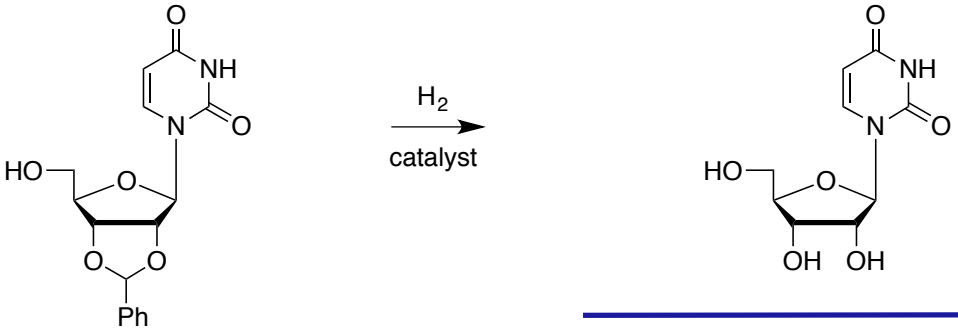
further hydrogenolysis of these products is possible


OBn
BnO
O
BnO
OBn
BnO
H2
catalyst
OH
HO
O
HO
OH
HO

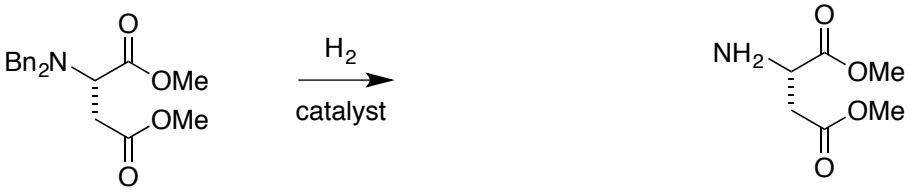

H
N
O
O
OMe
O
OBn
H2
catalyst
H
N
O
O
OMe
O
OH


H
N
O
O
OBn
O
OBn
H2
catalyst
H
N
O
O
OH
O
OH

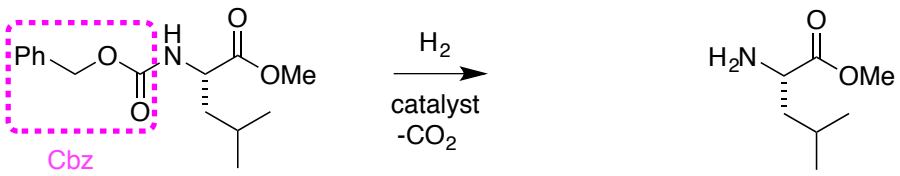

Ph
O
O
CO2Bn
CO2Bn
H2
catalyst
HO
HO
CO2H
CO2H



does not reduce the base



harder
Cbz.

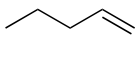


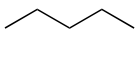
F. Double Bond Equivalents

1 and *2* molecules of H_2
4 molecules of H_2
can be calculated

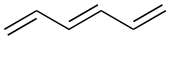
can
1 and *1*, respectively.

(*True*,
1 and *4*
0
True,

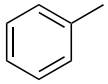

1


0


1


3


4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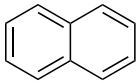
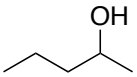
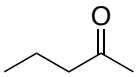

7

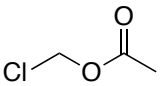

2



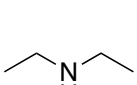
0



1



1



0

1

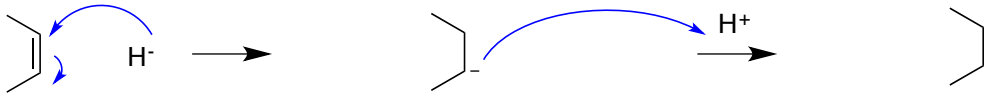
4

0

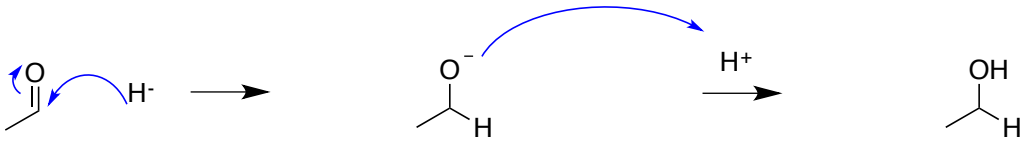
0

do not apply

G. Hydridic Reductions



hard



easy

Halogenation Of Alkenes

from chapter(s) _____ in the recommended text

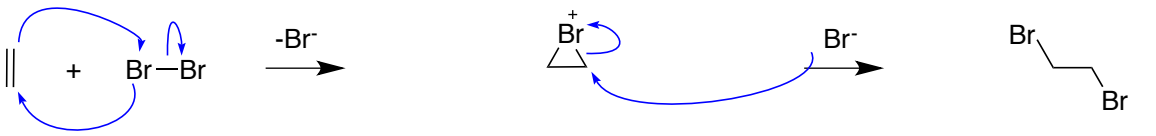
A. Introduction

B. Mechanism

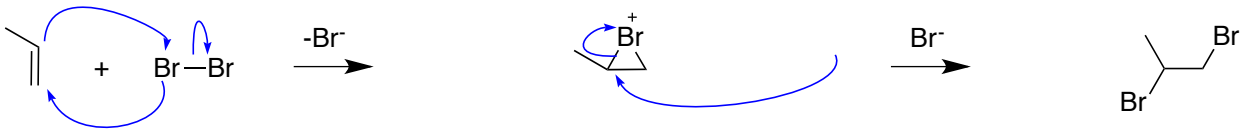
parallel
polarized
positively
is

Chlorination and Bromination

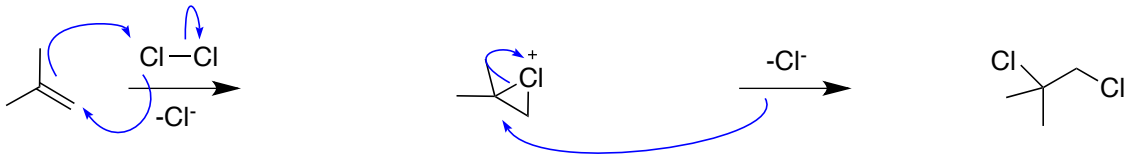
intermediates.



bromonium ion *1,2-dibromide*



bromonium ion *1,2-dibromide*



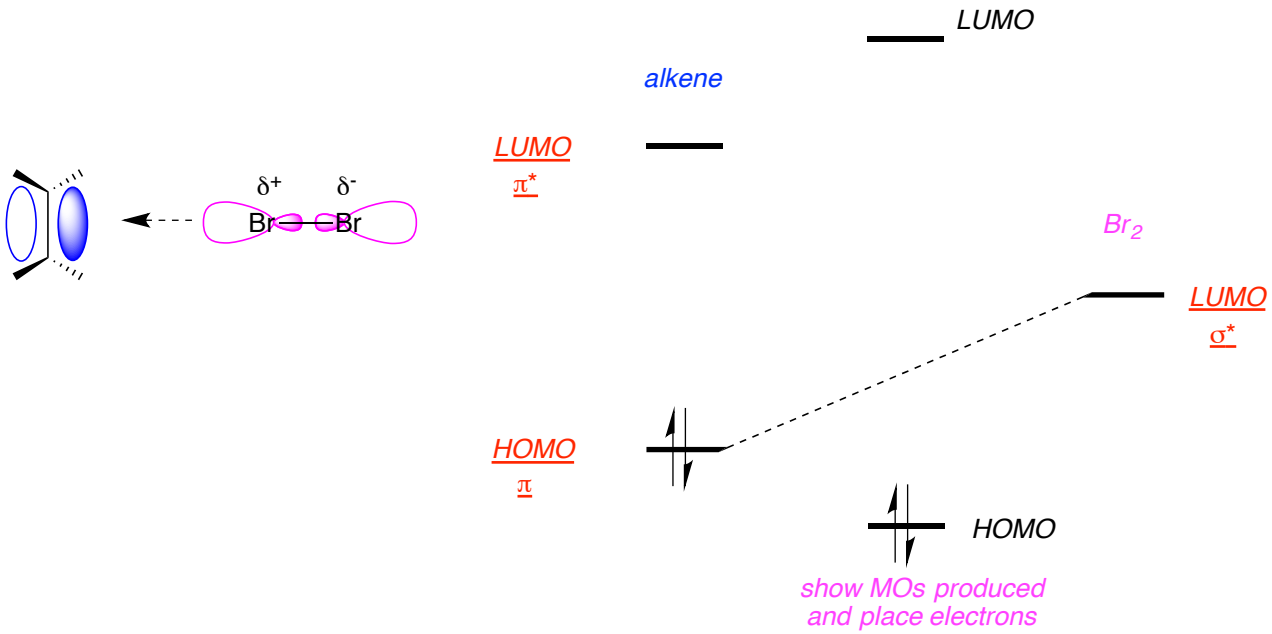
Halogens (X_2) are *electrophiles*
Nucleophiles
electrophile
becomes polarized in the presence of high electron density.

electrophilic
nucleophilic
faster

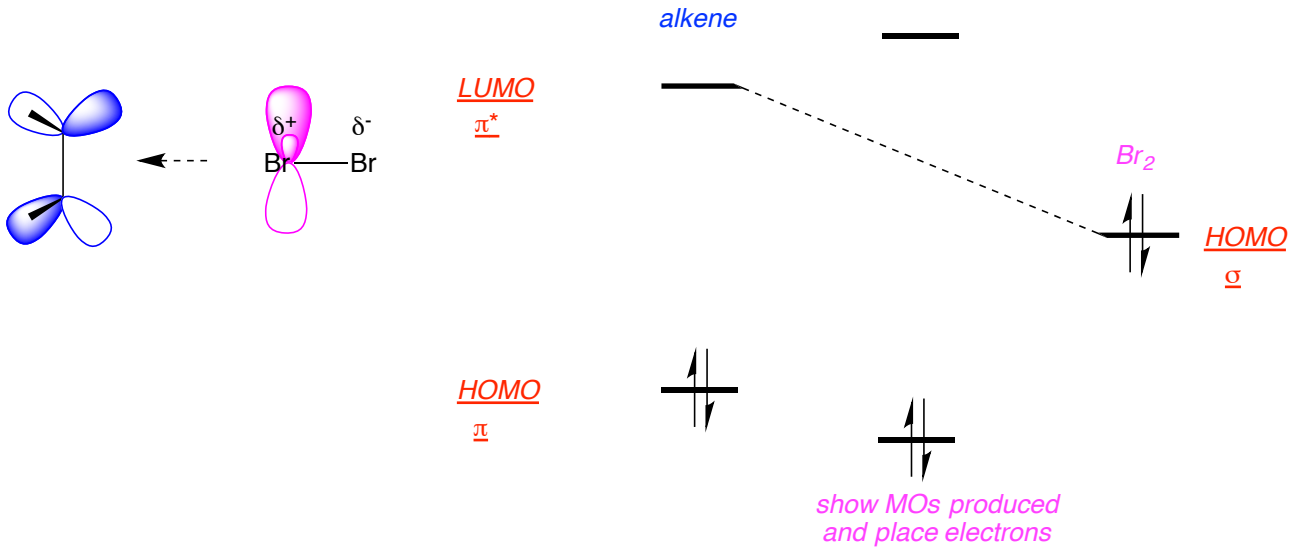
fastest bromination *slowest bromination*

addition

A MO View Of Halogenations



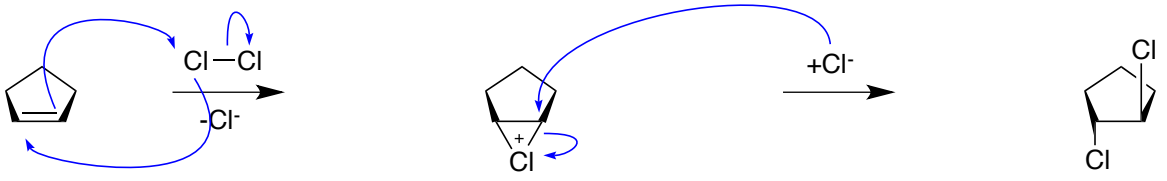
stabilizing,
primary
secondary

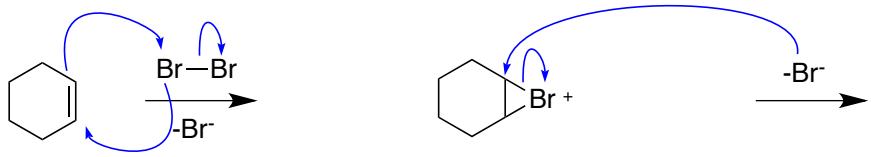


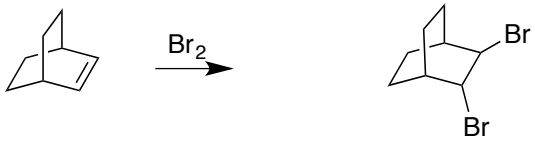
do not

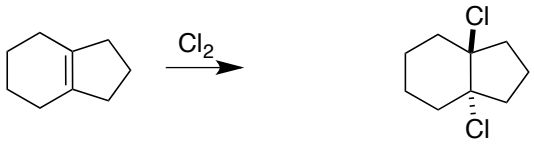
Stereospecificity
S_N2
anti
endocyclic
trans-

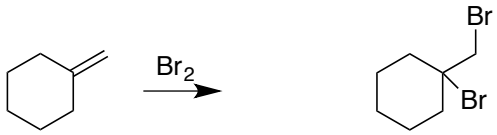
mostly trans-
opposite
stereospecifically-
always
.



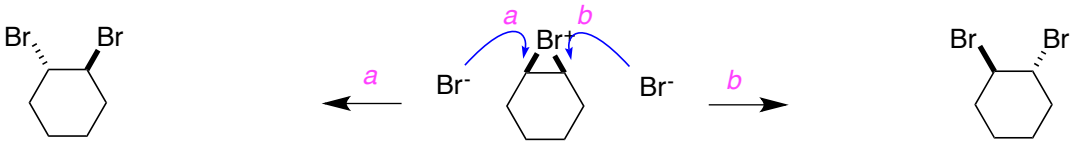








enantiomers

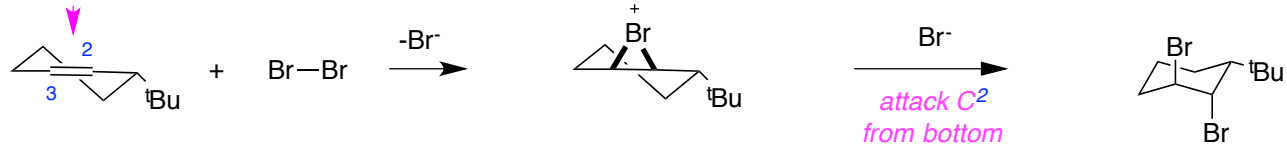


S,S *R,R*

equal
a racemate
is not

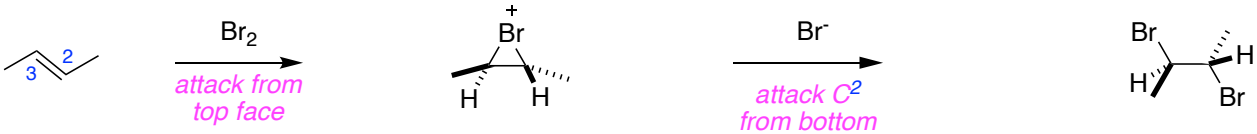
equal

bromonium ion formation



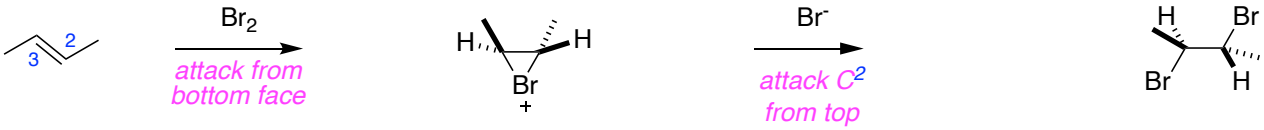
bromonium ion

1,2-dibromide



bromonium ion

dibromoalkane



bromonium ion

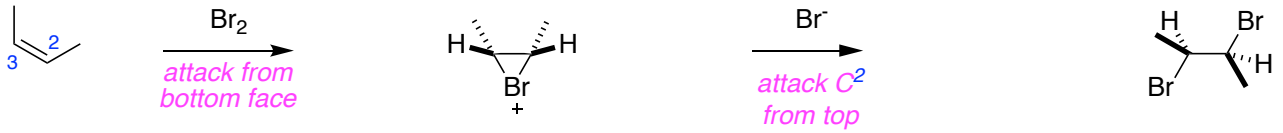
dibromoalkane

identical.

.

bromonium ion

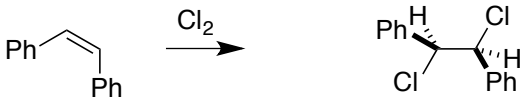
dibromoalkane

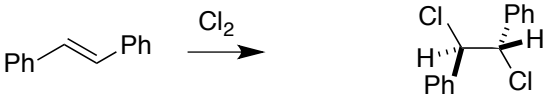


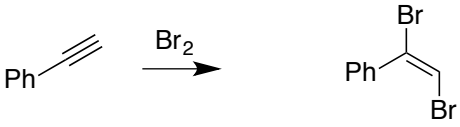
bromonium ion

dibromoalkane

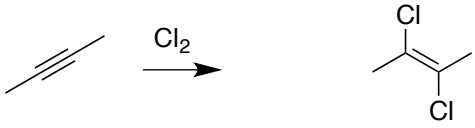
diastereomers.





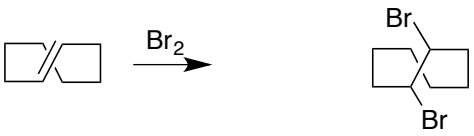


trans-1,2-dibromophenylethene

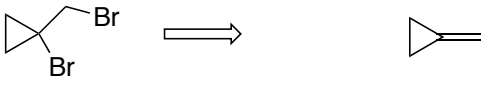


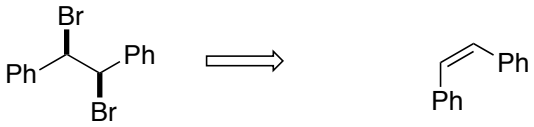
trans-2,3-dichlorobut-2-ene

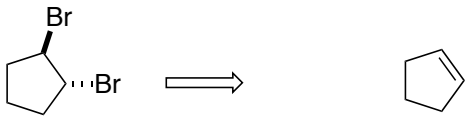
trans-

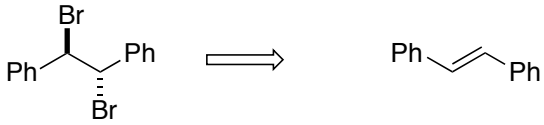


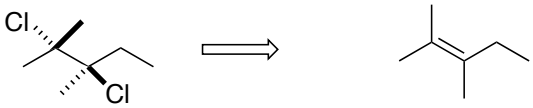
cis-

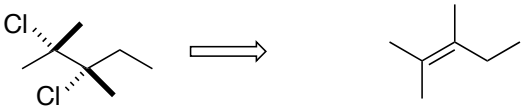








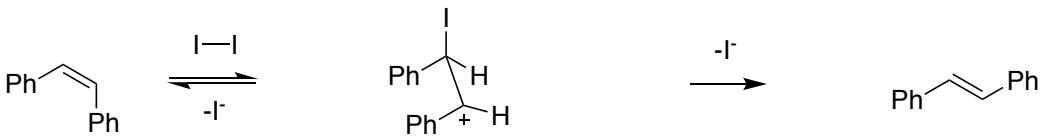




Iodination

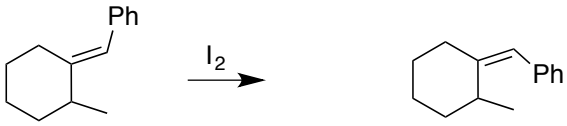
the product is thermodynamically unstable relative to ethene and iodine.

Following question in first edition is confusing so the question/answer will be simplified in the second edition to this:

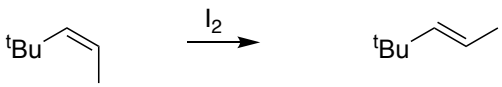


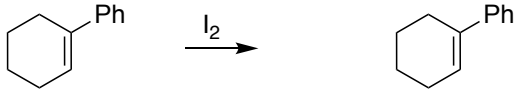
carbocation

E-1,2-diphenylethene



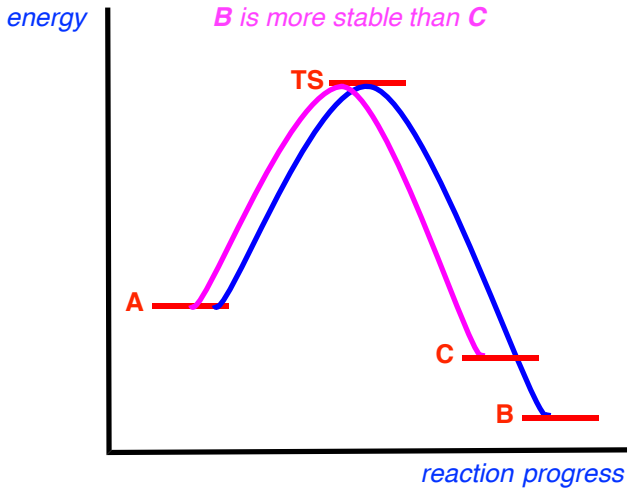
new question for 2nd edition

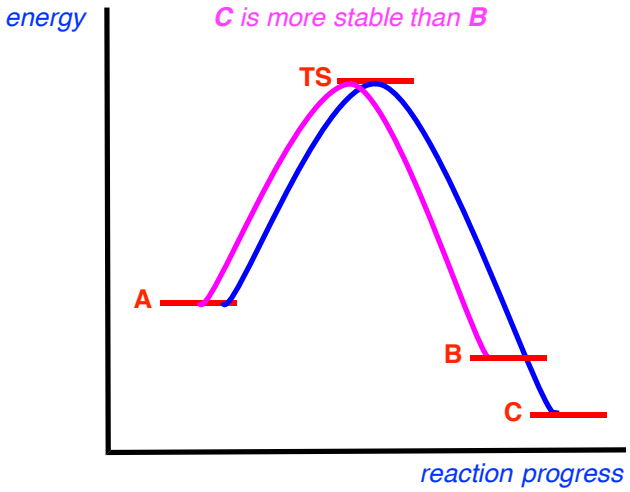




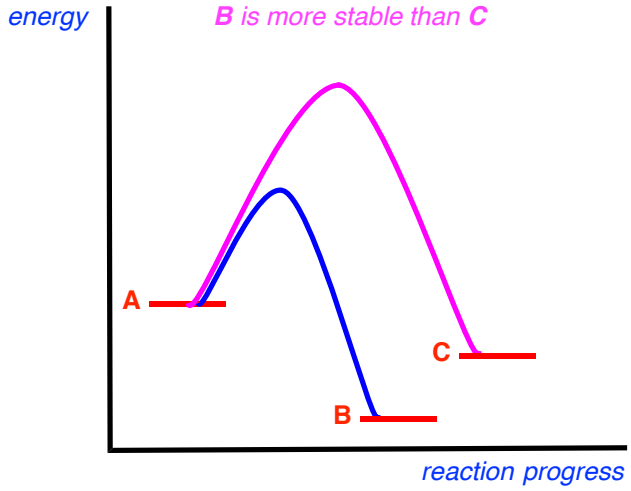
C. Kinetic And Thermodynamic Control

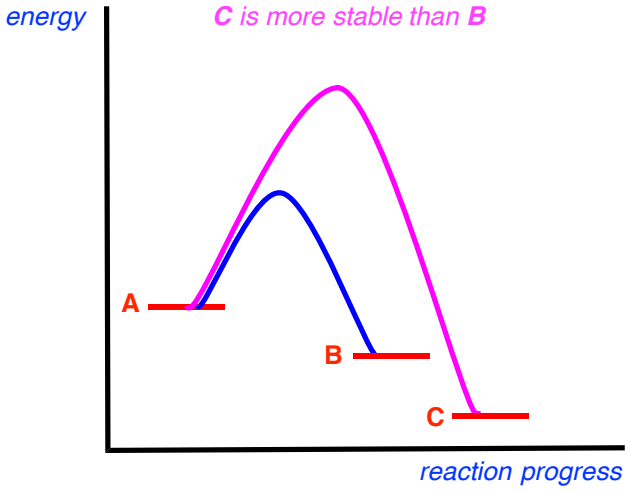
Kinetic Control





lower
cannot
is not
is dictated
1, and when **C** is more stable than **B** it will be *1*.





rates of formation,
be invariant
kinetic one.

Thermodynamic Control

reversible
>1.
will not

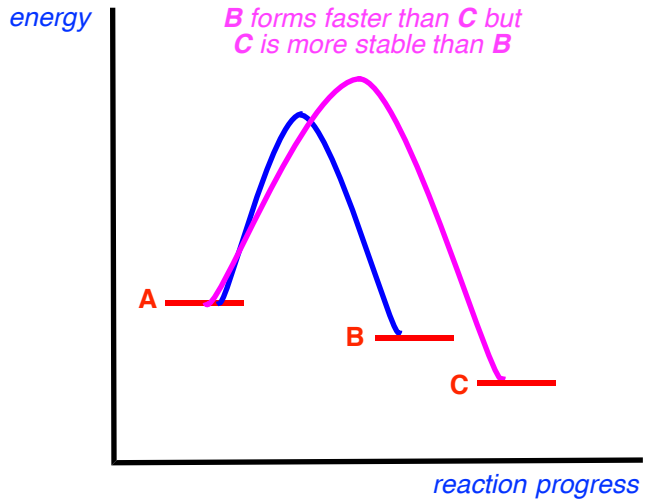
$$K_B = [\ B\ ] / [\ A\ ] \quad \text{and} \quad K_C = [\ C\ ] / [\ A\ ]$$

is another

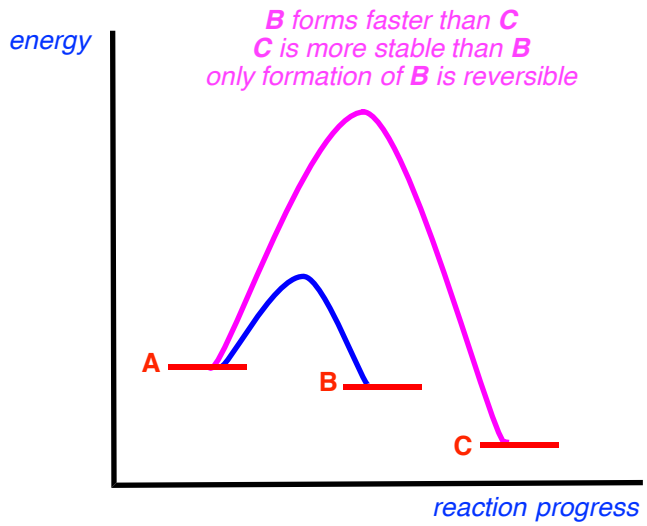
$$K_{BC} = [\ B\ ] / [\ C\ ]$$

independent of
coincident
activation energy barriers
stabilities of the products.
These ratios are *different*

Non-coincident Kinetic And Thermodynamic Control



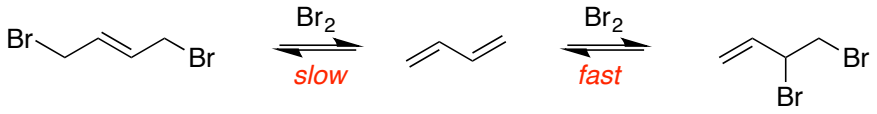
kinetic
reversibly.
thermodynamic
reversibly.
be disfavored because it will revert as the reaction proceeds and *reversibly* forms **C**.



kinetic product; only **B** forms *reversibly*.
thermodynamic product; it forms *irreversibly*.
not be observed because it will revert as the reaction proceeds and *irreversibly*

kinetic
thermodynamically

Bromination 1,3-Butadiene: Non-coincident Kinetic And Thermodynamic Control



1,4-dibromide more stable

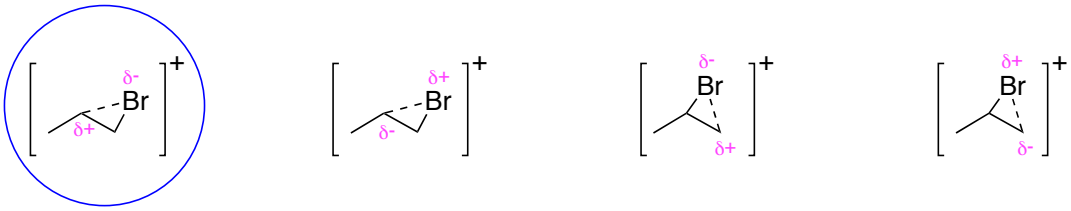
1,2-dibromide less stable

kinetic
decreases
increases.

the alkene products: 1,4-dibromide has two groups substituted on the alkene product while 1,2-isomer has only one group.

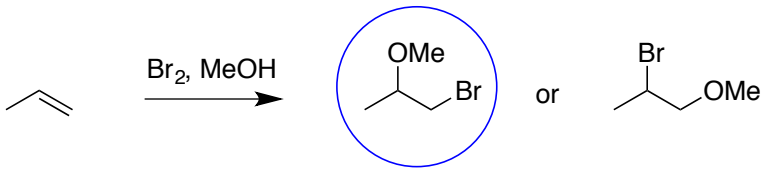
less
does not proceed

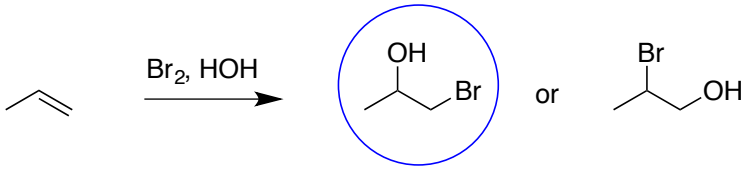
D. Halogenations In Nucleophilic Solvents



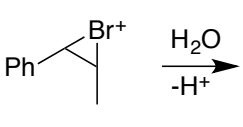
best

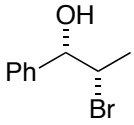
Regio--selectivity
regioisomers.

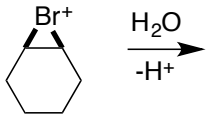


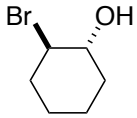


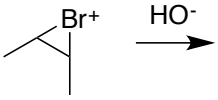
halohydrin
this is the precursor to the most stable cation.

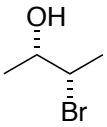


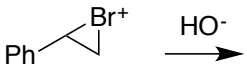


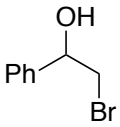












are

Epoxidation Of Alkenes, And Epoxides

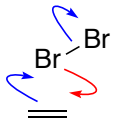
from chapter(s) _____ in the recommended text

A. Introduction

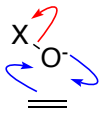
.

B. Reagents And Mechanism

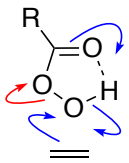
pushing



bromination

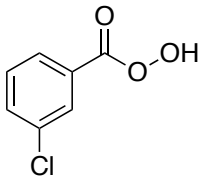


epoxidation general
X is leaving group

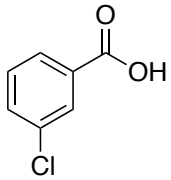


epoxidation with peracid

3
pushes
electrophilic



mCPBA



product after donation of oxygen

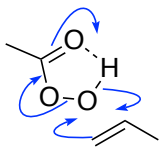
dimethyldioxirane

product after donation of oxygen

electrophilic
nucleophile.

addition reaction.

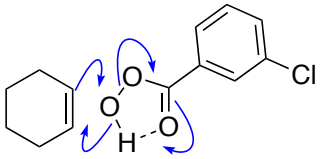
peracetic acid



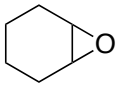
propene

propene oxide

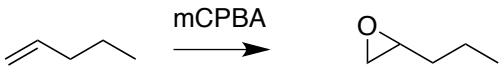
mCPBA

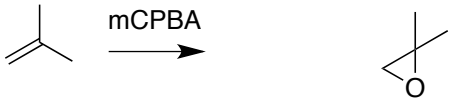


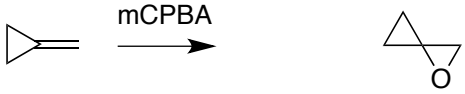
cyclohexene

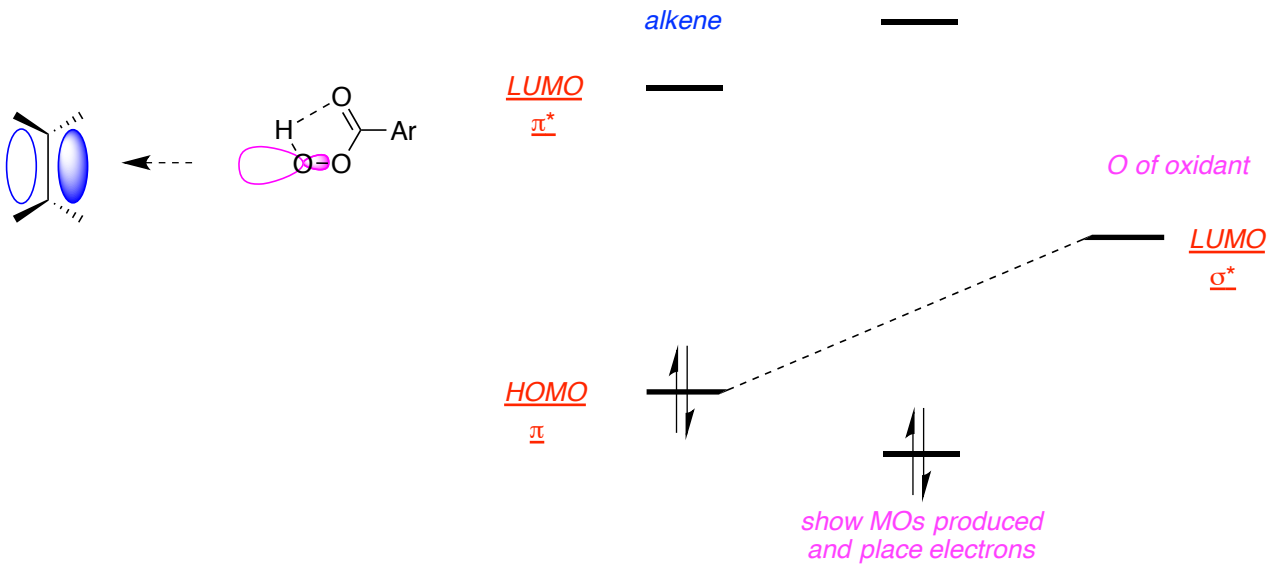


cyclohexene oxide





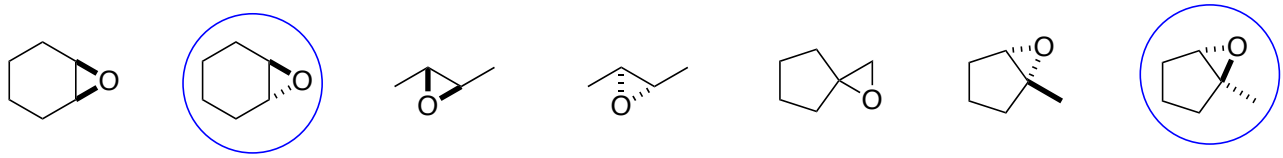




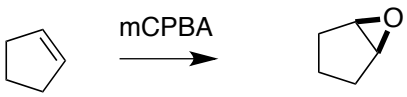
C. Rates Of Epoxidation

fastest epoxidation *slowest epoxidation*

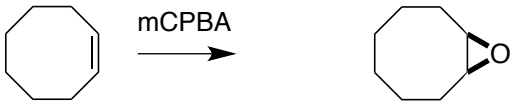
D. Stereospecificity



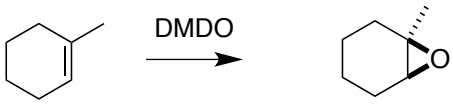
conserved



cis



cis



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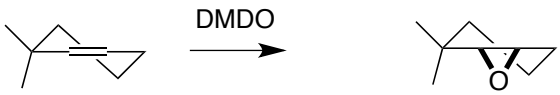

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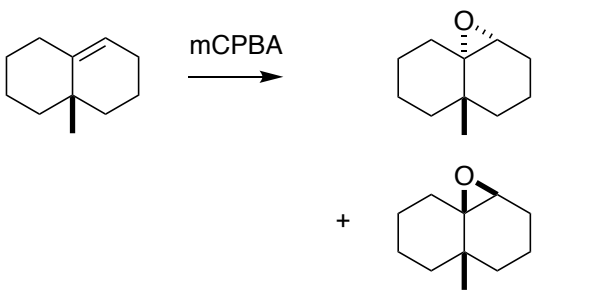
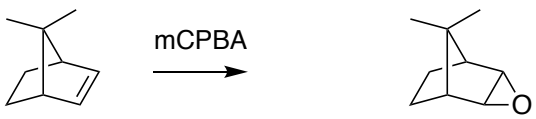
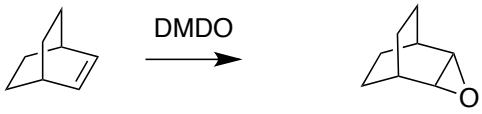


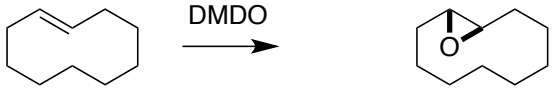
cis



cis
show stereically least hindered product



cis



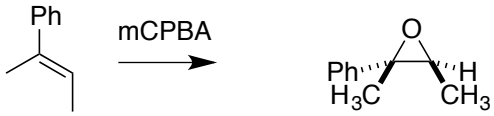
cis

always gives the *cis*

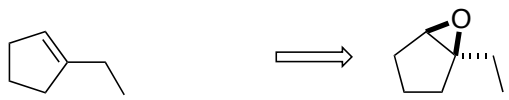
trans

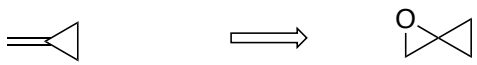
cis

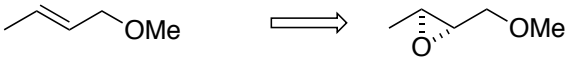
cis

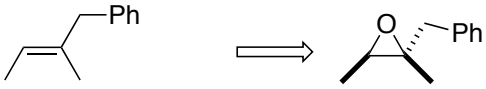


trans







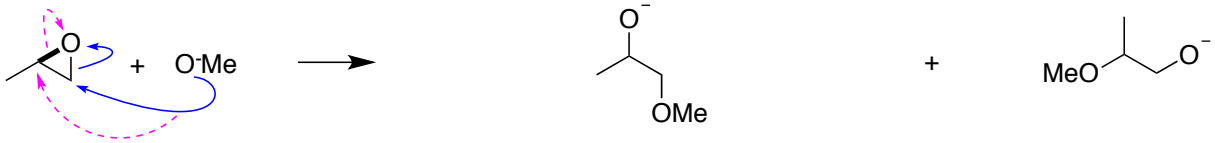


E. Regioselectivity Of Epoxide Ring Opening Reactions

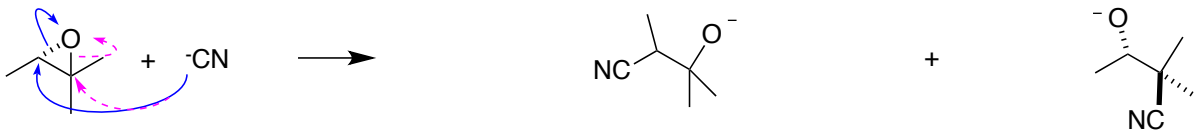
Under Neutral Or Basic Conditions

regioisomeric products

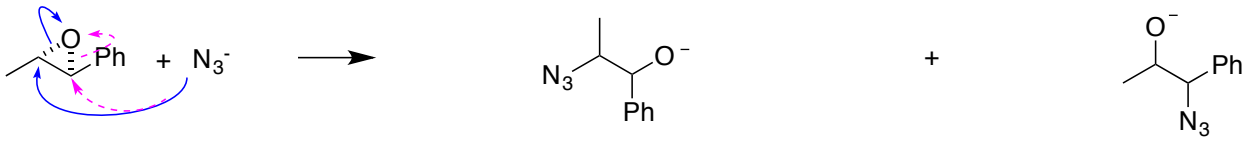
steric factors.



major *minor*



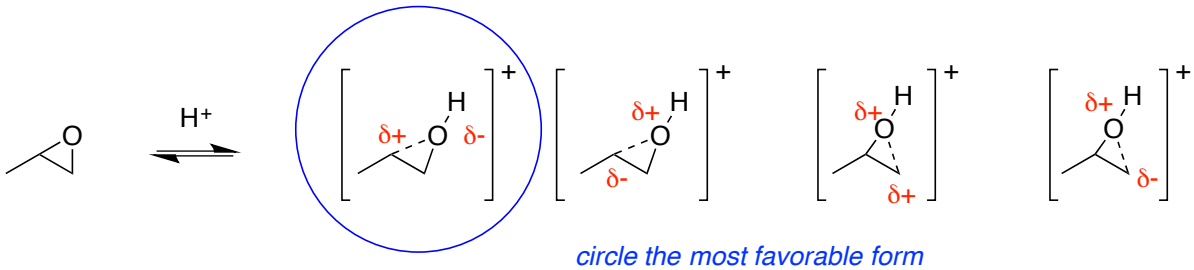
major *minor*



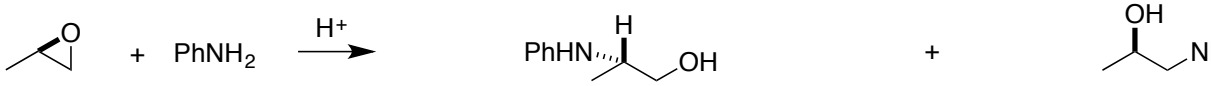
major *minor*

regioselective and not *regiospecific*.

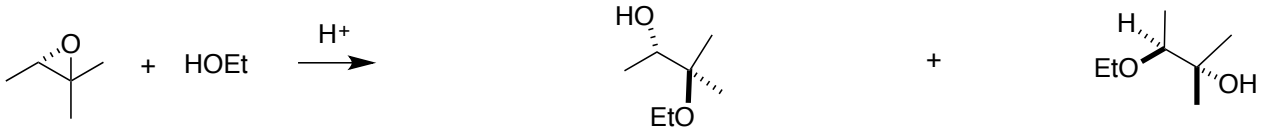
Under Acidic Conditions



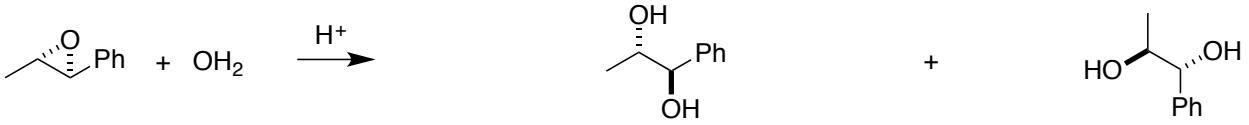
circle the most favorable form



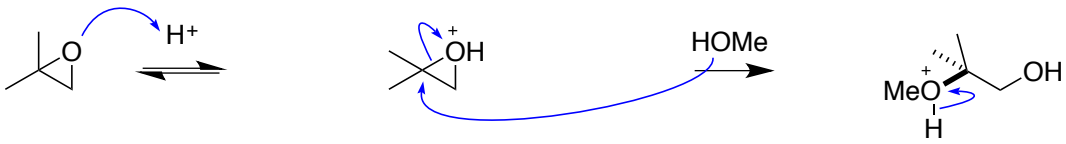
major *minor*

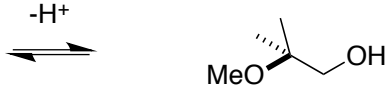


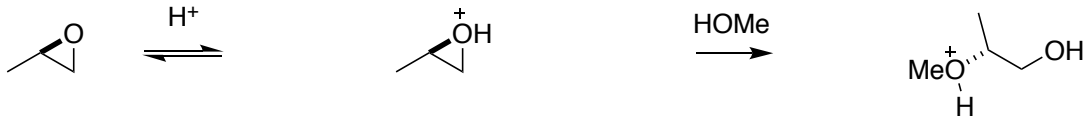
major minor

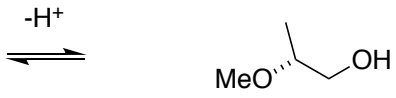


major minor






O
H+
OH
HOMe
MeO
H
OH


-H+
MeO
OH

Cycloadditions To Alkenes And Alkynes

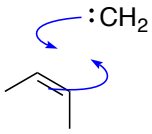
from chapter(s) _____ in the recommended text

A. Introduction

.

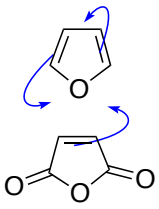
B. Nomenclature Of Cycloadditions

[3 + 2] could



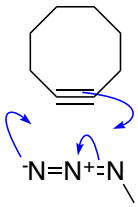
[2+1]

cyclopropanation



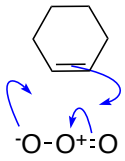
[4+2]

Diels-Alder



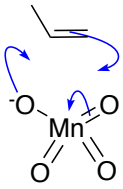
[2+3]

click reaction



[2+3]

ozonolysis



[2+3]

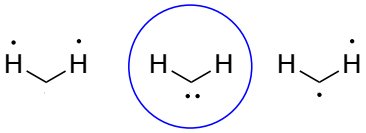
dihydroxylation

C. Carbene Additions [2 + 1] (Cyclopropanations)

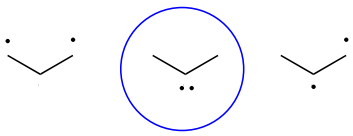
two: *true*.

6 electrons in the valence shell of carbon.
4.
is not

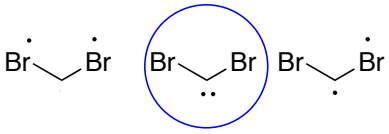
an empty p-orbital, *ie* *singlet*
a diradical structure, *ie* *triplet*



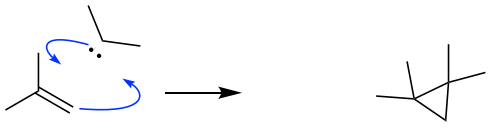
carbene

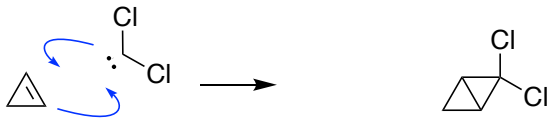


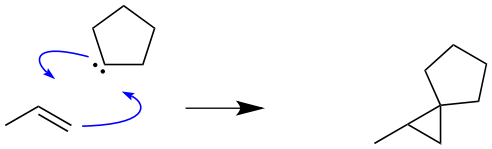
dimethylcarbene

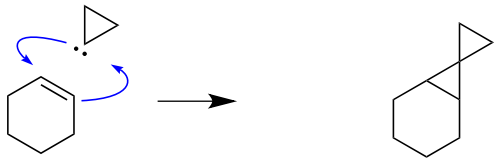


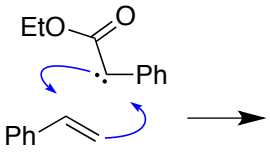
dibromocarbene

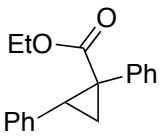




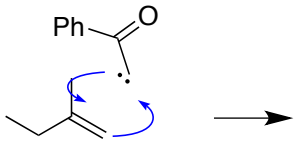


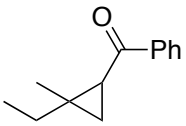






show only trans-product



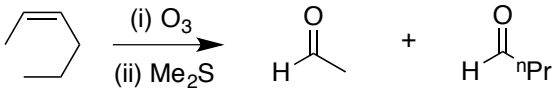


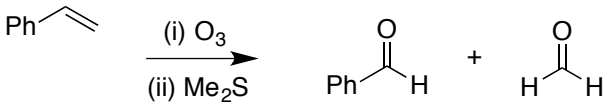
show only trans-product

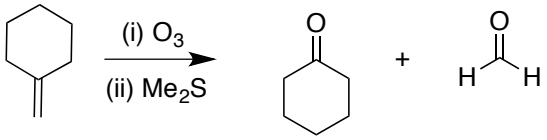
spiro-compounds.

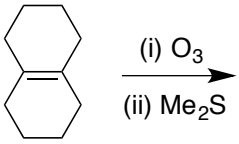
D. Ozonolysis [2 + 3]

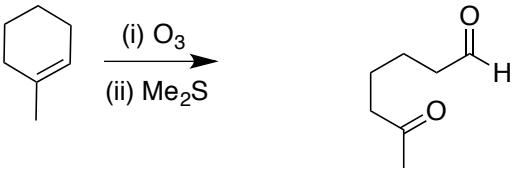
a sea breeze / don't smell it you clown, it's highly toxic (
ozonolysis,
aldehydes / ketones



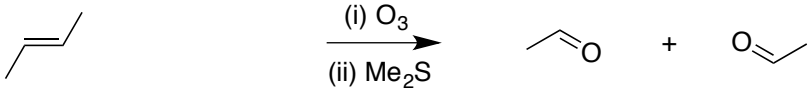


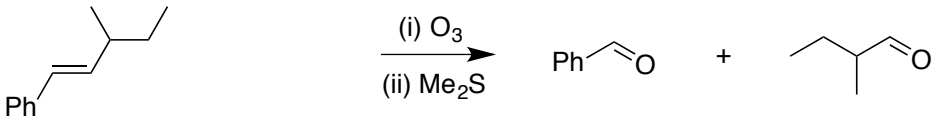


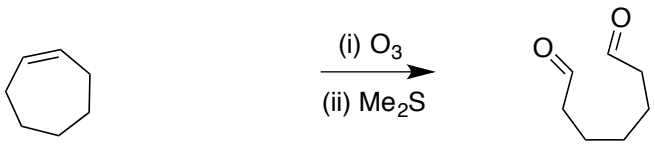


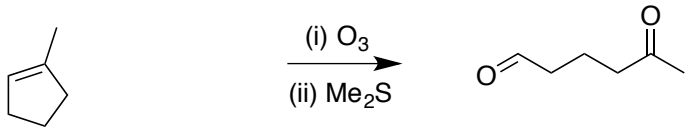


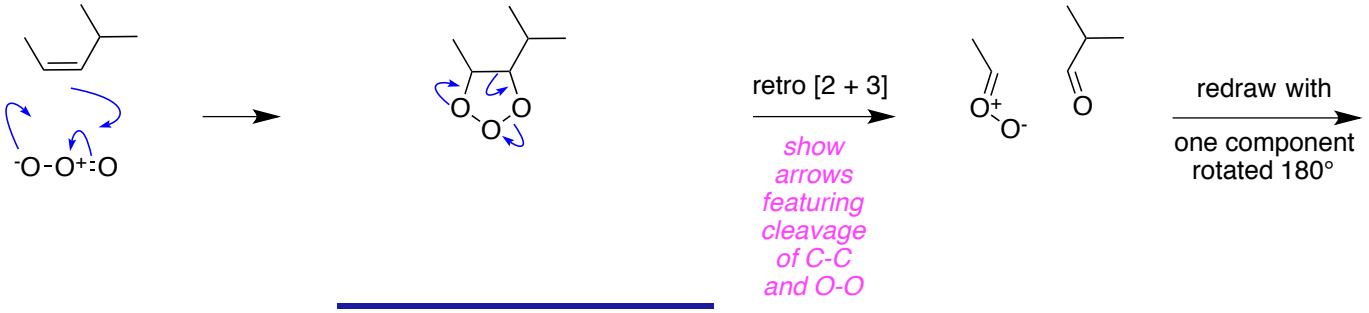
ring cleavage to 2 and 3 atoms components.

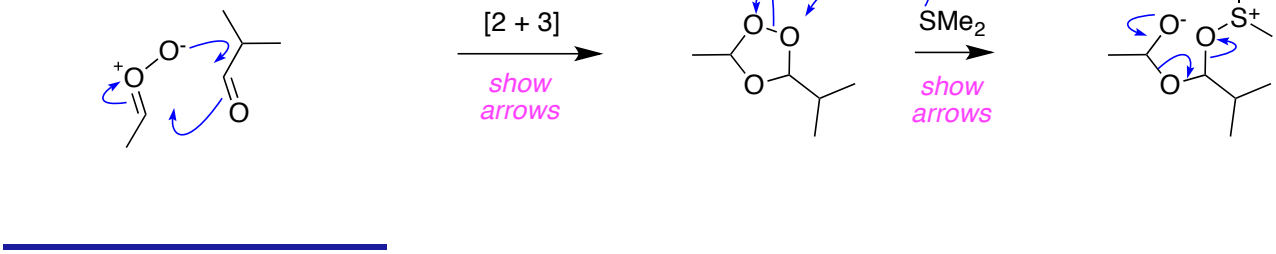

(i) O3
(ii) Me2S
O
+
O


Ph
(i) O3
(ii) Me2S
Ph
O
+
O

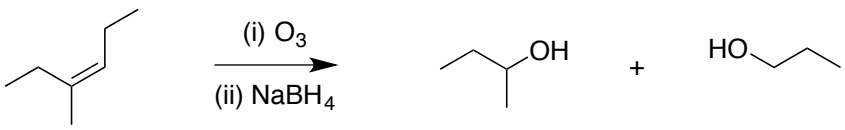

(i) O3
(ii) Me2S
O
O


(i) O3
(ii) Me2S
O
O


retro [2 + 3]
show arrows featuring cleavage of C-C and O-O
redraw with
one component rotated 180°

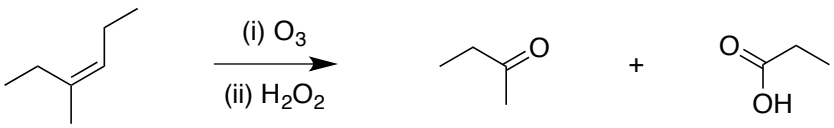

[2 + 3]
show arrows
SMe2
show arrows

reduced
oxidized



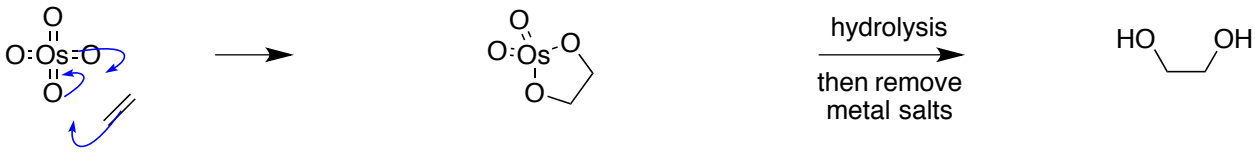

(i) O3
(ii) PPh3
O
+
O

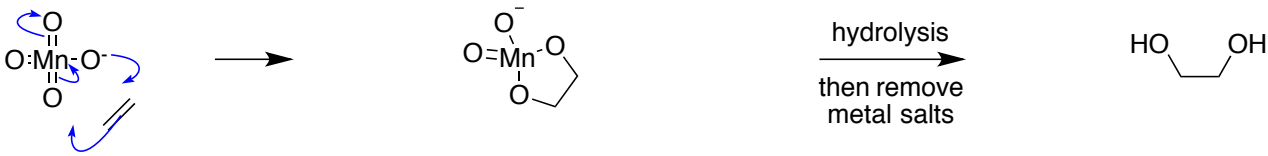

(i) O3
(ii) NaBH4
HO
OH


(i) O3
(ii) H2O2
O
+
O
OH

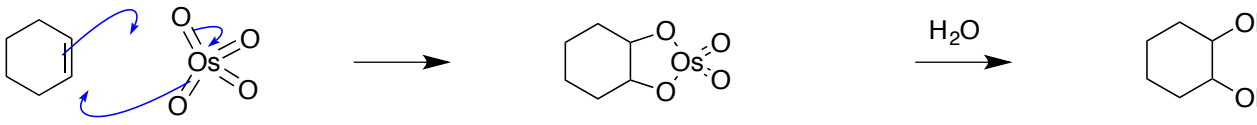
E. Dihydroxylation [2 + 3]

A dihydroxylation adds __2__

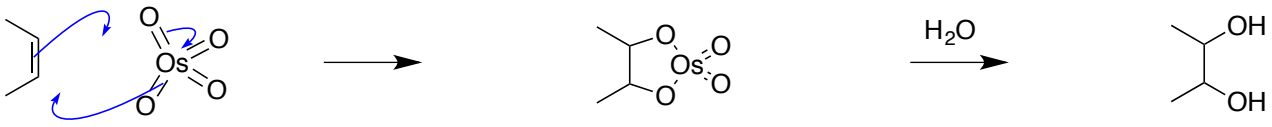




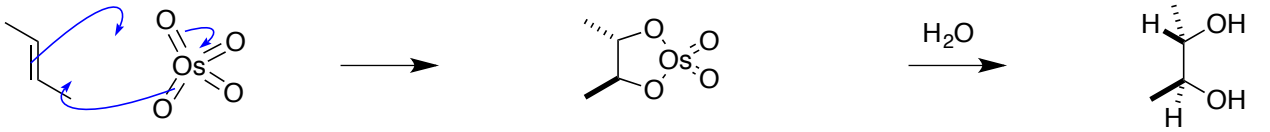
syn face specificity.



osmate ester *diol*

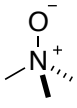


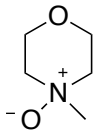
osmate ester *diol*



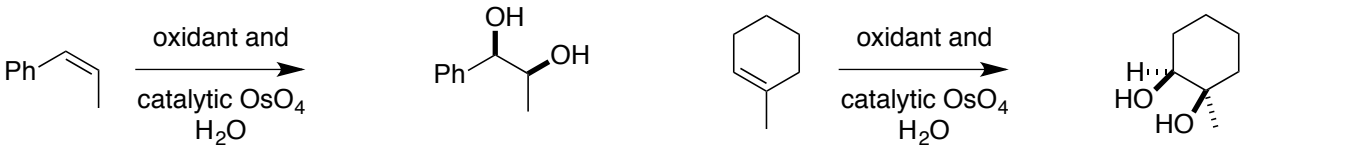
osmate ester *diol*

cis.
This is *unlike*
trans addition of

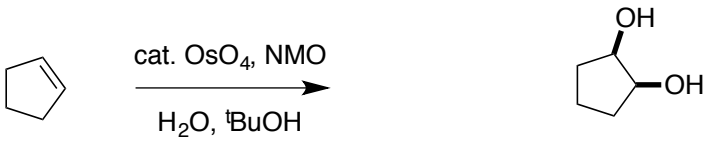


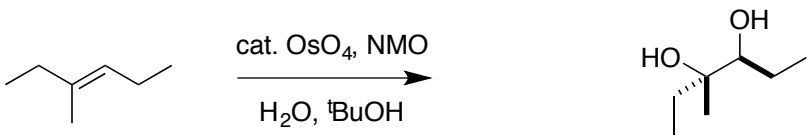


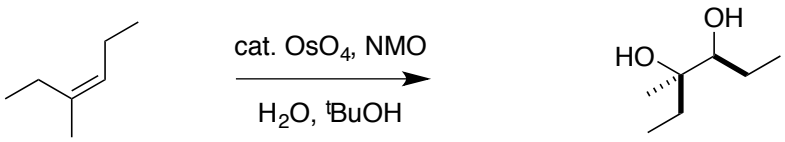
trimethylamine-N-oxide *NMO*



show stereochemistry



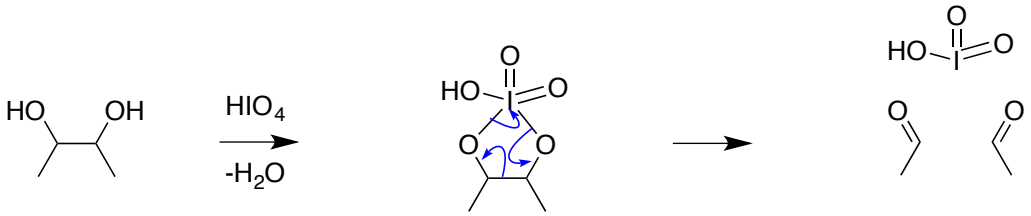


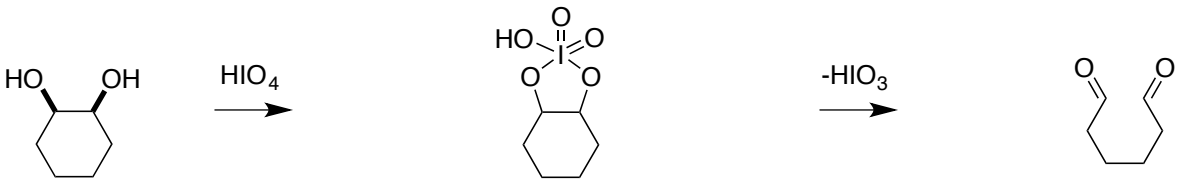


F. Periodate Cleavage

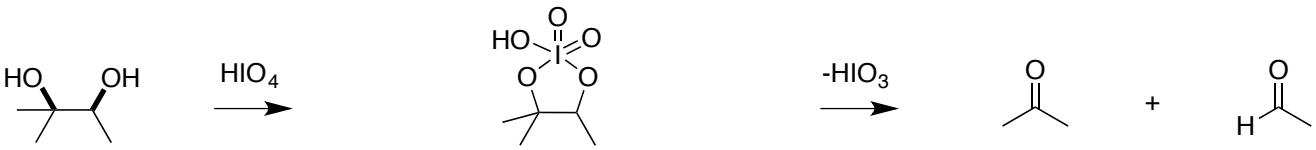
+7 oxidation state; it is reduced

+5





periodate intermediate *products*



periodate intermediate *products*

G. Azide-Alkyne "Click Reactions" [2 + 3]

at the end of a chain.

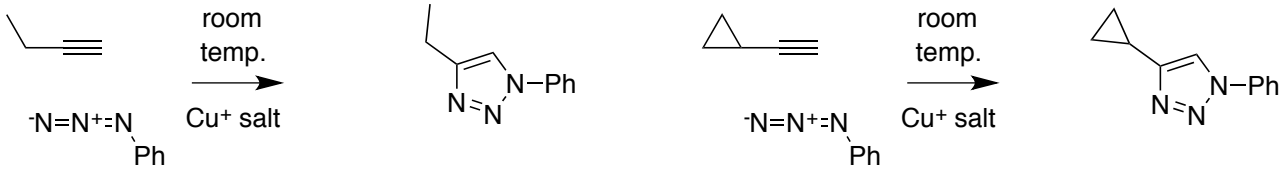
[3 + 2]

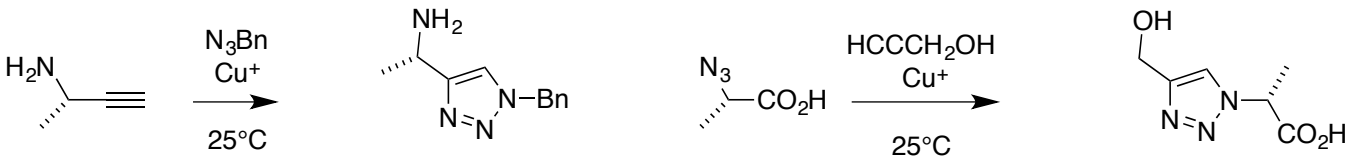
regioisomers

regioselective.

1,4-addition product *1,5-addition product*

chemoselective.

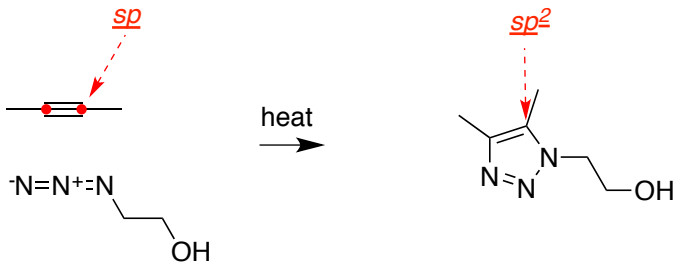




none

chemoselective.

less stable



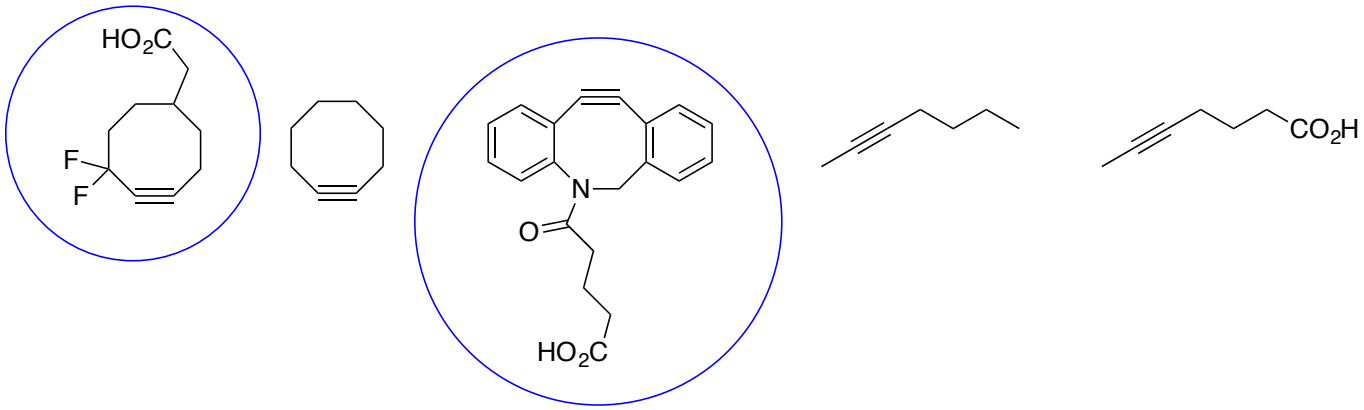
triazole product

180
120°.

cycloheptyne | cyclopropyne | cyclooctyne | cycloundodecyne

3 | 4 | 2 | 1

hydrogenation
most strained, *ie* cyclopropyne
sp^3, thereby making those carbon atoms
sp^3 (or sp^2 for partial hydrogenation) thereby making those carbon atoms more
sp^2, thereby making those carbon atoms more



can
do not need

Benzene And Aromaticity

from chapter(s) _____ in the recommended text

A. Introduction

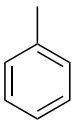
B. Common Aromatic Compounds

to smell.
differently to
a catalyst.

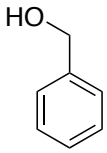
benzene

pyridine

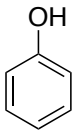
furan



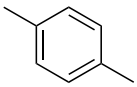
toluene



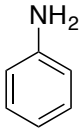
benzyl alcohol



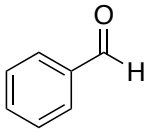
phenol



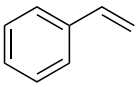
para-xylene



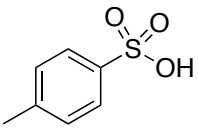
aniline



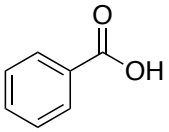
benzaldehyde



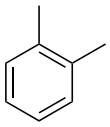
styrene



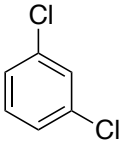
tosic acid



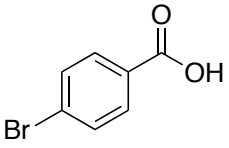
benzoic acid



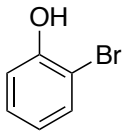
1,2-dimethylbenzene



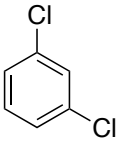
meta-dichlorobenzene



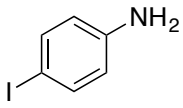
para-bromobenzoic acid



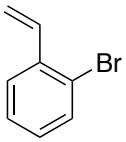
ortho-bromophenol



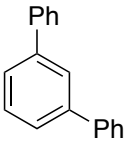
1,3-dichlorobenzene



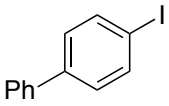
4-iodoaniline



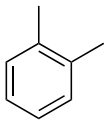
2-bromostyrene



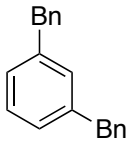
1,3-diphenylbenzene



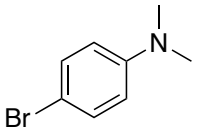
para-phenyliodobenzene



ortho-$Me_2C_6H_4$

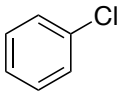


1,3-$Bn_2C_6H_4$

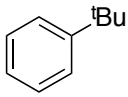


para-$(Me_2N)BrC_6H_4$

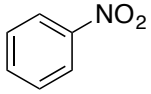
ie toluene.



chlorobenzene

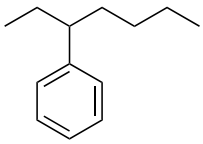


tert-butylbenzene

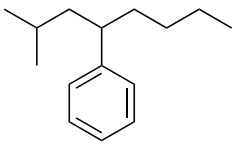


nitrobenzene

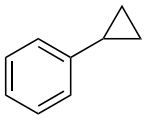
do not
lipophilic



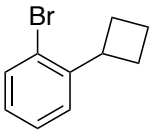
3-phenylheptane



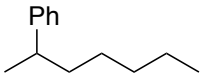
2-methyl-4-phenyloctane



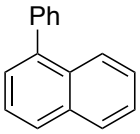
phenylcyclopropane



1-bromo-2-cyclobutylbenzene

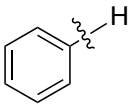


2-phenylheptane

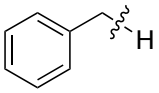


1-phenylnaphthalene

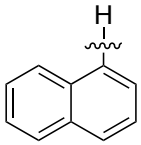
correct name: ____cycloproplybenzene_.



phenyl group in benzene



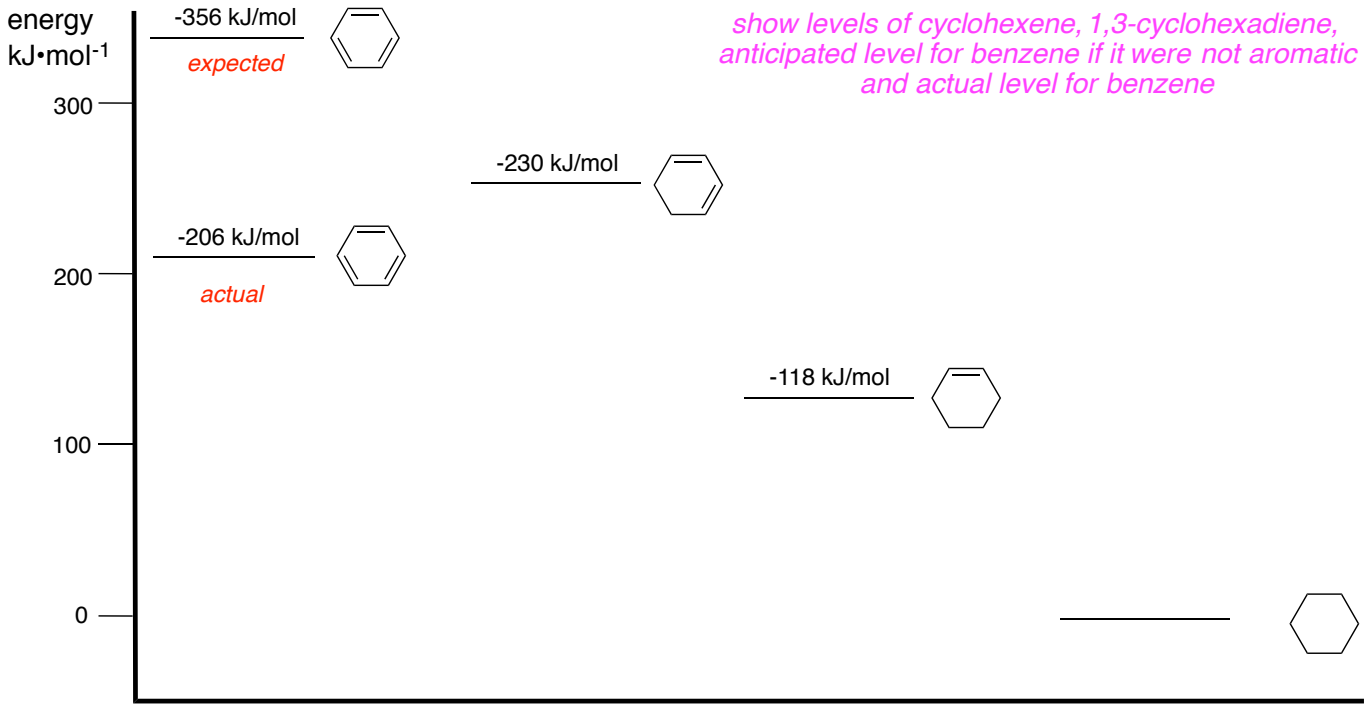
benzyl group in toluene



1-naphthyl group in naphthalene

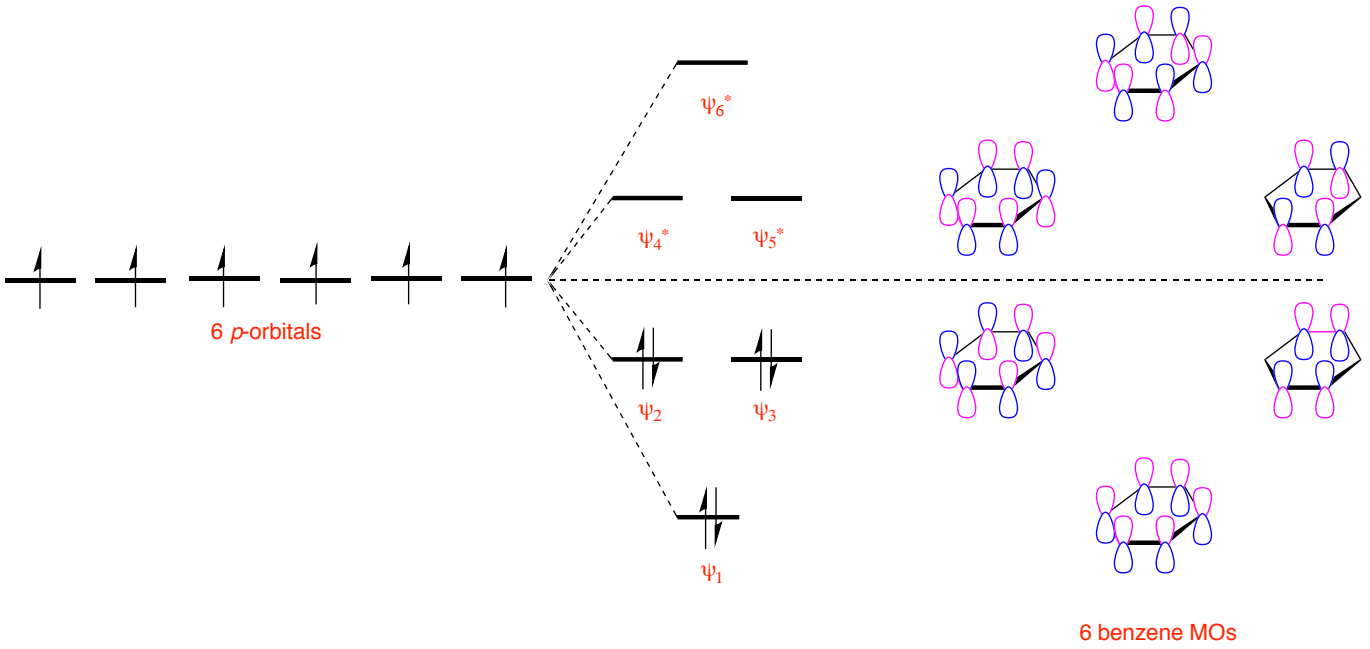
C. Heats Of Hydrogenation And Aromaticity

liberated
can
more
less than expected.
Cyclohexane
.



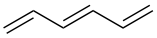
120°; each carbon is *sp^2* …. and has an empty *p*-orbital
equal.

6 molecular orbitals



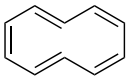
cyclic, *conjugated*, *planar*
The Hückel Rule

aromatic because it has {4(1)+2} = 6 π-electrons, follows Huckel Rule.



not aromatic because this is not cyclic compound.

aromatic because it has {4(1)+2} = 6 π-electrons, follows Huckel Rule.



aromatic because because it has {4(2)+2} = 10 π-electrons, follows Huckel Rule.

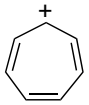
not aromatic because it has 4 π-electrons, does not follow Huckel Rule.

not aromatic because it has 4 π-electrons, does not follow Huckel Rule.

not aromatic because it has 4 π-electrons, does not follow Huckel Rule.

not aromatic because of nonplanarity of the methylene bridge

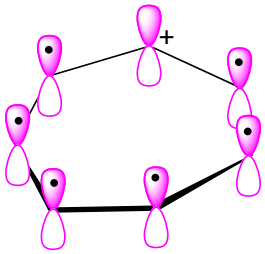
not aromatic because it has 8 π-electrons, does not follow Huckel Rule.



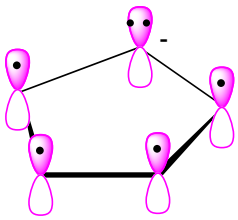
aromatic because the cation on methylene bridge gives planar structure and 6 π-electrons follow Huckel Rule.

D. Predicting Aromaticity

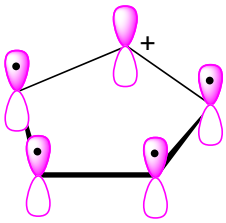
Carbocycles



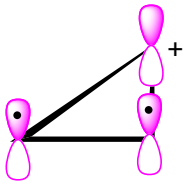
aromatic.



5 resonance structures
is *non-aromatic*.

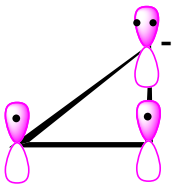


is *aromatic*.

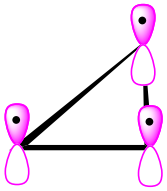


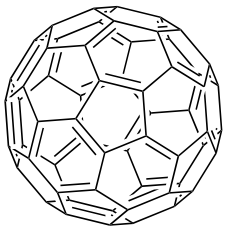
3 resonance
flat.

\ *non-aromatic*.

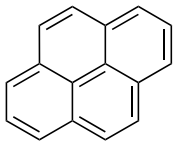


non-aromatic.

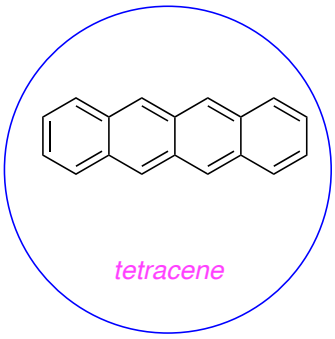




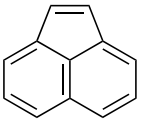
C_{60}



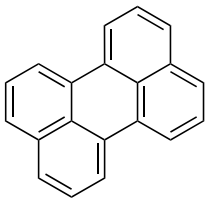
pyrene



tetracene



acenaphthalene



perylene

is not

Electrophilic Attack On Benzene

from chapter(s) _____ in the recommended text

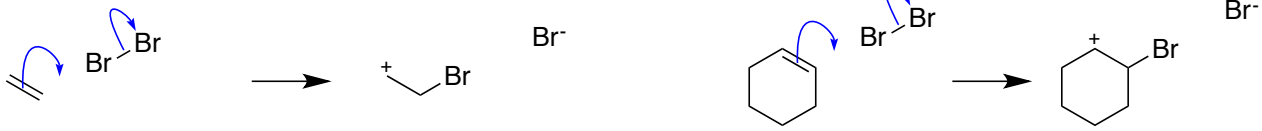
A. Introduction

.

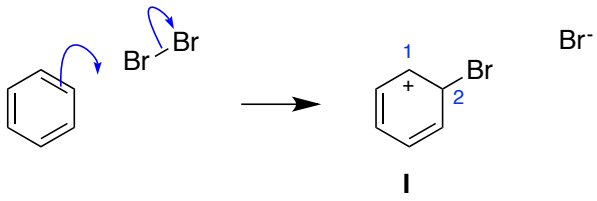
B. Electrophilic Bromination Of Alkenes And Benzene Compared

First Step: Approach Of Electrophile

is not



do distribute



I

1 hydrogen atoms on C^1 and *1* on C^2.

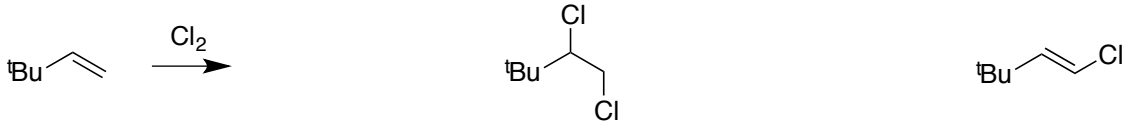
faster than on benzene because for benzene *aromatic*

Second Step: Loss Of Positive Charge

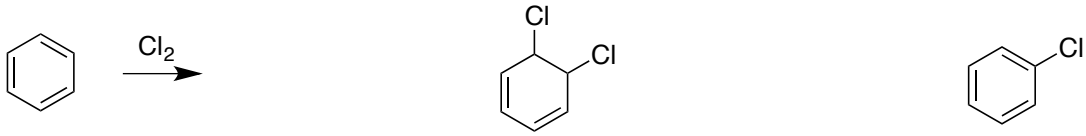
proton.

aromatic

addition *substitution*

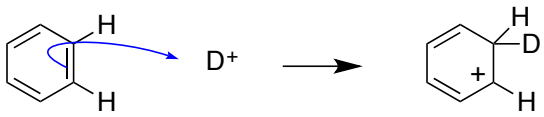


addition product *possible substitution product*



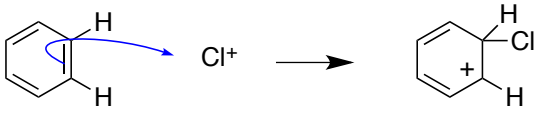
addition product *substitution product*

heavier isotope
the same as to
attracted to)

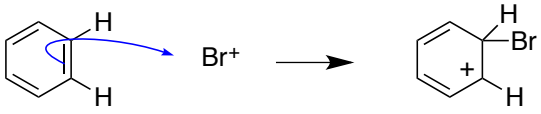


intermediate
non-aromatic.

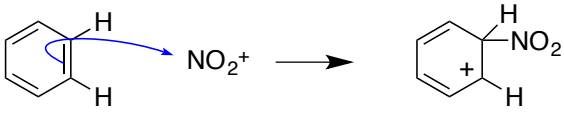
loses
slow.



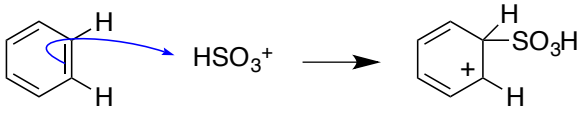
Cl+



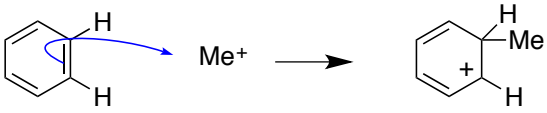
Br+



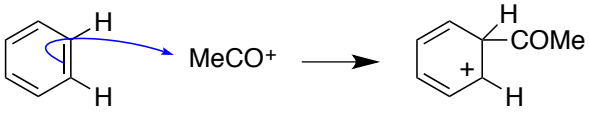
a nitronium ion, NO_2^+



a sulfonium ion, HSO_3^+

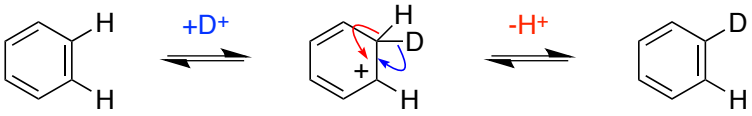


a methyl carbocation, Me^+



an acylium ion, $MeCO^+$

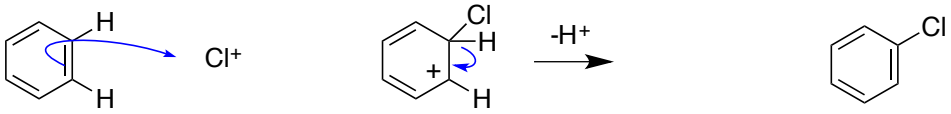
reversible.

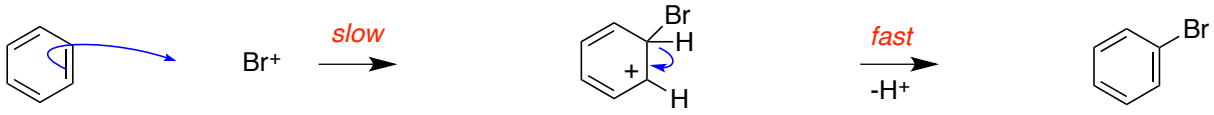


C. Halogenation Of Benzene

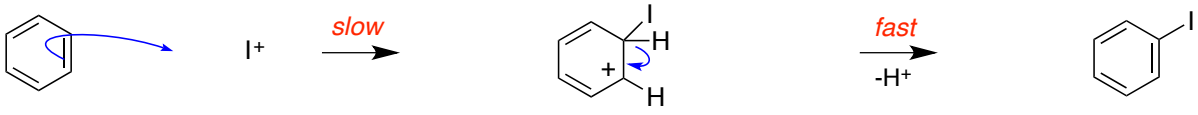
insufficiently

acid





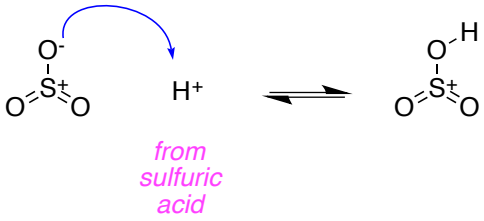
bromination

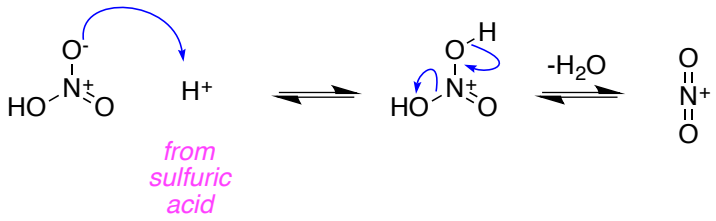


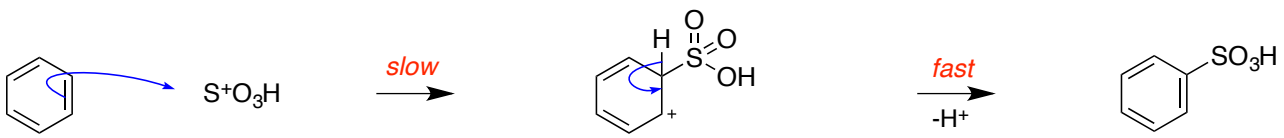
iodination

D. Sulfonation And Nitration Of Benzene

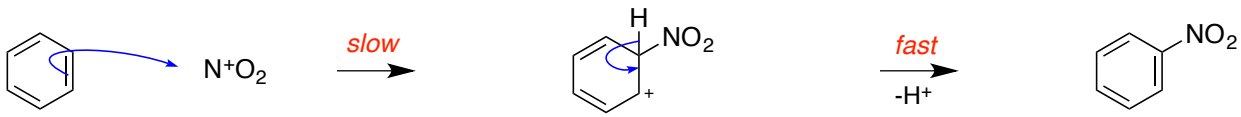
strong
oleum.
protonating.







sulfonation

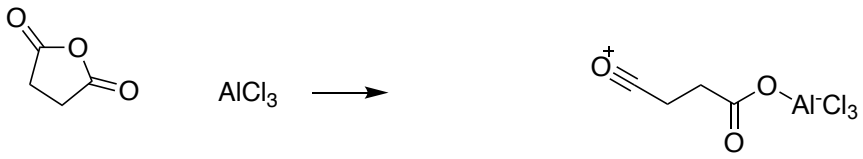


nitration

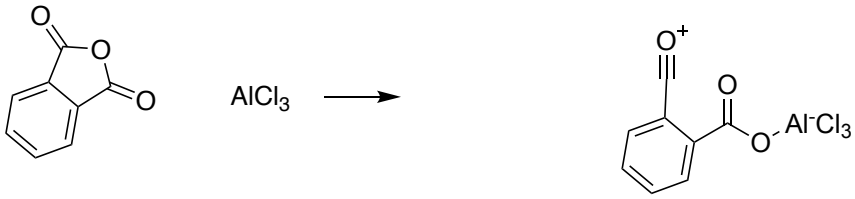
E. Acylation Of Benzene (Friedel-Crafts)

acylium ions

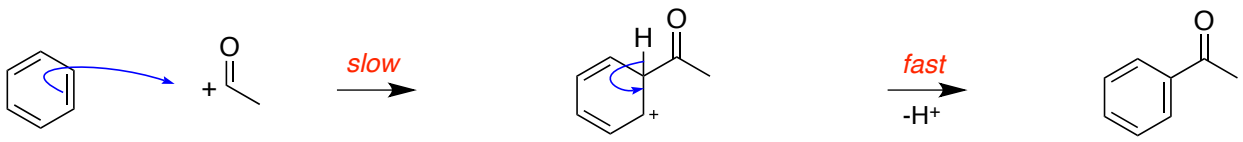
acylium *acylium*



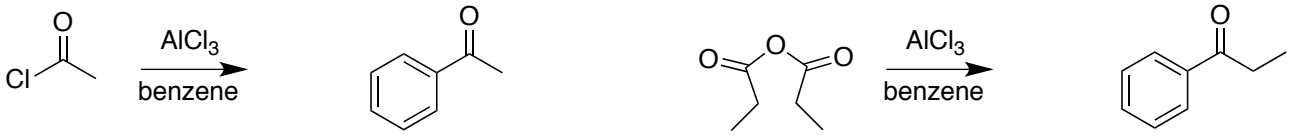
acylium



acylium



ketones.
less electron rich
do not tend to



equivalent.

F. Alkylation (Friedel-Crafts)

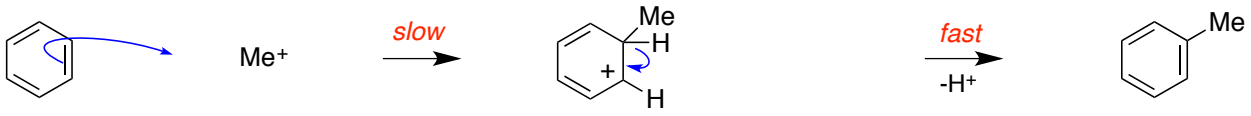
carbocations.

Lewis *acids*

do not

not to be

is not a concern



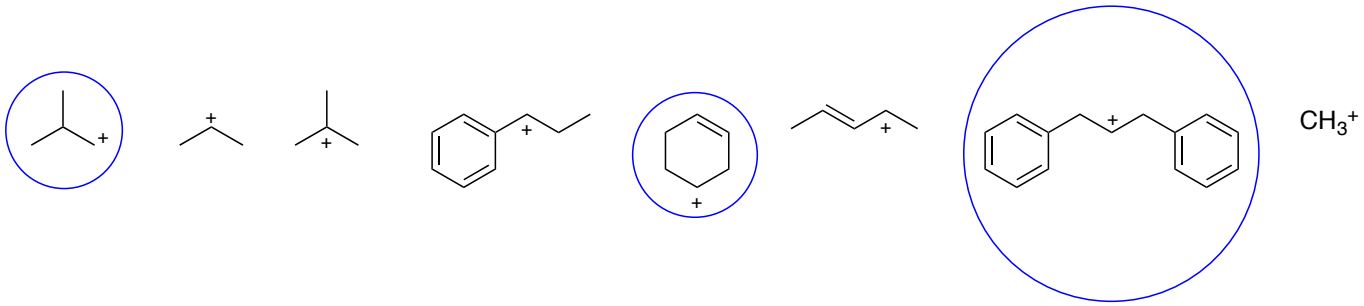
methylation

alkylbenzenes, these are *more*
do
are

Carbocation Rearrangements Revisited

hydride

more



decreases

Ultraviolet And Fluorescence Spectroscopy

from chapter _____ in the recommended text

A. Introduction

B. Fundamental Physics

more
X-ray

ground state energy level to a(n) *excited*

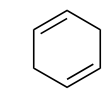
inversely proportional to the *energies*
directly related to their *number*.

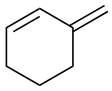
broad
IR-vibrational

Chromophores
cross-section and the *more*

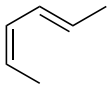
C. Molecular Orbital Diagrams Of Alkenes, Dienes, and Polyenes

just one

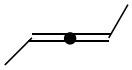

non-conj'd


conj'd


conj'd

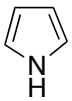

conj'd


non-conj'd


non-conj'd

$H_2C{=}CH_2$
non-conj'd

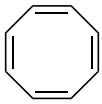

conj'd



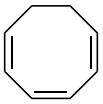
conj'd

conj'd

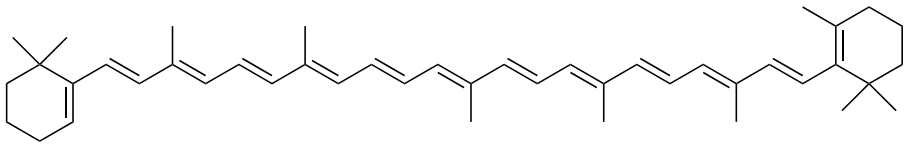
non-conj'd

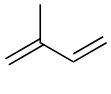

conj'd

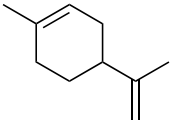

non-conj'd

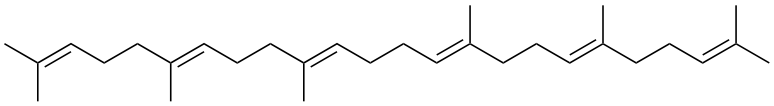

conj'd

Thank you to Dr Syed Hussaini of U Tulsa who pointed out that 4H-pyran (4 th example) is conjugated of its oxygen is sp^2 hybridized.

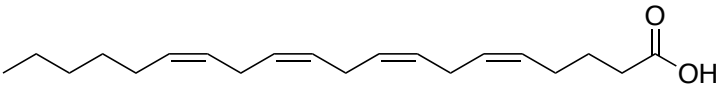

β-carotene *conj'd*


isoprene
conj'd

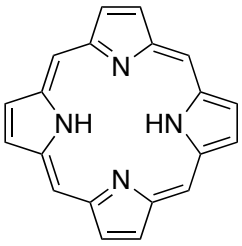

limonene
non-conj'd



squalene *non-conj'd*

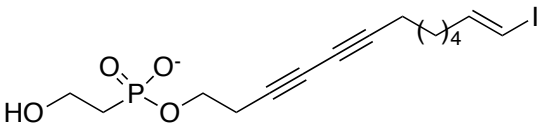


arachidinoic acid *non-conj'd*

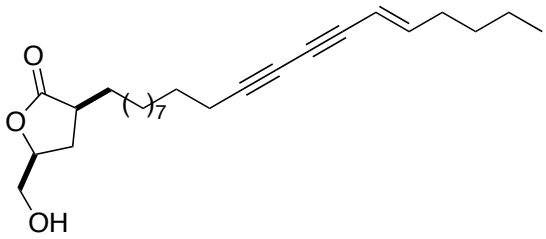


porphyrin *conj'd*

is



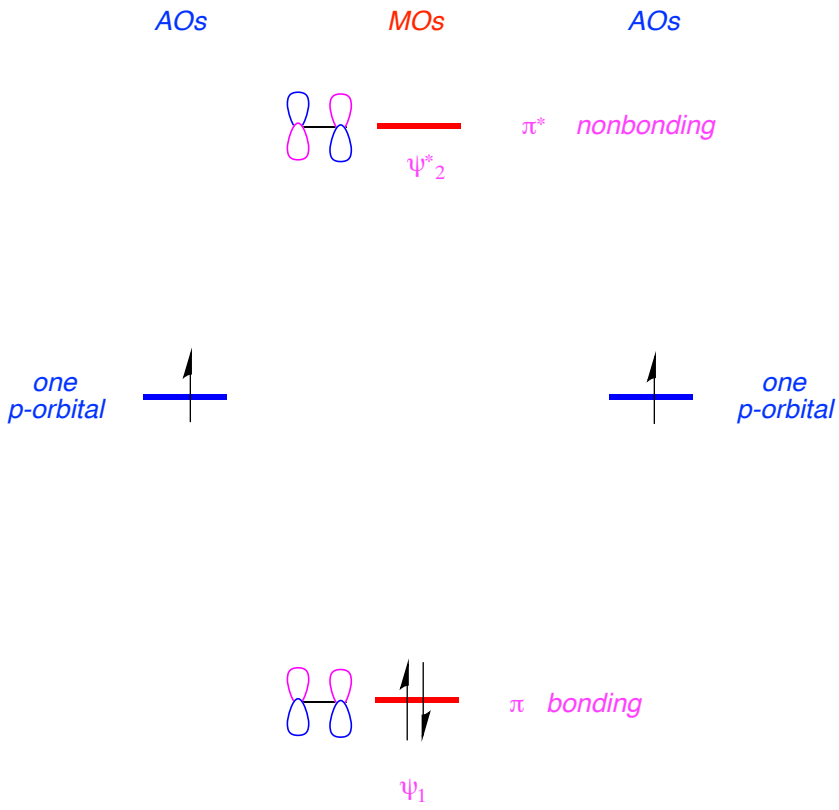
phosphoiodyns A
non-conj'd



debilisone
conj'd

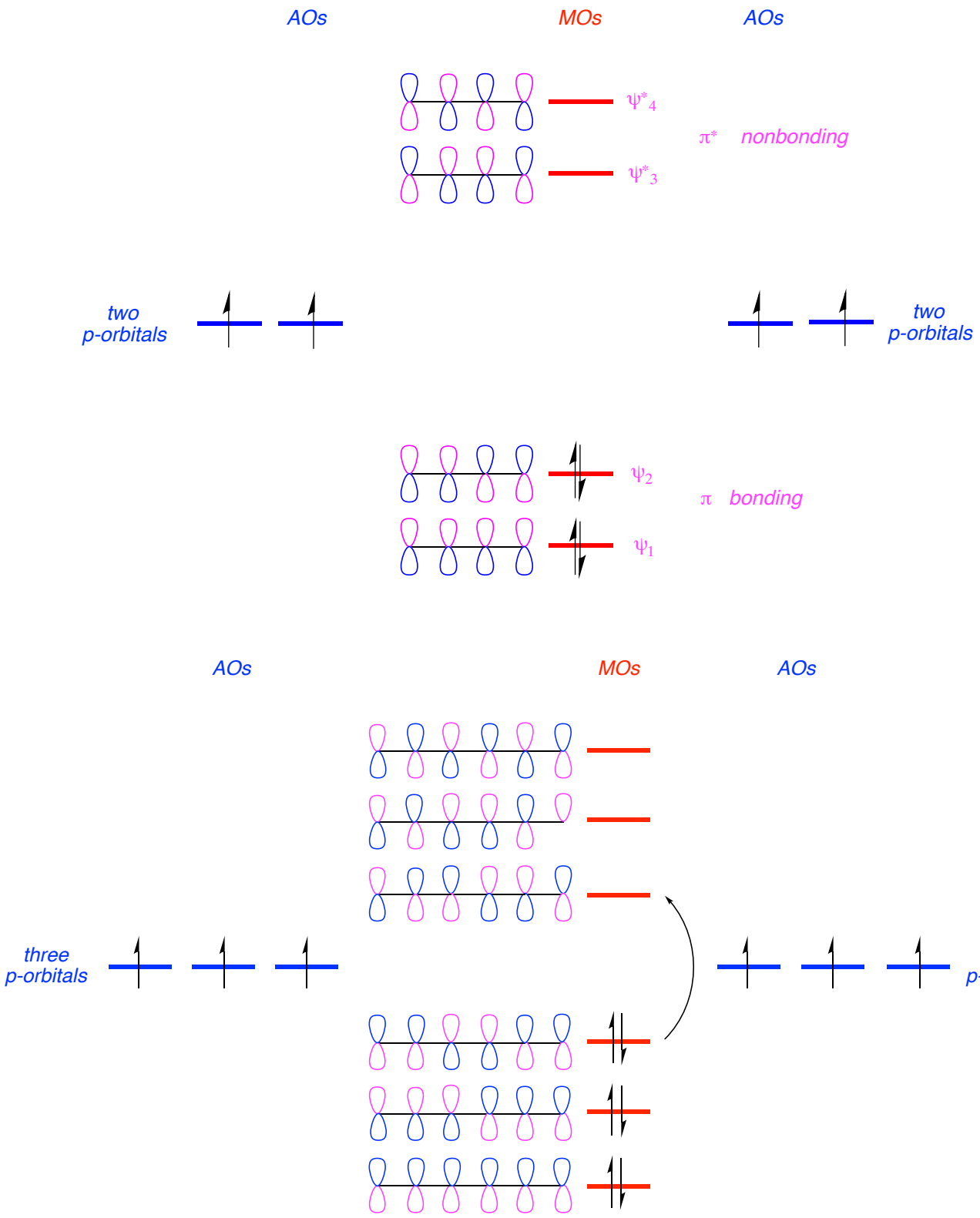
an alternative to
n

2
bonding π- and *antibonding*
Maximal



ultraviolet region resulting in an *excited*
IR energy

larger cross-sections, therefore they absorb *more*
absorbance of the *chromophore*
larger

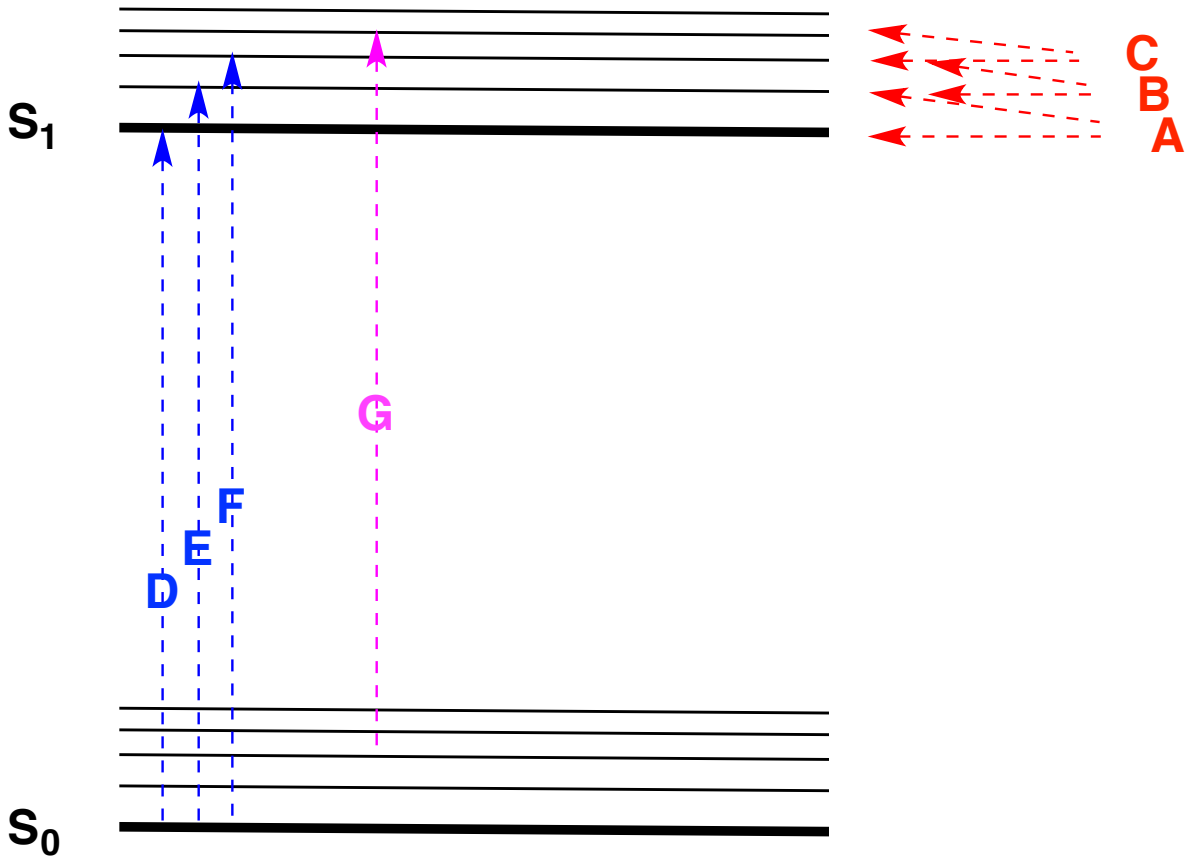

AOs
MOs
AOs
ψ*4
π*
nonbonding
ψ*3
two
p-orbitals
two
p-orbitals
ψ2
π
bonding
ψ1
AOs
MOs
AOs
three
p-orbitals
three
p-orbitals

decreases
lower energy quanta of *increased*

vibrational energy states, while *electronic*
IR
UV quanta.

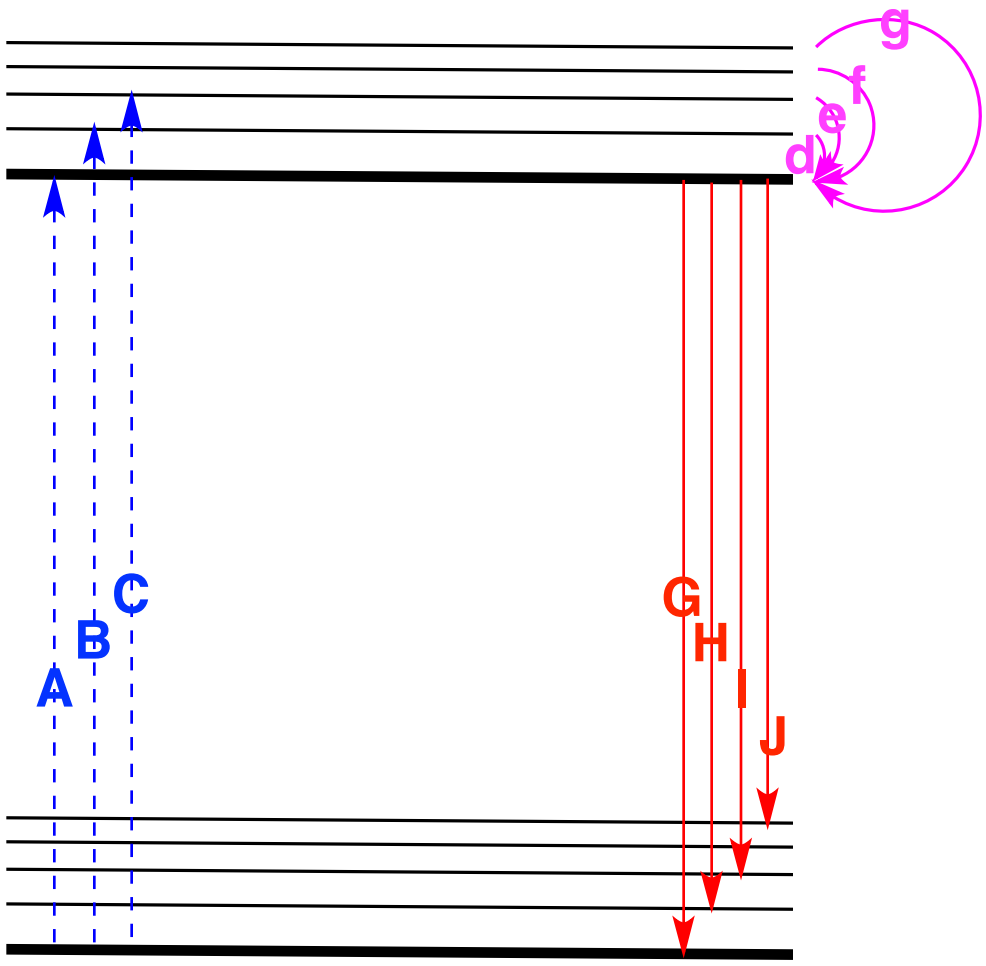
UV
IR.

IR
UV
greater than for transitions like **G**.



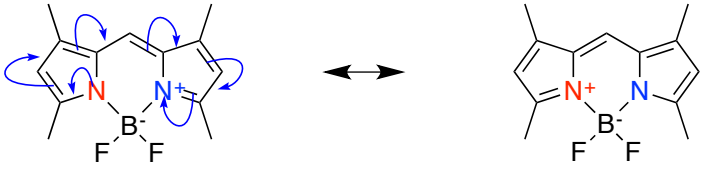
multiple
smaller
UV and transitions between *electronic*
vibrational emissions.

nano-second
fluorescent radiation
rigid molecules

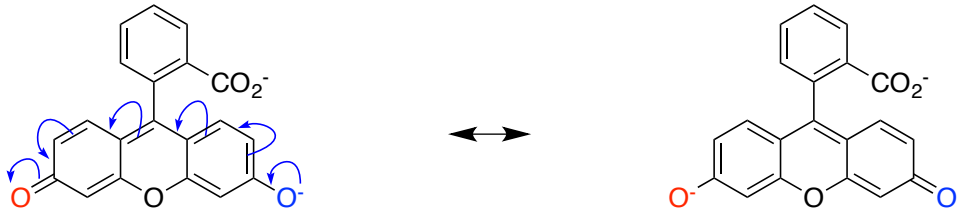


sensitive
higher
higher
fluorescence spectroscopy
fluors.
less

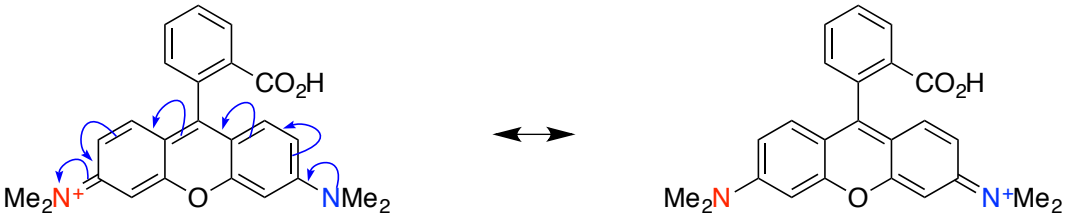
rigid



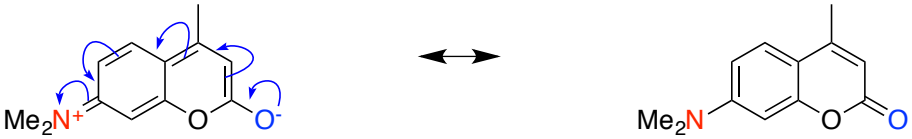
a BODIPY



a fluorescein



a rhodamine



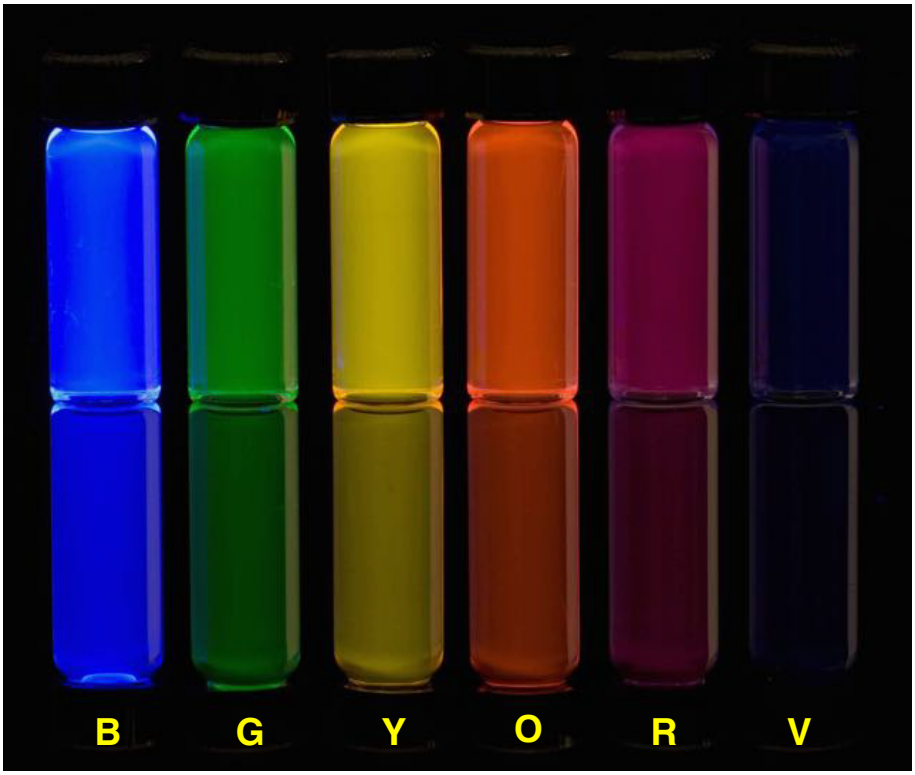
a coumarin

Of the probes shown above, the ones which has fluorescence that is most sensitive to reduced pH is the *fluorescein and coumarin*, whereas the *BODIPY* is least sensitive to pH.

This is because *fluorescein and coumarin* contain phenoate-O^- groups that can be protonated as the pH is reduced from 7.0.

Fluorescence of the *coumarin* is likely to be most sensitive to the dipole moment of the solvent it is in because the oscillation of charge in this molecule is unsymmetrical.

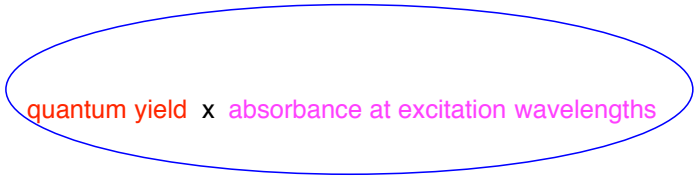
Which of the fluor solutions below emit the highest energy light *V*, and which of them emit at the longest wavelength *R*.



Circle the correct definition of fluorescence quantum yield from the following choices:

$$\frac{\#\text{ photons absorbed}}{\#\text{ photons emitted}} \qquad \frac{\#\text{ photons emitted}}{\#\text{ photons absorbed}} \qquad \frac{\#\text{ photons lost as heat}}{\#\text{ photons absorbed}}$$

Circle the correct descriptor of fluor brightness:



quantum yield x absorbance at λ_{max}

absorbance at excitation wavelengths only

quantum yield only

absorbance at λ_{max} only

Infrared (IR) Spectroscopy

from chapter(s) _____ in the recommended text

A. Introduction

B. Origin Of IR Absorbance

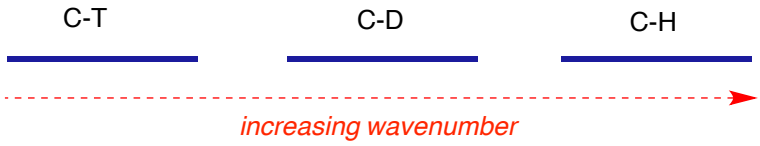
less
lower

accumulated after multiple scans

dipole
unsymmetrical
greater
faster
higher
cm^{-1}.

slower
lower wavenumber.

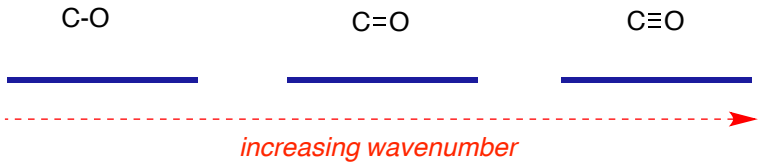
write C-H, C-D, and C-T
above the appropriate lines



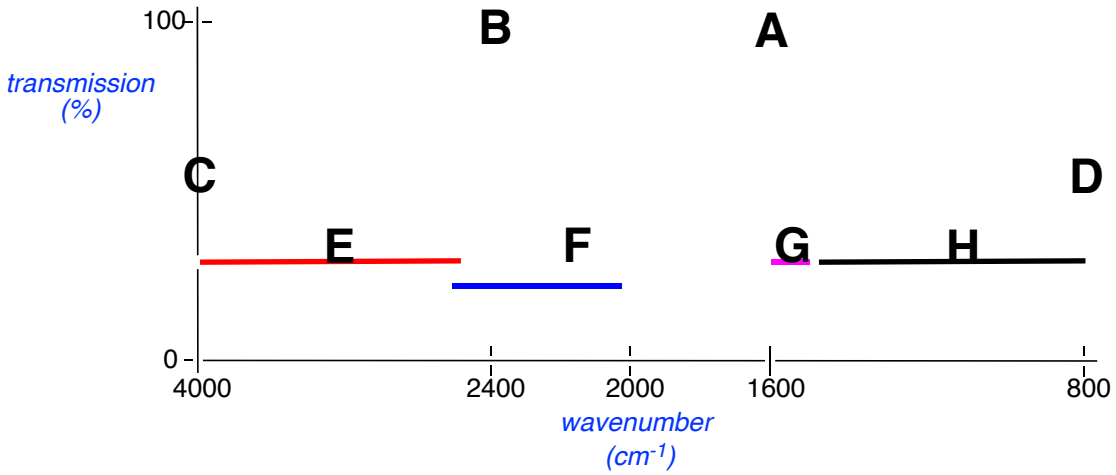
write

C≡O C−O C=O

above the appropriate lines



are
inversely
the same
expanded below 2000 relative to the 4000 – 2000 cm^{-1}.
can



3000 cm^{-1}
3300 cm^{-1}
3500 cm^{-1}

1600 - 1500 cm^{-1}
1900 – 1500 cm^{-1}.

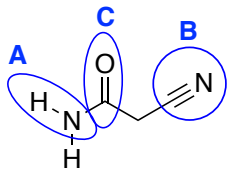
1640 cm^{-1} and absorb much *less*
lower

1550 & 1350 cm^{-1}.

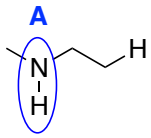
1030 – 1080 cm^{-1}.

the ___fingerprint____ region

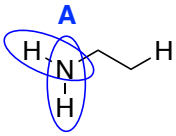
C. Functional Group Assignments



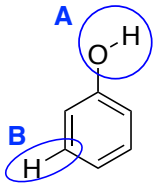
A 3300; **B** 2300; **C** 1690 cm^{-1}



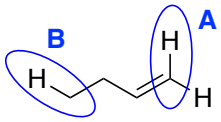
A 3300 cm^{-1}



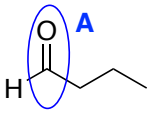
A 3300 and 3250 cm^{-1}



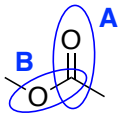
A 3400; **B** 3050 cm^{-1}



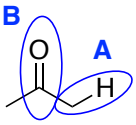
A 3050; **B** 2950 cm^{-1}



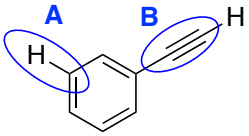
A 1730 cm^{-1}



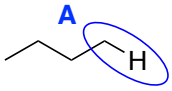
A 1735; **B** 1250 cm^{-1}



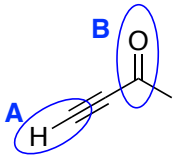
A 2950; **B** 1715 cm^{-1}



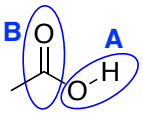
A 3050; **B** 2100 cm^{-1}



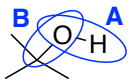
A 2950 cm^{-1}



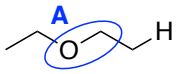
A 3300; **B** 1680 cm^{-1}



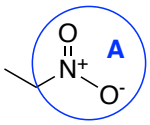
A 2900 (br); **B** 1690 cm^{-1}



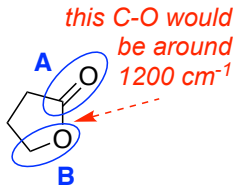
A 3400 (br); **B** 1100 cm^{-1}



A 1100 cm^{-1}



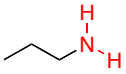
A 1560 and 1380 cm^{-1}



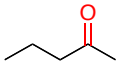
A 1770; **B** 1100 cm^{-1}

a "the "fingerprint region"

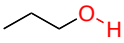
b



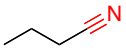
c



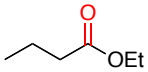
d



e

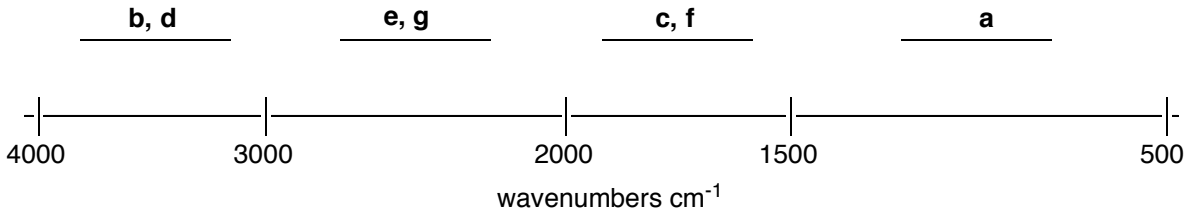


f



g

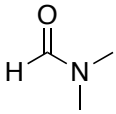
put letters on these lines to indicate the functional groups that absorb here



D. Assigning Structures From Spectra

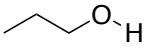
acetone

acetonitrile



DMF

DMSO



n-propyl alcohol

pyridine

is ____acetone_____ .

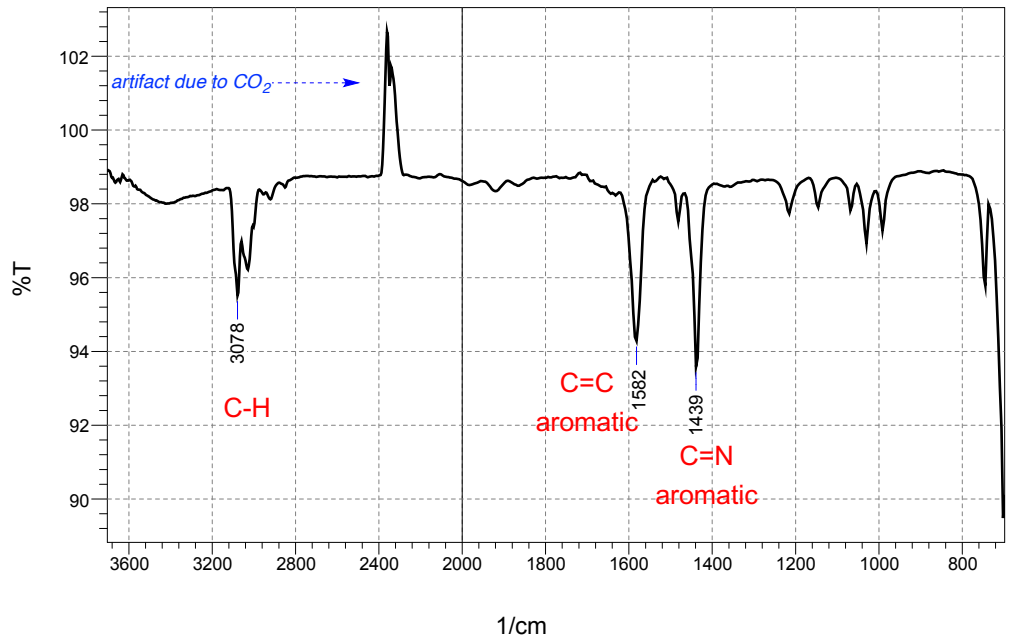
a ____C-H___ bond.

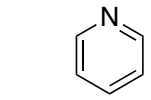
a ____C=O_____ bond.

is _____acetonitrile_____ .

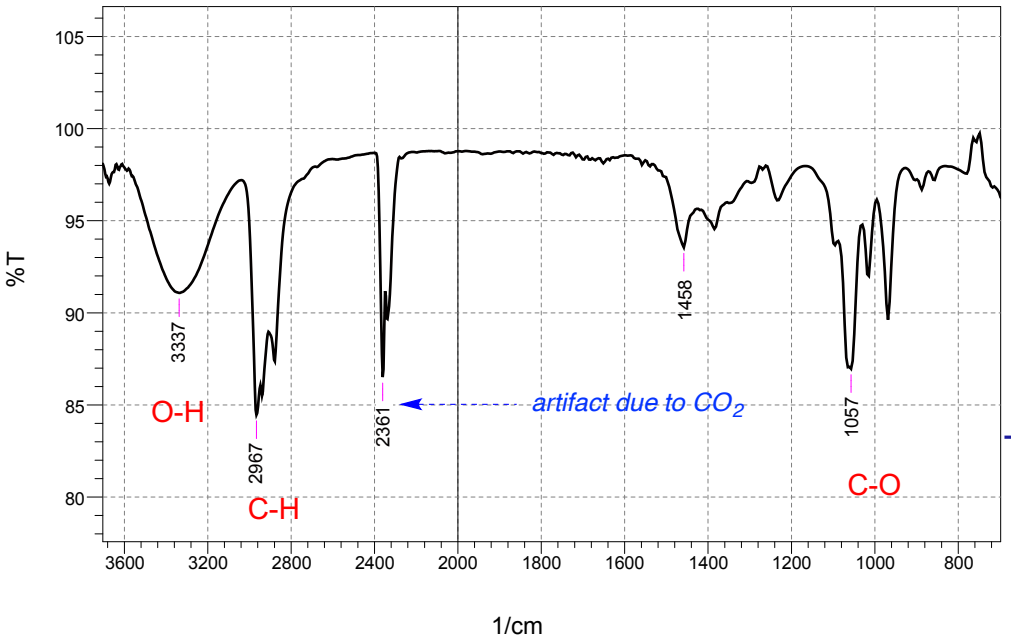
a _____C-H____ bond.

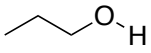
a ____C≡N_____ bond.



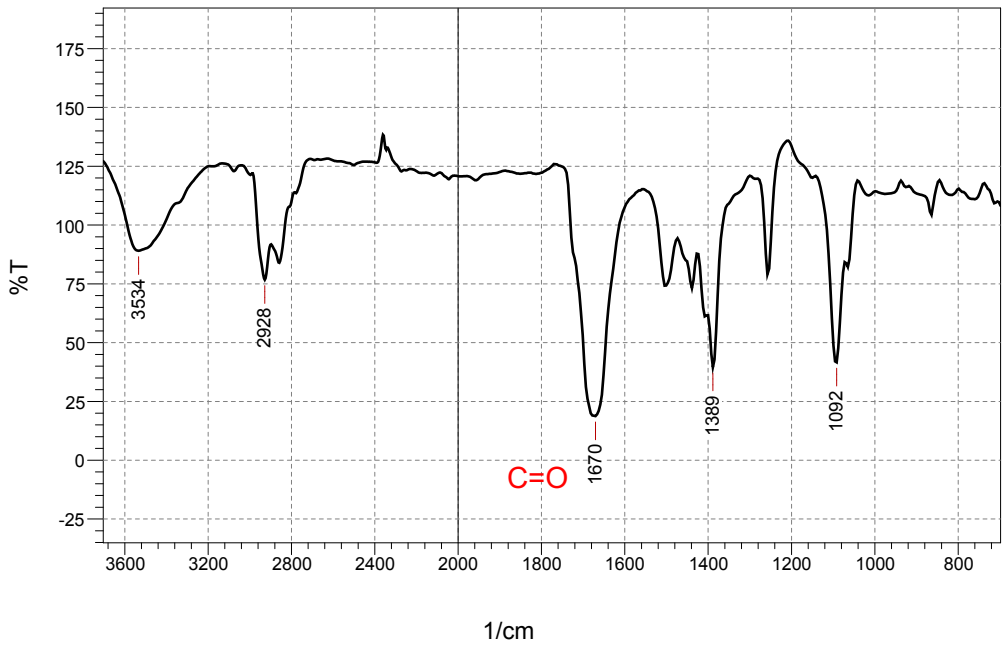


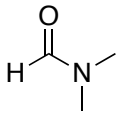
draw structure and attribute numbered IR stretches to particular bonds



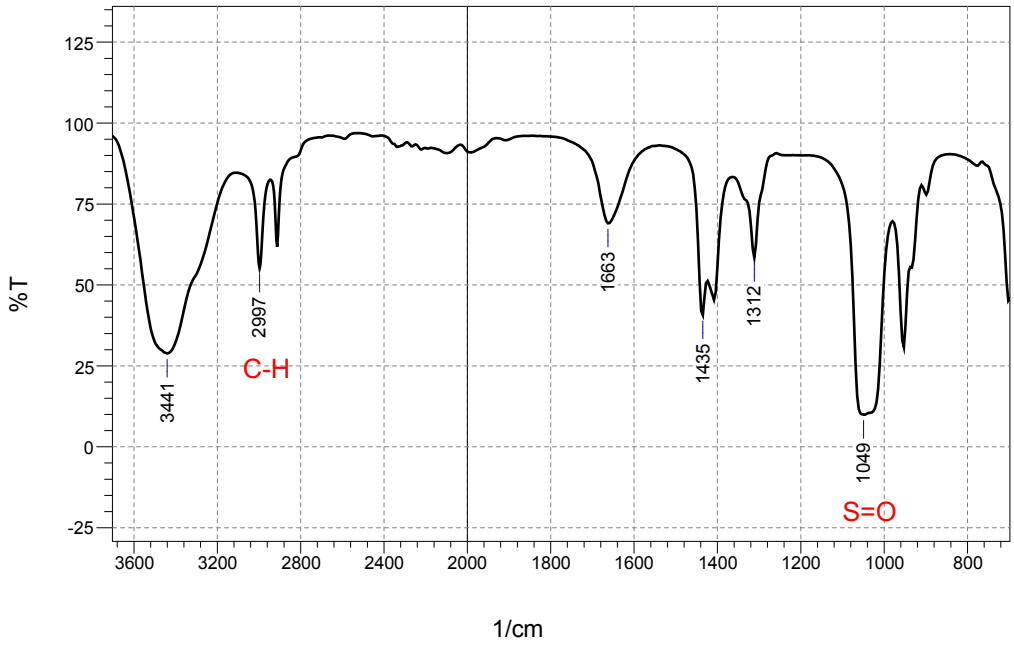


draw structure and attribute numbered IR stretches to particular bonds

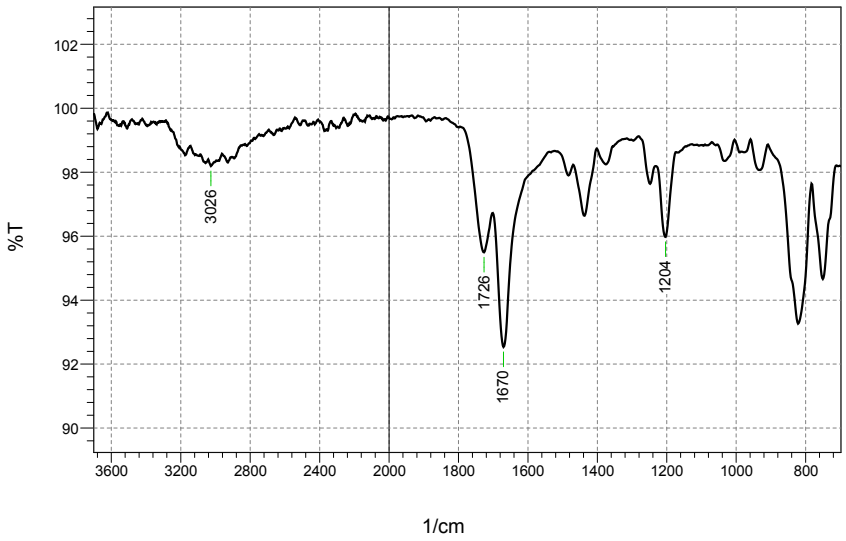




draw structure and attribute numbered IR stretches to particular bonds

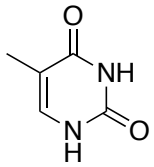


draw structure and attribute numbered IR stretches to particular bonds

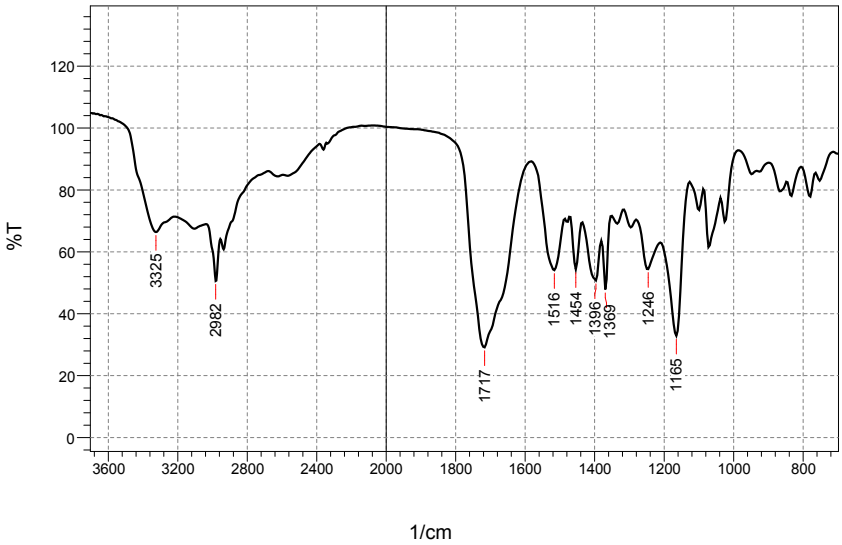


thymine

compound name

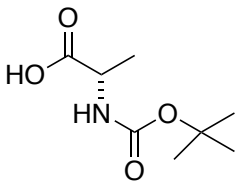


compound structure

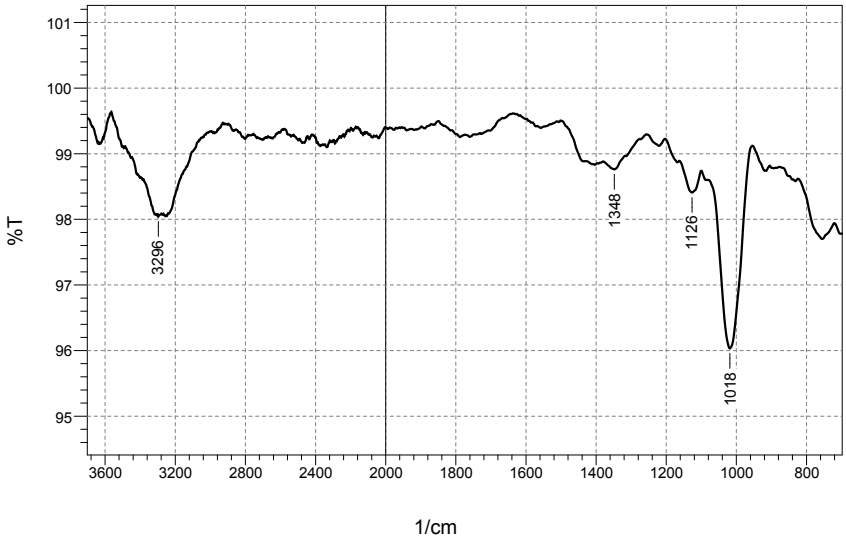


Boc-Ala

compound name

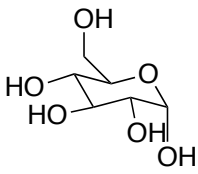


compound structure



glucose

compound name



compound structure

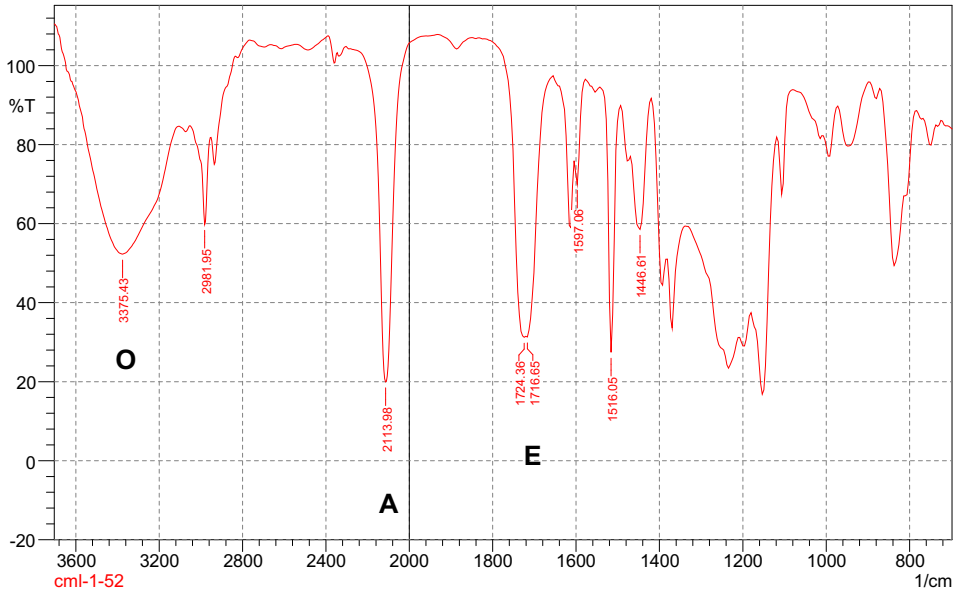
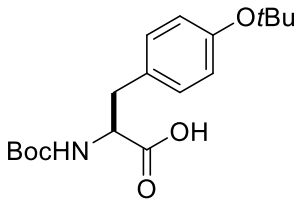
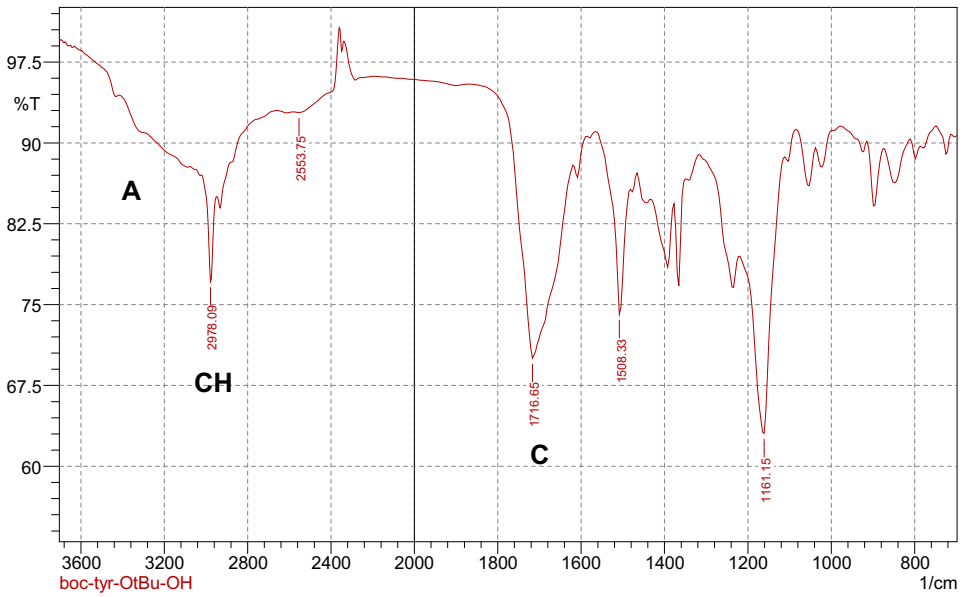


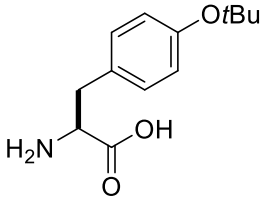
plate).



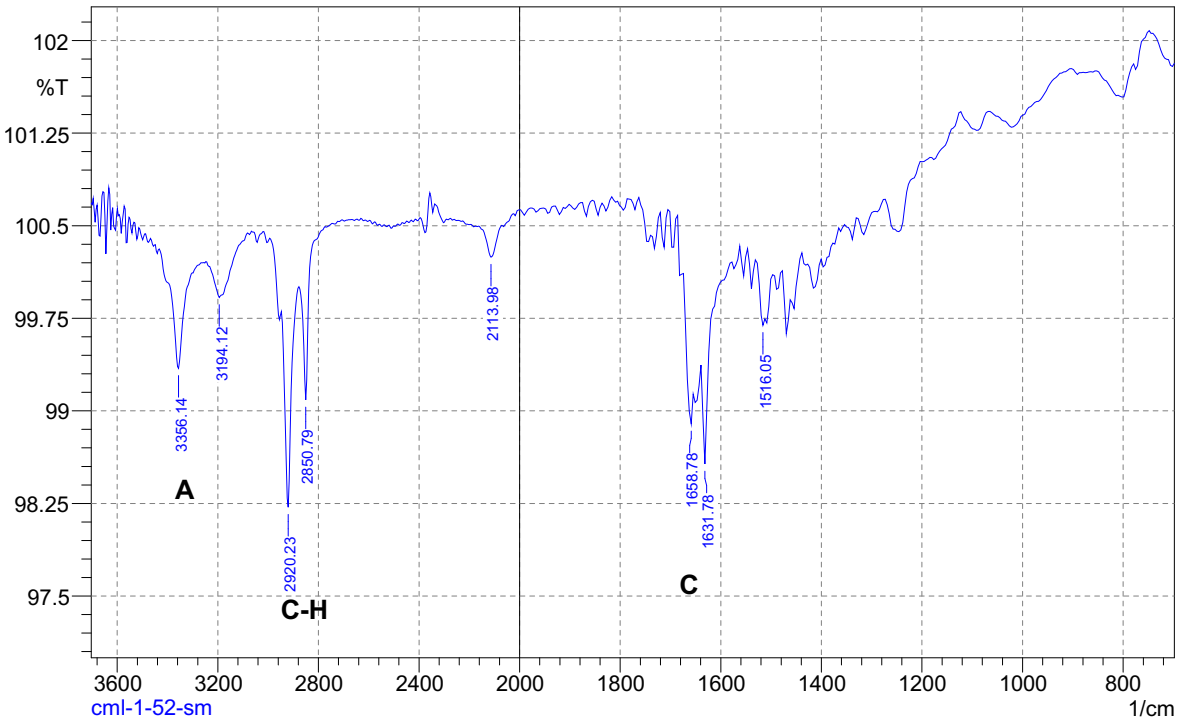
boc-tyr-OtBu-OH



The following is an FT-IR of compound “cml-1-52-sm”. Write **A** on the absorbances corresponding to the amine N-H stretches, **C** on that for the CO stretches, and **CH** for the C-H stretches (taken as a thin film on a NaCl plate).



cml-1-52-sm


102
%T
101.25
100.5
99.75
99
98.25
97.5
3356.14
3194.12
2920.23
2850.79
2113.98
1658.78
1631.78
1516.05
A
C-H
C
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
cml-1-52-sm
1/cm

^{13}C NMR Spectroscopy

from chapter _____ in the recommended text

A. Introduction

B. Fundamental Physics Of NMR (Nuclear Magnetic Resonance)

Nuclear spin

flipping these spins between aligned and counter-aligned states by applying a *radiofrequency* *low* energy range of the electromagnetic spectrum, *ie* *low* frequency and *high*

½, and for ^{12}C the nuclear spin is *0*.

high, but that of ^{13}C is *low* (*1.1*

averaged over multiple scans to increase *both these parameters*.

less than those between vibrational states in IR, and *less*
are sensitive to large external magnetic fields
zero

larger the energy gap between nuclear spin states.

both these parameters.

are sensitive to the electron density and proximal NMR active nuclei in the same molecule, hence these nuclei in different parts of the molecule flip when *different*

"*shield* each other

deshielded relative to

C. Chemical Shifts In General

$SiMe_4$.

δ on this scale reflects how much less the frequency is for an NMR active nuclei to flip, or *resonate*,

$$\frac{\text{frequency of 0 on scale - frequency for nucleus}}{\text{frequency of 0 on scale}}$$

positive.
deshielded
the operating frequency of the machine
200,000,000 Hz.
200 so on
200, *ie* *200* Hz.

on a 250 MHz machine, 1 ppm corresponds to ___250___ Hz in proton NMR spectra
on a 400 MHz machine, 1 ppm corresponds to ___400___ Hz in proton NMR spectra
on an 800 MHz machine, *10 ppm* corresponds to __8000____ Hz in proton NMR spectra

_25_ Hz.
difference of __0.1__ ppm.
___0.1___ ppm.

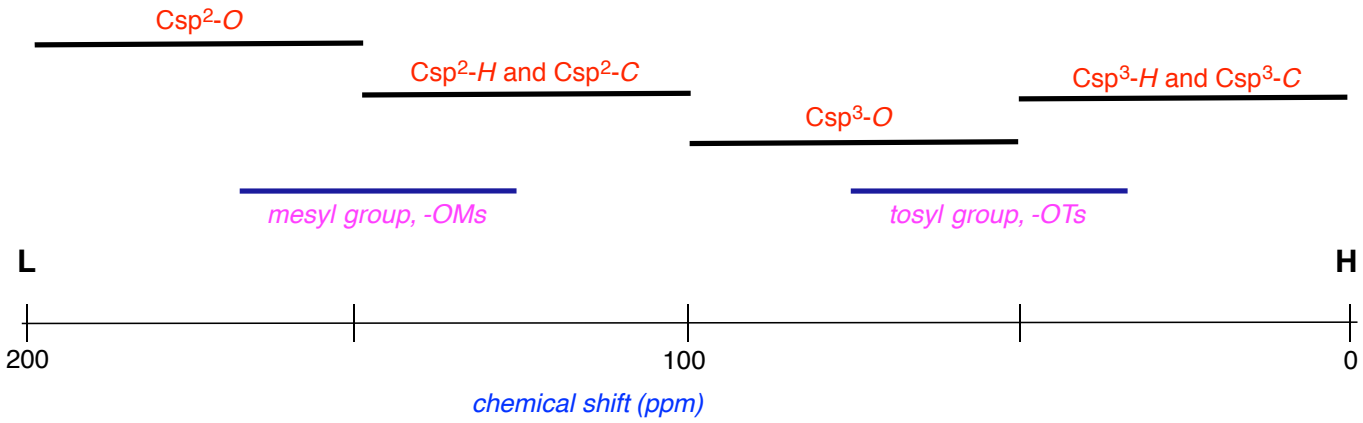
greater on a 60 MHz

greater on a 100 MHz

less as the operating frequency

D. Chemical Shifts In ^{13}C Spectra

upfield region and corresponds to *shielded*



downfield region and corresponds to *deshielded*
attract electron density tend to *deshield*
deshield

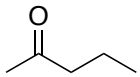
less shielded

inequivalent except

the same chemical shifts, and inequivalent ones usually resonate at *different*

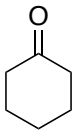
the same as

NOTE FROM KB: it is difficult to be sure about exactly which chemical shift range for some of these carbons, in other words some are borderline. When the book is re-printed I will make the ranges broader.



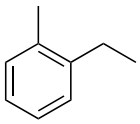
__5__
inequivalent C

number of resonances (ppm):
0 - 50 __4__
50 - 100 _0__
100 - 150 _0__
above 150 _1__



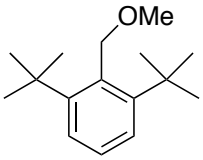
__4__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _0__
above 150 _1__



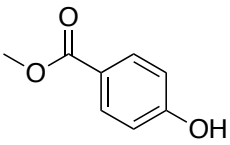
__9__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _6__
above 150 _0__



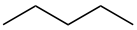
__8__
inequivalent C

number of resonances (ppm):
0 - 50 _2__
50 - 100 _2__
100 - 150 _4__
above 150 _0__



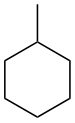
__6__
inequivalent C

number of resonances (ppm):
*0 - **40** _0__*
***40** - 100 _1__*
100 - 150 _3__
above 150 _2__



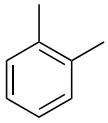
__3__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _0__
*above 150 __0_*



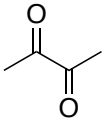
__5__
inequivalent C

number of resonances (ppm):
0 - 50 _5__
50 - 100 _0__
100 - 150 _0__
above 150 _0__



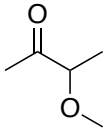
__4__
inequivalent C

number of resonances (ppm):
0 - 50 _1__
50 - 100 _0__
100 - 150 _3__
above 150 _0__



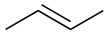
__2__
inequivalent C

number of resonances (ppm):
0 - 50 _1__
50 - 100 _0__
100 - 150 _1__
above 150 _1__



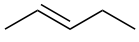
__5__
inequivalent C

number of resonances (ppm):
0 - 50 _2__
50 - 100 _2__
100 - 150 _0__
above 150 _1__



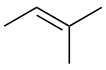
__2__
inequivalent C

number of resonances (ppm):
0 - 50 _1__
50 - 100 _0__
100 - 150 _1__
above 150 _0__



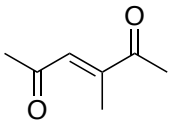
__5__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _2__
above 150 _0__



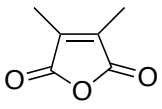
__5__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _2__
above 150 _0__



__7__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _2__
above 150 _2__



__3__
inequivalent C

number of resonances (ppm):
0 - 50 _1__
50 - 100 _0__
100 - 150 _1__
above 150 _1__

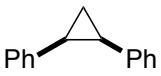
NOTE FROM KB: it is difficult to be sure about exactly which chemical shift range for some of these carbons, in other words some are borderline. When the book is re-printed I will make the ranges broader. HOWEVER the number of inequivalent *C* have been checked several times. They are right I believe, but sometimes the symmetry of the molecules is hard to see. Look out of for planes of symmetry, C2 axes, and diastereotopic groups.

__1__
inequivalent C

number of resonances (ppm):
0 - 50 _1__
50 - 100 _0__
100 - 150 _0__
above 150 _0__

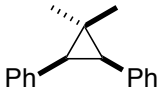
__3__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _0__
above 150 _0__



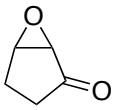
__6__
inequivalent C

number of resonances (ppm):
0 - 50 _2__
50 - 100 _0__
100 - 150 _4__
above 150 _0__



__8__
inequivalent C

number of resonances (ppm):
0 - 50 _4__
50 - 100 _0__
100 - 150 _4__
above 150 _0__

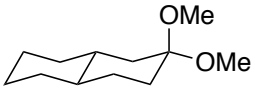


__5__
inequivalent C

number of resonances (ppm):
0 - **40** _2__
40 - 100 _2__
100 - 150 _0__
above 150 _1__

__6__
inequivalent C

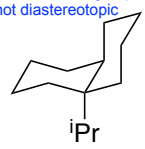
number of resonances (ppm):
0 - 50 _4__
50 - 100 _2__
100 - 150 _0__
above 150 _0__



__12__
inequivalent C

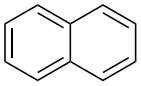
number of resonances (ppm):
0 - 50 _9__
50 - 100 _3__
100 - 150 _0__
above 150 _0__

flipping of cis-decalins is fast on the 13C NMR time scale, so iPr Me groups are not diastereotopic



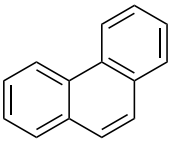
__8__
inequivalent C

number of resonances (ppm):
0 - 50 _8__
50 - 100 _0__
100 - 150 _0__
above 150 _0__



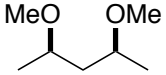
__3__
inequivalent C

number of resonances (ppm):
0 - 50 _0__
50 - 100 _0__
100 - 150 _3__
above 150 _0__



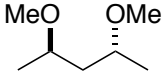
__7__
inequivalent C

number of resonances (ppm):
0 - 50 _0__
50 - 100 _0__
100 - 150 _7__
above 150 _0__



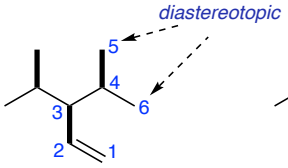
__4__
inequivalent C

number of resonances (ppm):
0 - 50 _2__
50 - 100 _2__
100 - 150 _0__
above 150 _0__



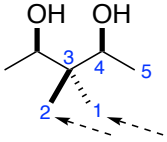
__4__
inequivalent C

number of resonances (ppm):
0 - 50 _2__
50 - 100 _2__
100 - 150 _0__
above 150 _0__



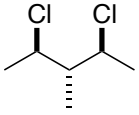
__6__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _2__
above 150 _0__



__5__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _1__
100 - 150 _0__
above 150 _0__

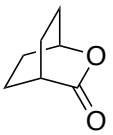


__4__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _1__
100 - 150 _0__
above 150 _0__

__2__
inequivalent C

number of resonances (ppm):
0 - 50 _2__
50 - 100 _0__
100 - 150 _0__
above 150 _0__

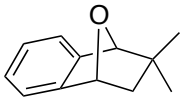


__5__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _1__
100 - 150 _0__
above 150 _1__

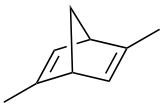
__3__
inequivalent C

number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _0__
above 150 _0__



__12__
inequivalent C

number of resonances (ppm):
0 - 50 _4__
50 - 100 _2__
100 - 150 _6__
above 150 _0__

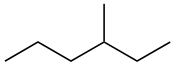


__5__
inequivalent C

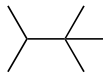
number of resonances (ppm):
0 - 50 _3__
50 - 100 _0__
100 - 150 _2__
above 150 _0__

__1__ ^{13}C resonances.

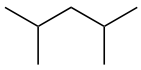
cannot be



7 inequivalent C



4 inequivalent C



3 inequivalent C

E. Coupling In ^{13}C NMR

^{13}CH Spin Systems

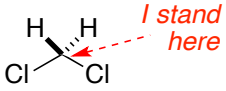
The ^{1}H nucleus *is*
different to
into *two* peaks of almost equal intensity; this is called a *doublet*.
The chemical shift of that carbon is *exactly at the center of*

coupling with protons

doublet and a singlet, respectively.
In that experiment it *would*

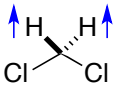
^{13}CH$_2$ Spin Systems

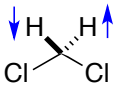
the same

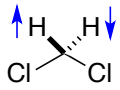


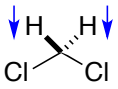
I stand here

and experience.....









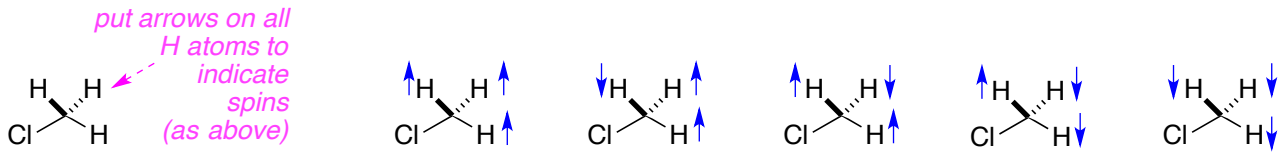
magnetic effect feels same

3 different magentic field strengths influence that ^{13}C, ratio 1:2:1

three different magnetic fields and the relative probability is *1:2:1*.
triplet for the carbon and it *could*

$^{13}CH_3$ Spin Systems

quartet for the carbon and it *could*



__4__ different magentic field strengths influence that ^{13}C, ratio __1:3:3:1__

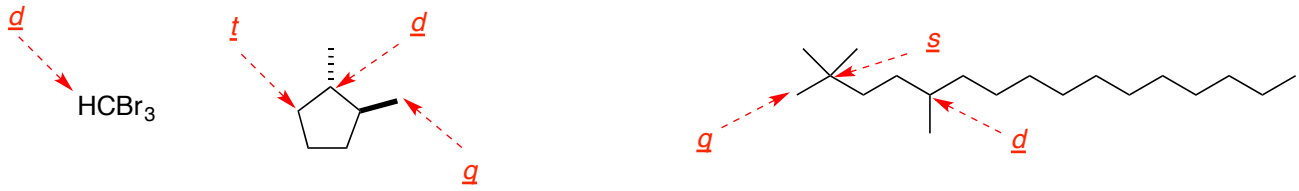
The relative probabilities for finding the spins in *a* or *o* states is *1:3:3:1*.

n + 1 peaks.
doing the splitting and not those *being observed*.

follows Pascal's triangle.

rare and *can* be ignored.

Differentiating CH, CH_2, And CH_3 In ^{13}C Spectra



coupling constant and it is expressed in *Hz*.
different on machines operating at different field strengths, so they are *never*

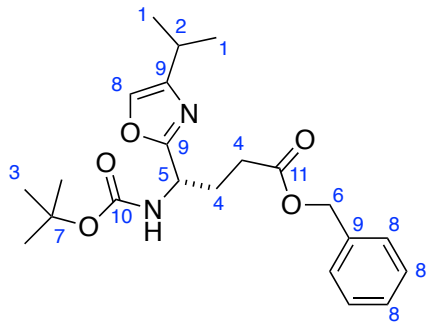
DEPT Spectra To Differentiate Quaternary, Methine-, Methylene-, and Methyl-Carbons

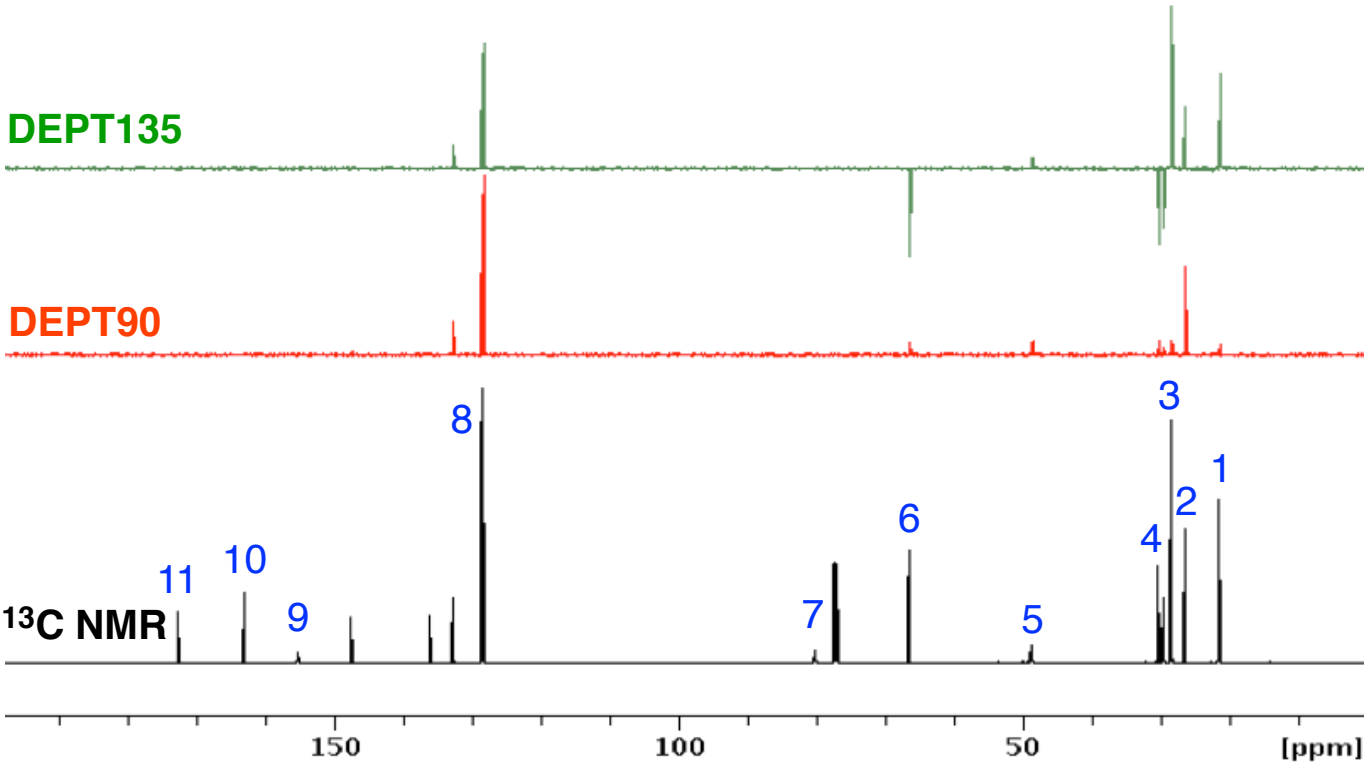
quaternary, *do not*
positive peaks, and resonances for CH_2 carbons *negative*.

CH peaks.

can
more

(Some inequivalent carbon atoms are given the same number if they are indistinguishable in the spectra, *eg* C^4, C^8 and C^9). This will be made clear in the next edition.





nearly always shown.

^{1}H-NMR signals of the protons attached to them.

^{1}H NMR Spectroscopy

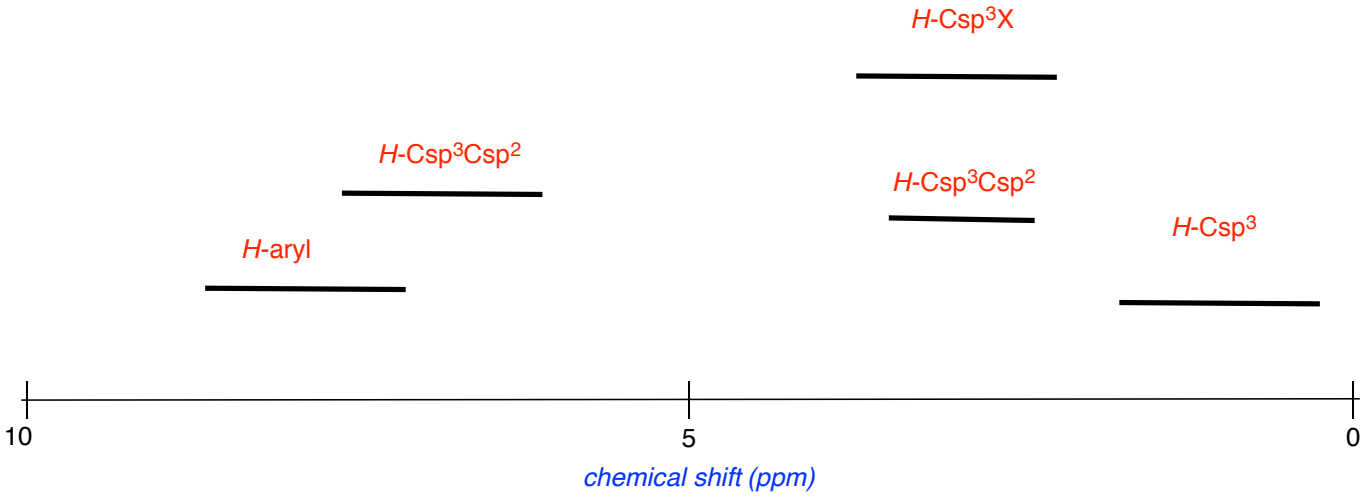
from chapter _____ in the recommended text

A. Introduction

.

B. Chemical Shifts In ^{1}H Spectra

smaller

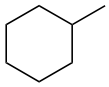


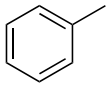
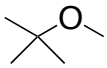
high field region
low field region from 5 – 6.5 ppm

lower field than *H*C-Csp^3 atoms
allylic and benzylic
higher chemical shifts than *H*C-Csp^3

higher

lower

$H_2C{=}CH_2$

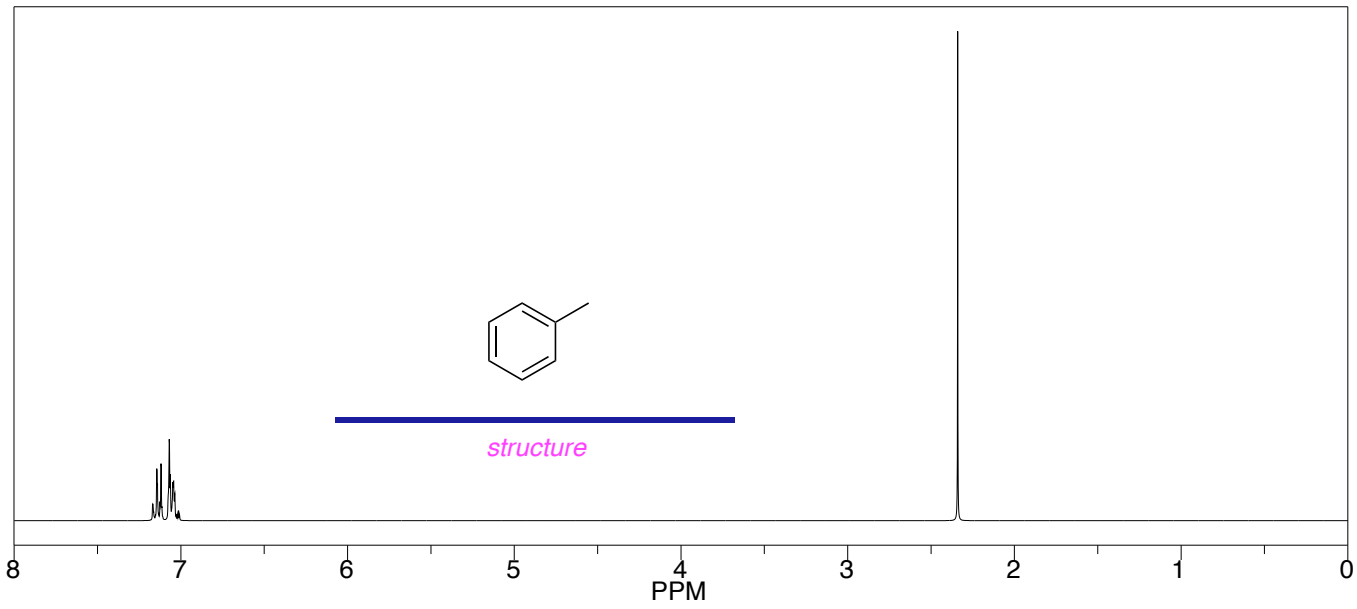
1.4 - 1.2 | 1.4 - 1.2 and 0.9 | 7.5 | 7.5 and 2.3 | 3.5 and 1.4 - 1.2 | 0.9 | 5.2

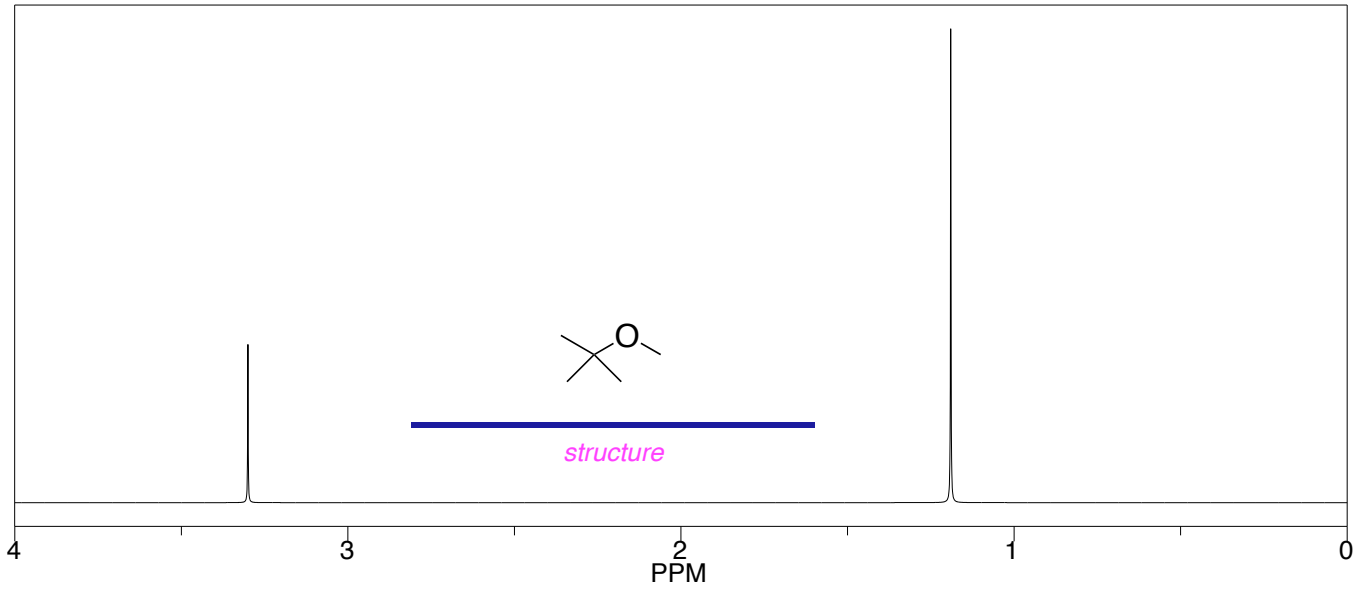
select from δ = 7.5, 5.2, 3.5, 2.3, 1.4 - 1.2, and, or 0.9

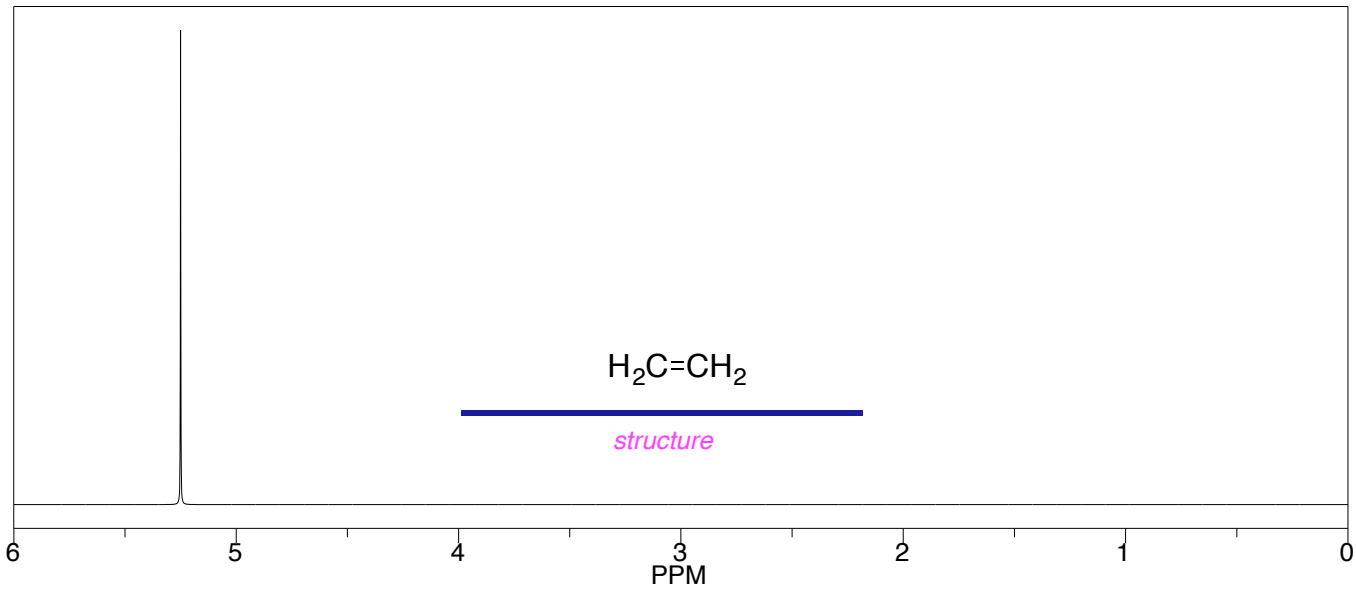
__1__ __5__ __1__ __4__ __2__ __1__ __1__

indicate number of H environments

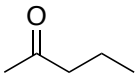
x.




O
structure
4
3
2
1
0
PPM

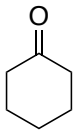

H2C=CH2
structure
6
5
4
3
2
1
0
PPM

NOTE FROM KB: it is very difficult to be sure about the chemical shift ranges for some of these protons, in other words some are borderline. When the book is re-printed I will make the ranges broader.



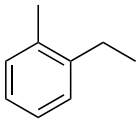
__4___
inequivalent H

number of resonances (ppm):
0 - 2 _2__
2 - 3 _2__
3 - 4 _0__
4 - 7 _0__
7 - 9 _0__



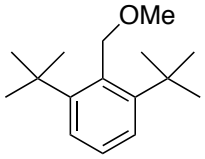
__3___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__



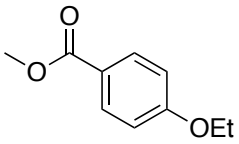
___7__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __2__
3 - 4 __0__
4 - 7 __0__
7 - 9___4_



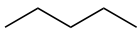
__5___
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __1__
4 - 7 __1__
7 - 9___2_



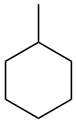
___5__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9__2__



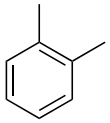
__3___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__



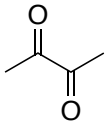
___8__
inequivalent H

number of resonances (ppm):
0 - 2 __8__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__



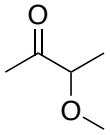
___3__
inequivalent H

number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___2_



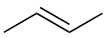
___1__
inequivalent H

number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_



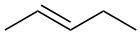
___4__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __1__
3 - 4 __1__
4 - 7 __1__
7 - 9__0__



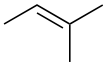
___2__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_



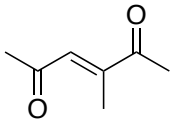
___5__
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __0__
4 - 7 __2__
7 - 9___0_



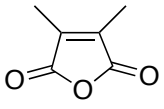
__4___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_



__4___
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __2__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_



__1___
inequivalent H

number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__

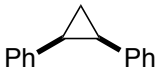
NOTE FROM KB: it is very difficult to be sure about the chemical shift ranges for some of these protons, in other words some are borderline. When the book is re-printed I will make the ranges broader.

___1__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_

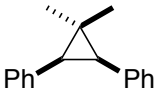
___4__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_



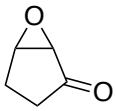
__6___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___3_



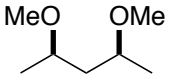
___6__
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___3_



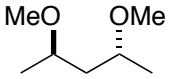
__6___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __2__
3 - 4 __1__
4 - 7 __1__
7 - 9__0__



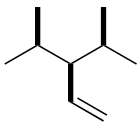
__5___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9___0_



__4__
inequivalent H

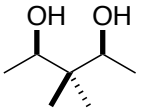
number of resonances (ppm):
0 - 2 __2__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9___0_



__7___
inequivalent H

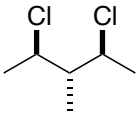
number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __3__
7 - 9___0_

note OH resonance
chemical shift varies



__5___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __1__
4 - 7 __1__
7 - 9___0_



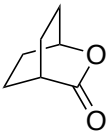
___4__
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __1__
4 - 7 __0__
7 - 9__0__

__2___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_

note plane of symmetry

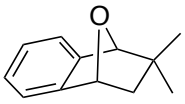


___6__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __1__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_

__4___
inequivalent H

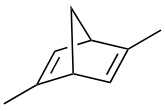
number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_



___10__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __2__
7 - 9___4_

note C2 axis



___4__
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_

C. Coupling In ^{1}H NMR

two bond couplings

Heteronuclear Coupling To ^{13}C Is Unimportant

1.11

are not

NMR silent).

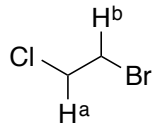
hetero-

Homonuclear ^{1}H Coupling

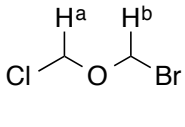
is not removed

2 and 3 bond *homo*nuclear couplings.

ie 4 bond homonuclear



A



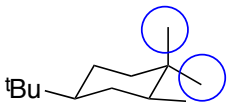
B

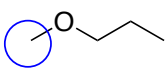
3 bonds and *do*

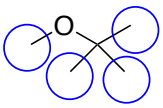
4 bonds between them and *do not*

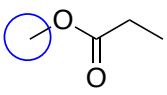
do not appear to be split.

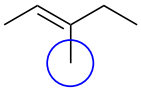
singlets.

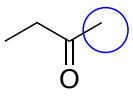


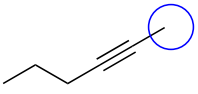


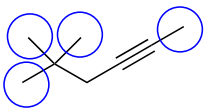


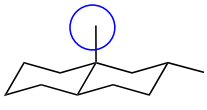


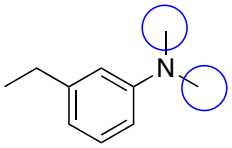


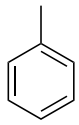




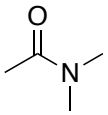








molecule 1



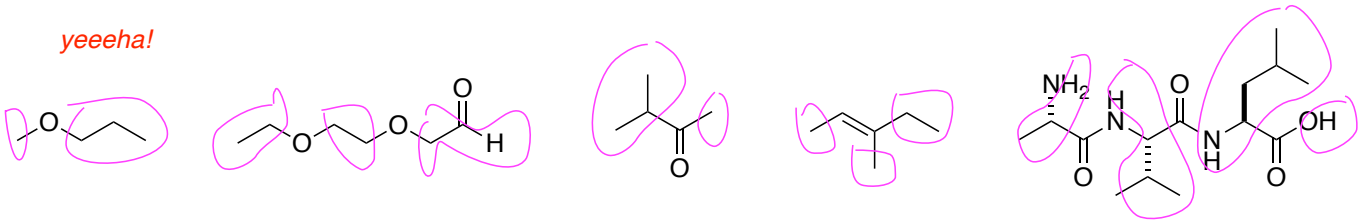
molecule 2

molecule 3

Spin Systems

any number >1 NMR

yeeeha!



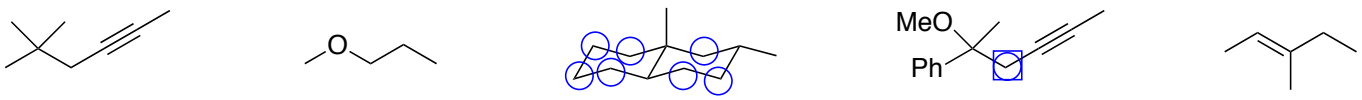
n + 1
does not
does
follows Pascal's triangle.

H^a-C-H^b Spin Systems

will
doublet.

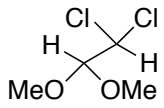
sometimes
will

will
appear as a *doublet*.

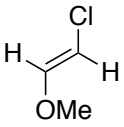


H^a-C-C-H^b Spin Systems

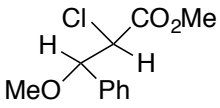
smaller than



isolated H^aCCH^b



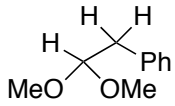
molecule 1



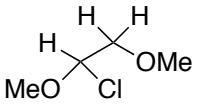
molecule 2

will
triplet
doublet

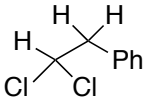
H^aC-CH^b_2 Spin Systems



isolated $H^aCCH^b_2$



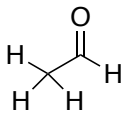
molecule 1



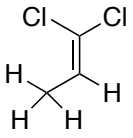
molecule 2

H^aC-CH^b_3 Spin Systems

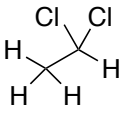
will
quartet, and *H^b* appears as a *doublet*.



isolated $H^aCCH^b_3$



molecule 1



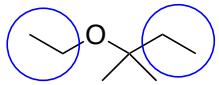
molecule 2

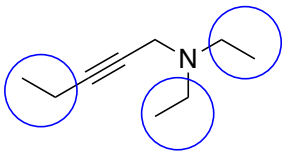
$H^a_2C\text{-}CH^b_3$ Spin Systems (Isolated Ethyl Groups)

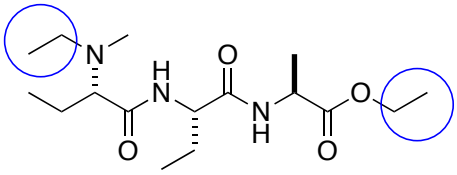
does not

do not

triplet, and the methylene is a *quartet*.



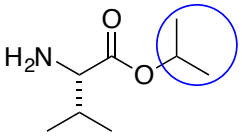


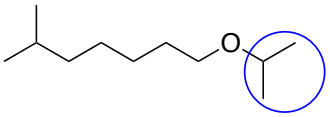


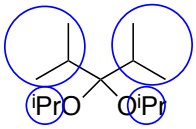
$(H^a_3C)_2CH^b$ Spin Systems (Isolated ^{i}Pr Groups)

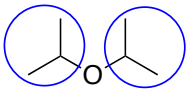
heptet with a relative intensity of _1:6:15:20:15:6:1

doublets.

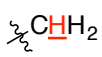








Common Splitting Patterns In Organic Molecules

A 

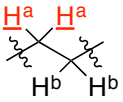
s

B 

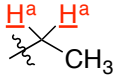
s

C 

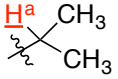
d

D 

t

E 

q

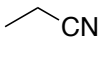
F 

hept

s = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *quin* = quintet, *sex* = sextet, *hept* = heptet, *oct* = octet

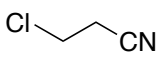
methyl | methylene | methylene | ethylene | ethyl | iso-propyl

fragment name possible fragment names: ethyl, ethylene, *iso*-propyl, methyl, methylene



E

3



D

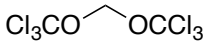
4

F

5

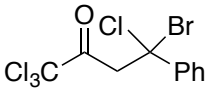
A

2



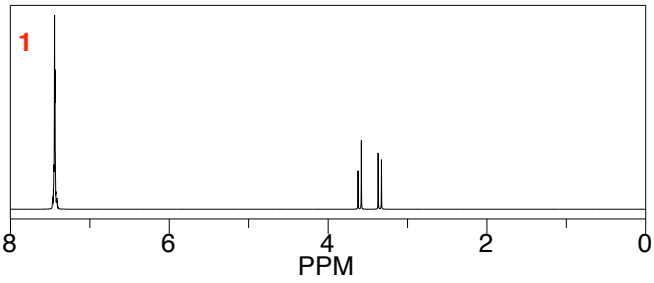
B

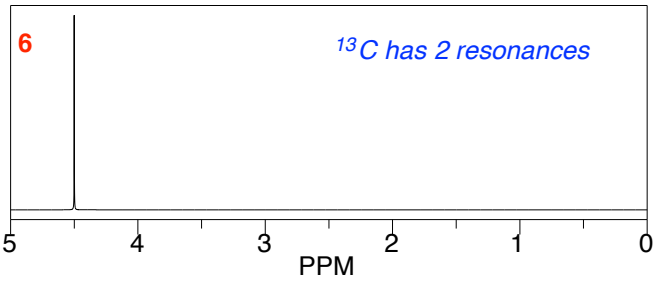
6

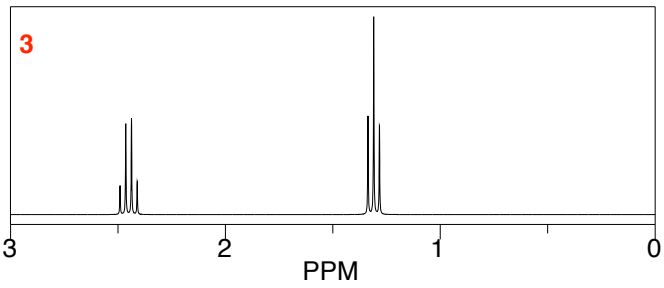


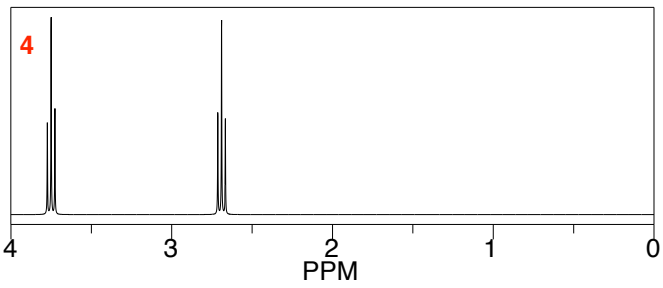
C

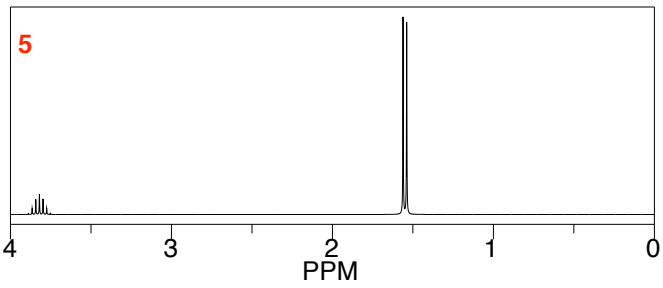
1

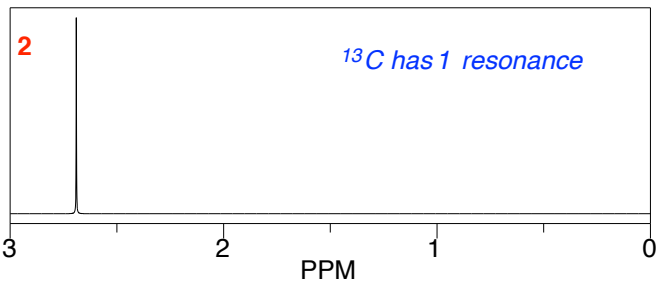


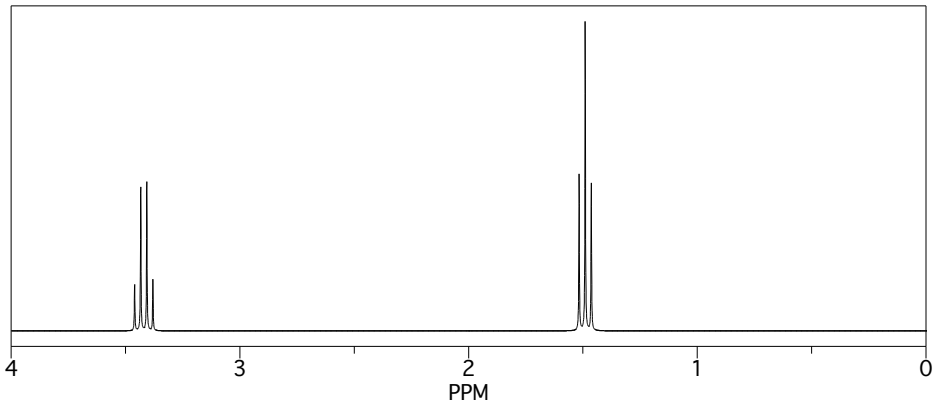




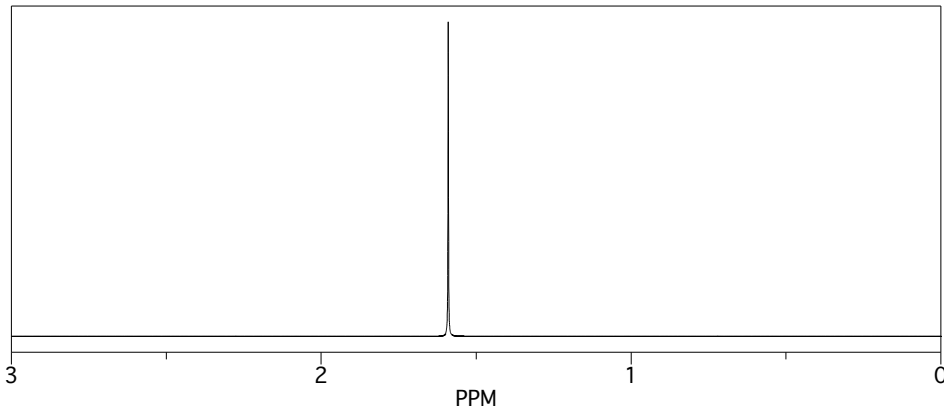




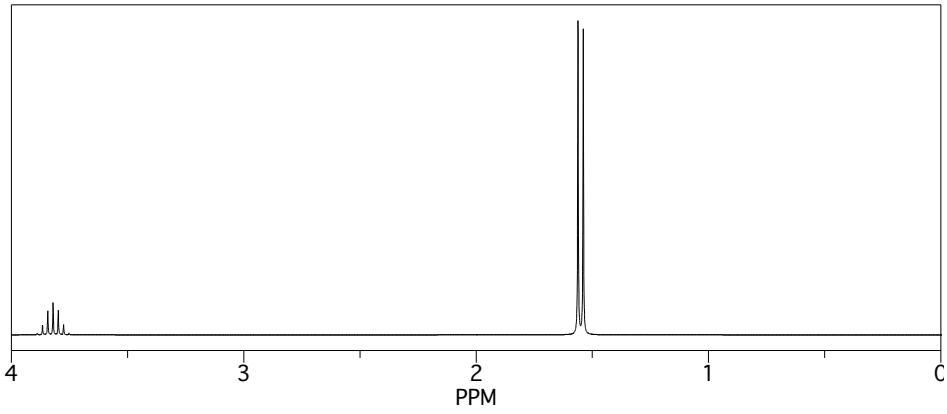




structure

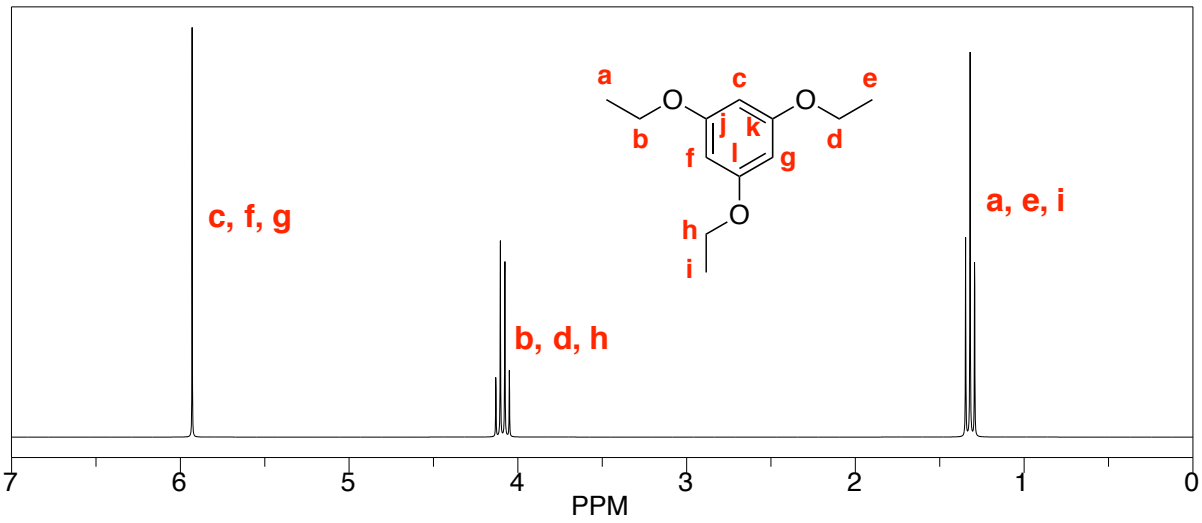


structure

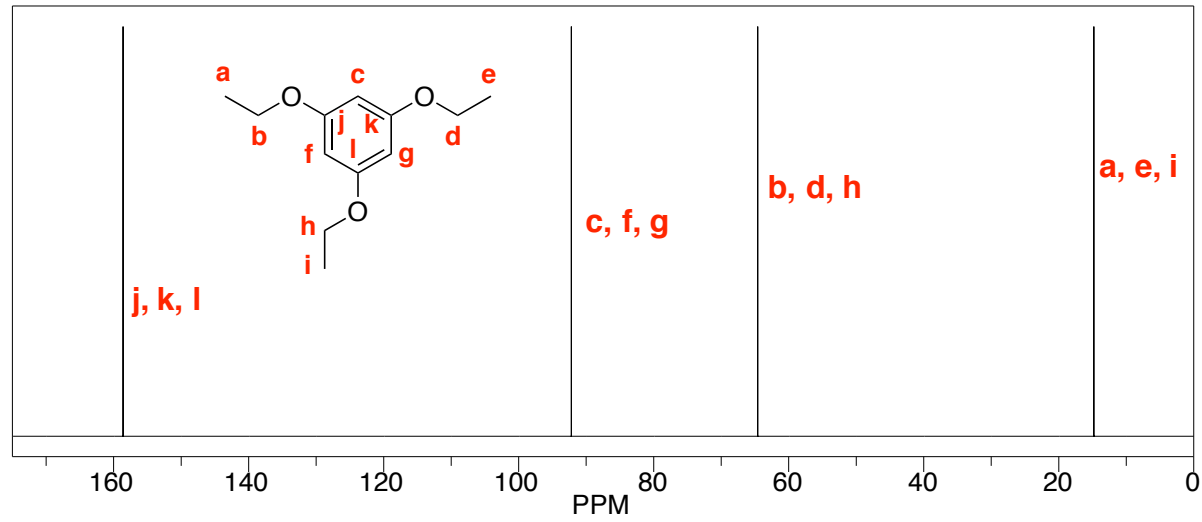


structure

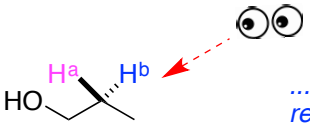
^{1}H NMR



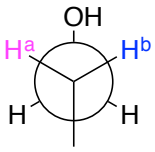
^{13}C NMR



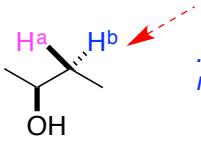
D. Diastereotopic Protons



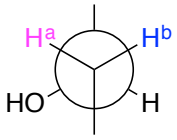
..... can be represented as



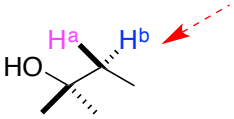
where H^a and H^b <u>are</u> equivalent



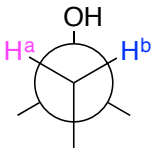
..... can be represented as



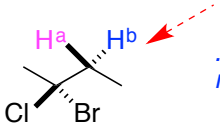
where H^a and H^b <u>are not</u> equivalent



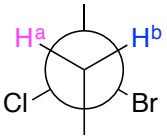
..... can be represented as



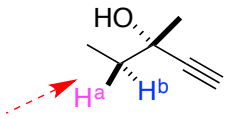
where H^a and H^b <u>are</u> equivalent



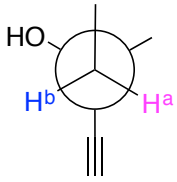
..... can be represented as



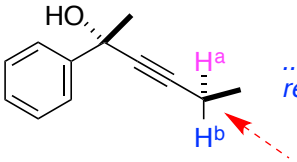
where H^a and H^b <u>are not</u> equivalent



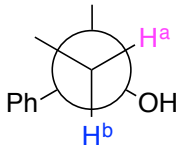
..... can be represented as



where H^a and H^b <u>are not</u> equivalent

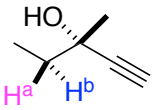


..... can be represented as

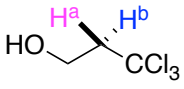


where H^a and H^b <u>are not</u> equivalent

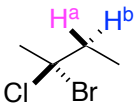
<u>inequivalent</u>



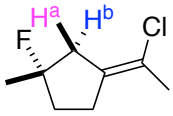
H^a: __doublet of quartets__
H^b: __doublet of quartets__



H^a: __triplet__
H^b: __triplet__

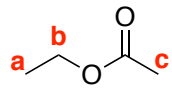


H^a: __doublet of quartets__
H^b: __doublet of quartets__

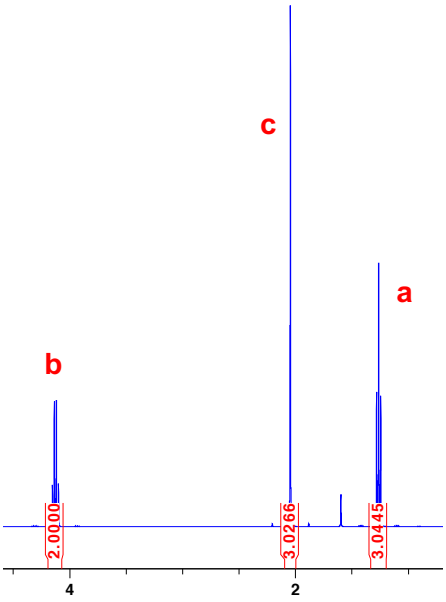


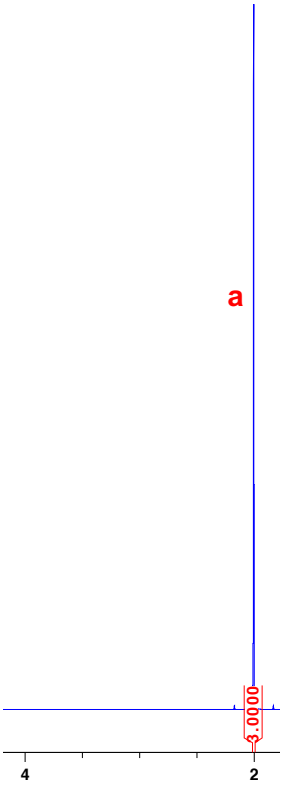
H^a: __doublet of doublets___
H^b: __doublet of doublets___

E. Some Problems Involving Spectral Interpretation



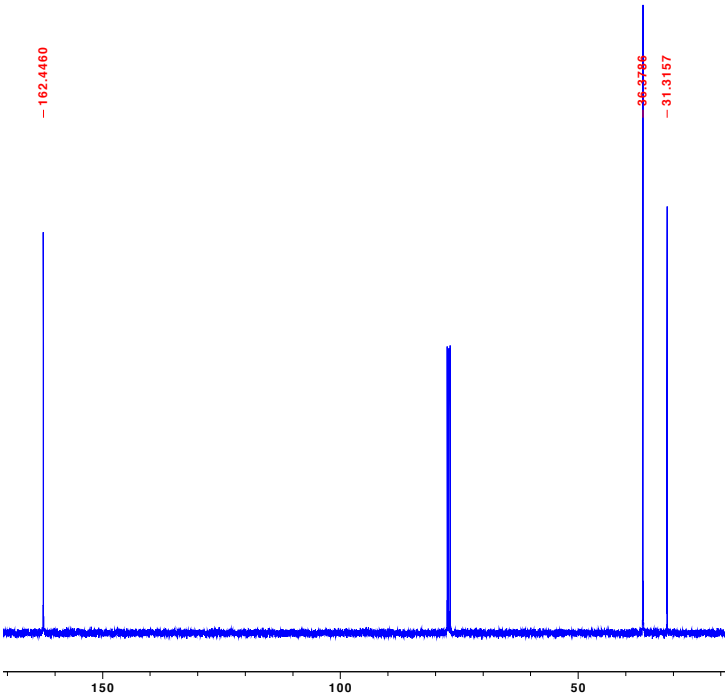
structure

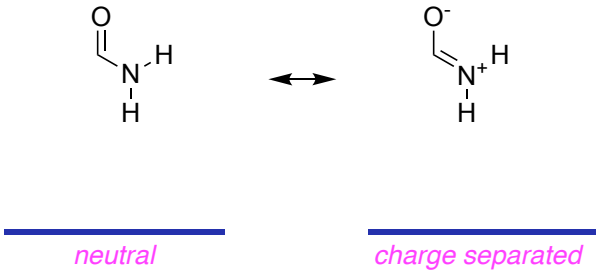




structure

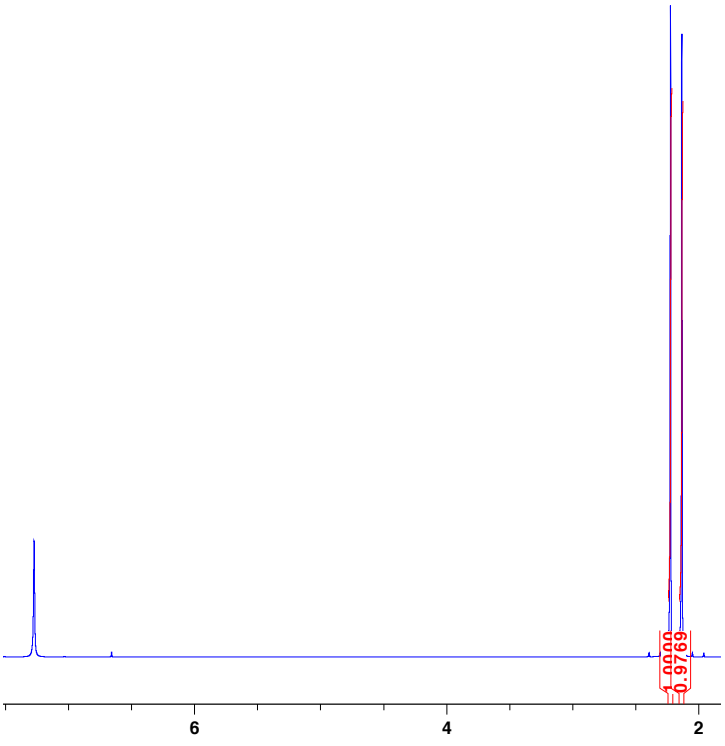
Here are the proton and carbon spectra of dimethyl formamide (DMF). Draw a resonance structure of DMF that shows a charge separation between *O* and *N*.





Explain why *two* methyl resonances are seen in each spectrum:

because rotation around the OC-N bond is slow on the NMR time scale, due to this resonance effect___



…

Mass Spectrometry (MS)

from chapter(s) _____ in the recommended text

A. Introduction

B. Components Of Mass Spectrometers

mass-to-charge.

molecular mass

without fragmentation).

- create ions in the gas phase
- separate ions on the basis of *m/z* (*ie* an analyzer)

- detect the number of ions of each *m/z*

an ionization source / an analyzer / a detector.

ionization.

for *analysis*.

or *analysis*.

for *analysis*.

or *ionization*.

Fourier transform (FT) analysis.

Electron Impact (EI) ionization.

Detectors in MS *electron multipliers*.

MALDI-TOF is a valid description but *ESI-MALDI* is not.

C. Primary Ions Formed In Different Ionization Techniques

MALDI
ie $[M + 1]^+$.

ESI
$[M + 1]^+$

MALDI ESI EI

an electron from molecules to give *radical cations*
ie $[M]^+$.

Resolution
sensitivity.

most sensitive forms of MS.

D. Isotopes In Mass Spectrometry

Element	Isotope	Abundance (%)	Mass number	Exact mass
hydrogen	^{1}H	99.99	1	1.00783
carbon	^{12}C	98.89	12	12.00000
carbon	^{13}C	1.11	13	13.00335
nitrogen	^{14}N	99.64	14	14.00307
oxygen	^{16}O	99.76	16	15.99492
fluorine	^{19}F	100	19	18.99840
phosphorus	^{31}P	100	31	30.97376
sulfur	^{32}S	95.00	32	31.97207
chlorine	^{35}Cl	75.77	35	34.96886
chlorine	^{37}Cl	24.23	37	36.96590
bromine	^{79}Br	50.69	79	78.91835
bromine	^{81}Br	49.31	81	80.91635
iodine	^{127}I	100	100	126.904468

CO	C_2H_4	$C_2H_5{}^{35}Cl$
27.99492	28.03132	64.00801
exact mass	*exact mass*	*exact mass*

$CH_3{}^{79}Br$	$CH_3{}^{81}Br$	$C_2H_5{}^{37}Cl$
93.94184	95.93984	66.00505
exact mass	*exact mass*	*exact mass*

can distinguish

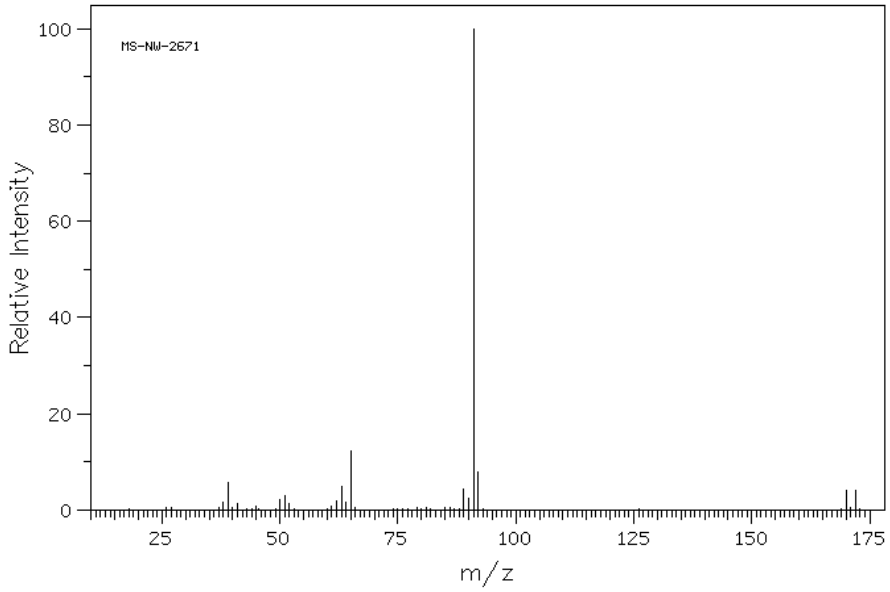
1.99704 atomic mass units (amu's) in a ratio of 3.13:1
1.99800 amu's in a ratio of 1.03:1.

3 molecular ions in a 1:2:1
4 molecular ions in a 1:3:3:1

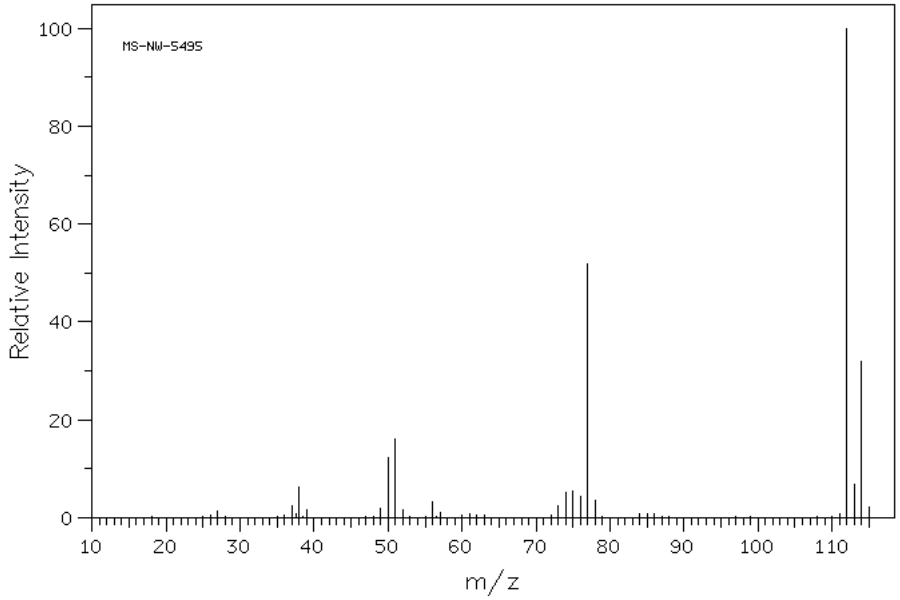
Illustrative Interpretation Of Isotopes In MS

the chlorine-containing compound A is number: __2_____
the bromine-containing compound B is number: __1_____
the non-halogenated compound C is number: ____3_____

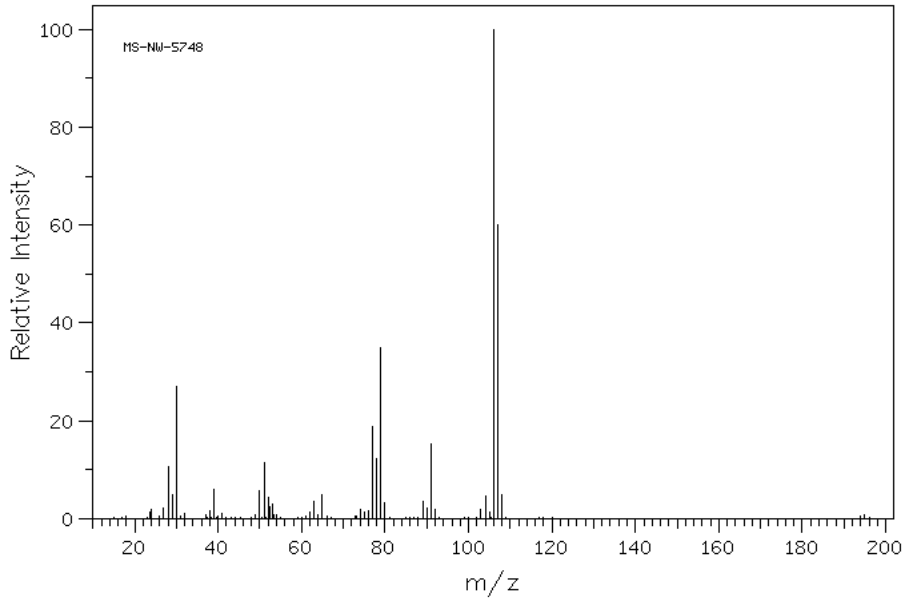
1 (m/z = 170 and 172):



2 (m/z = 112 and 114):



3 (m/z = 107):



always have odd molecular ion m/z values.

E. Fragmentation

radicals

the *most* stable one that is most likely to be observed.

electron impact

ESI does not.

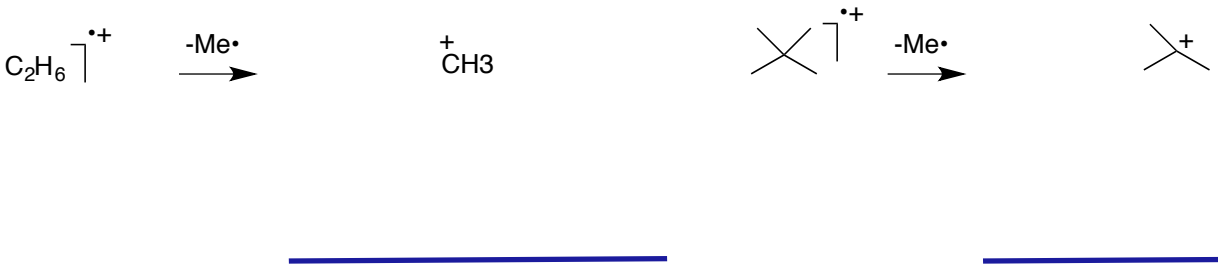
ESI is widely used in contemporary MS, but *EI*

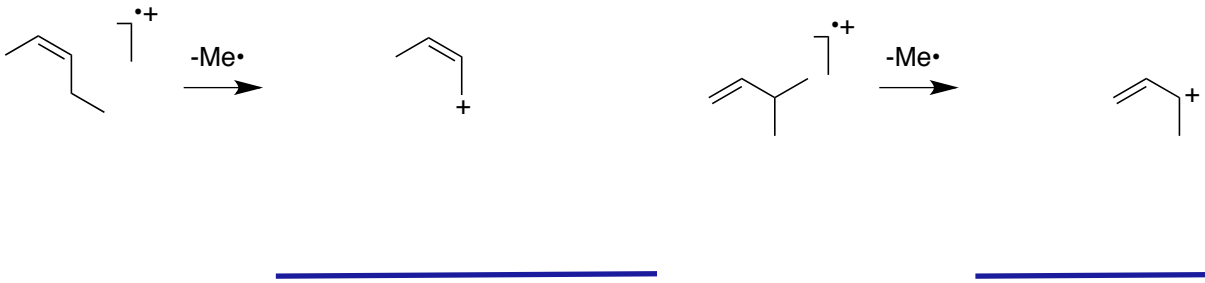
Fragmentation is usually *undesirable*

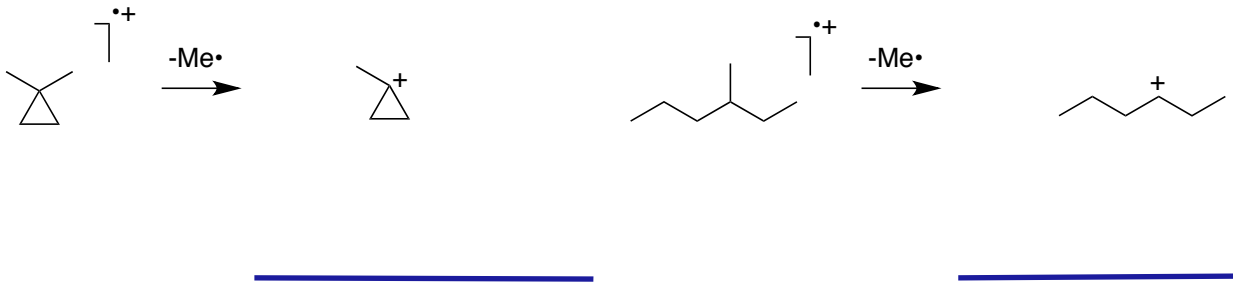
is useful when complementary methods

MS/MS

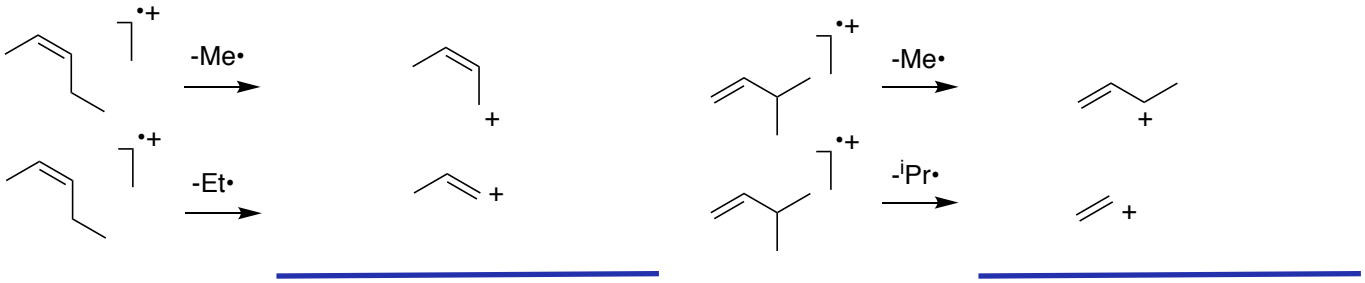
tandem

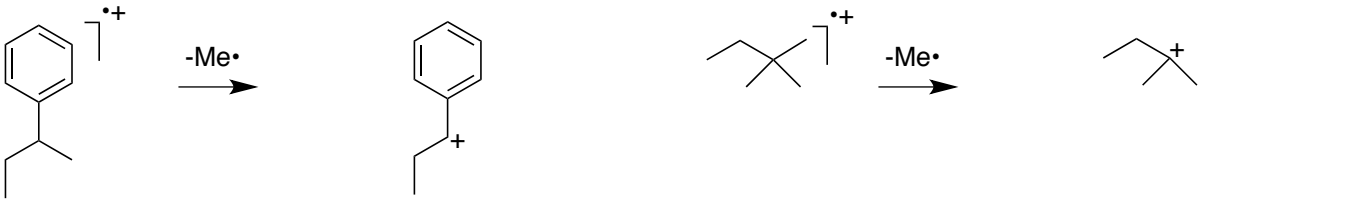


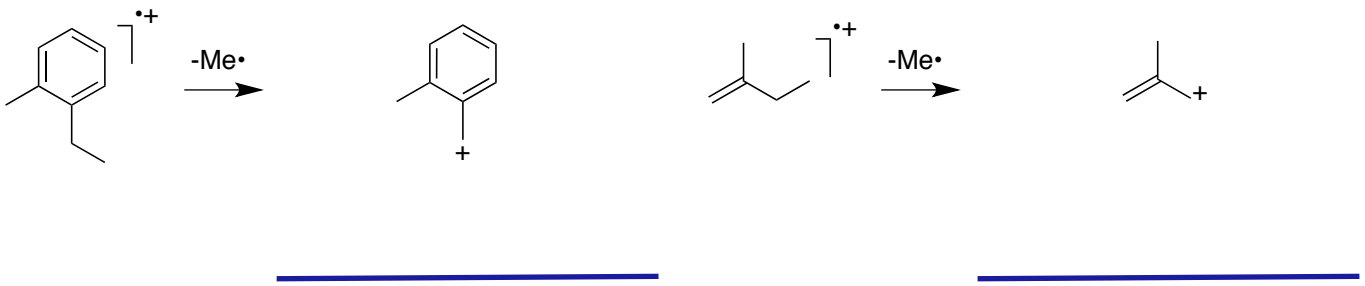


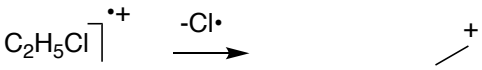


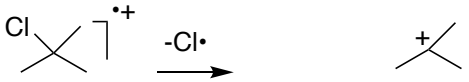
sorry, intended question was -Me• but then there was overrlap with another question. This one will be deleted in later editions

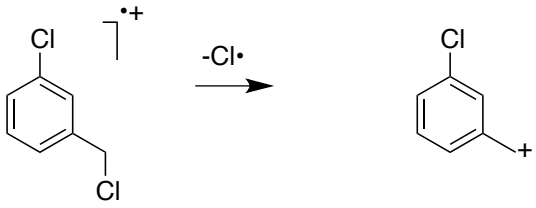


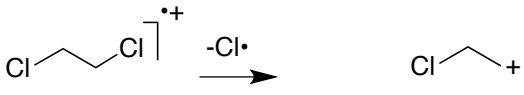


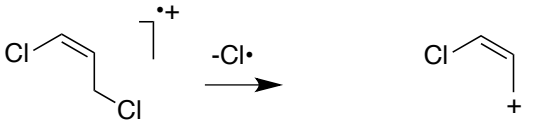


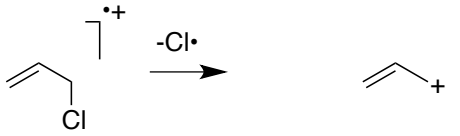

C2H5Cl
-Cl•


Cl
-Cl•

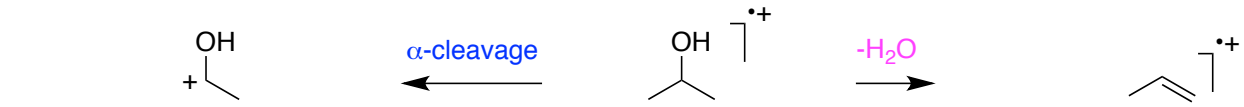

Cl
-Cl•
Cl
Cl

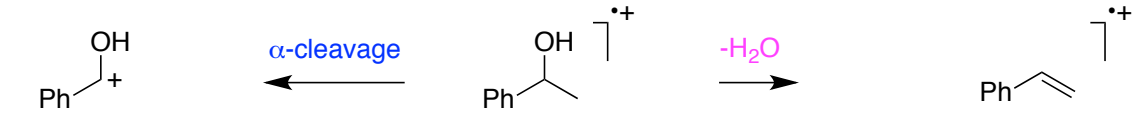

Cl
Cl
-Cl•
Cl

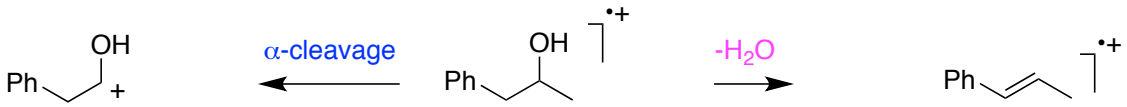

Cl
-Cl•
Cl

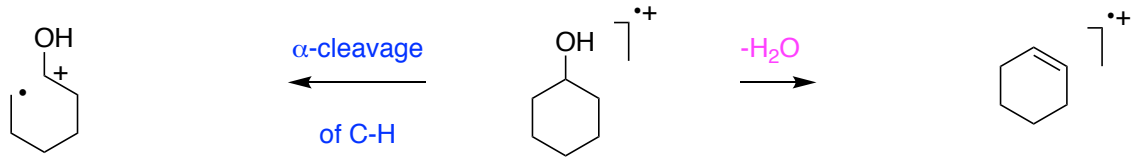

-Cl•
Cl

α-Cleavage

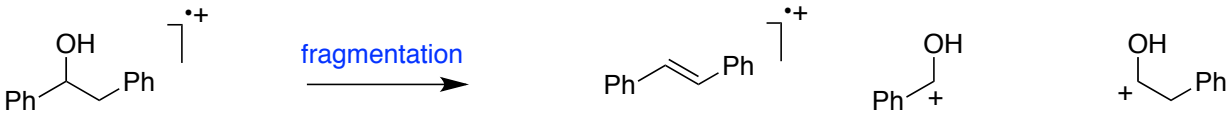

OH
α-cleavage
OH
-H2O


OH
Ph
+
α-cleavage
OH
Ph
•+
-H2O
Ph
•+

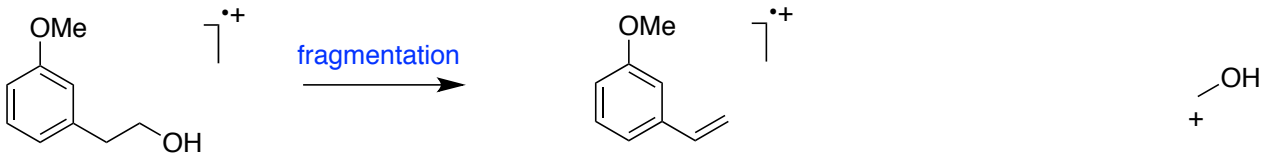

OH
Ph
+
α-cleavage
OH
Ph
•+
-H2O
Ph
•+


OH
+
α-cleavage
of C-H
OH
•+
-H2O
•+


OH
Ph
Ph
fragmentation
OH
Ph


OH
Ph
Ph
fragmentation
Ph
Ph
OH
Ph
OH
Ph


HO
fragmentation
HO

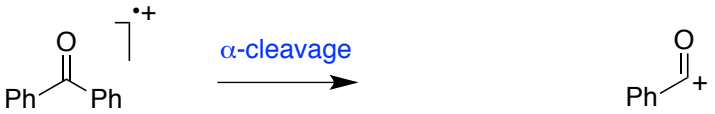

OMe
OH
fragmentation
OMe
OH

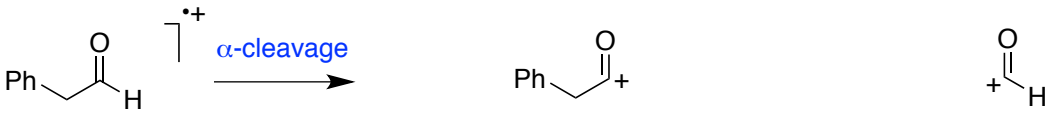

NH2
Ph
Ph
α-cleavage
NH2
Ph
Ph
NH2
Ph

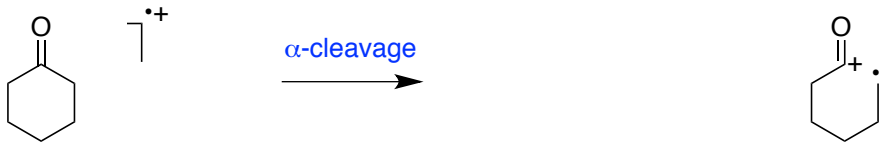

NH
α-cleavage
NH
NH


NH
α-cleavage
NH
NH


NEt3
α-cleavage
N

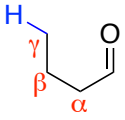

α-cleavage

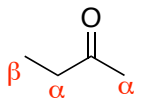

α-cleavage

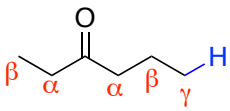

α-cleavage

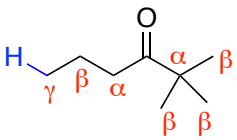

α-cleavage

The McLafferty Rearrangement

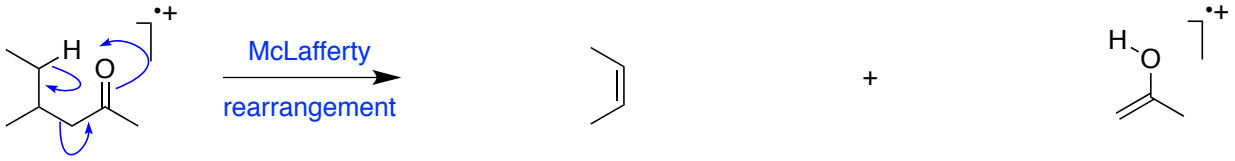




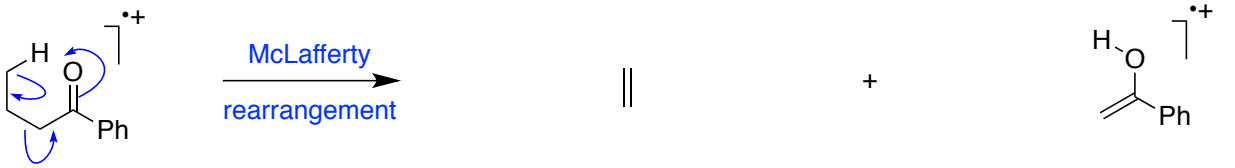




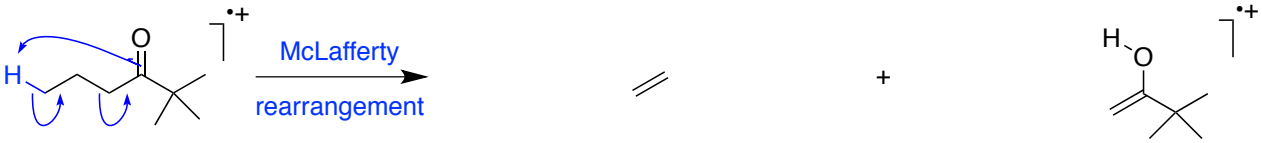
α and β fragments

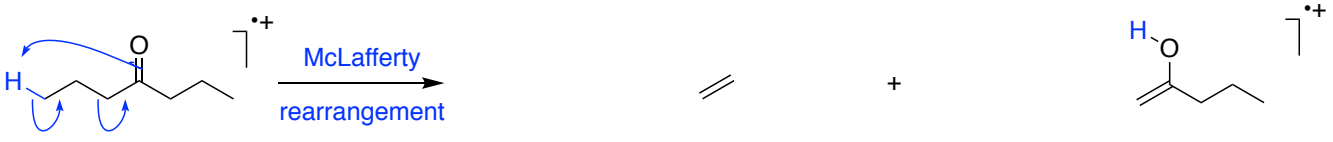


alkene *radical cation*



alkene *radical cation*





Molecule on the left can undergo *McLafferty rearrangement* since it has γ-hydrogen whereas molecule on the right does not.