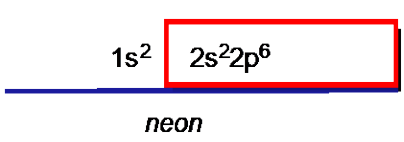
1. Hybridization

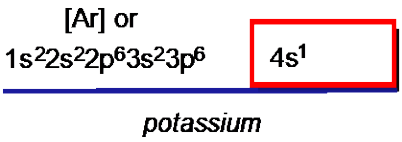
A. Intro

B. Electron Counting

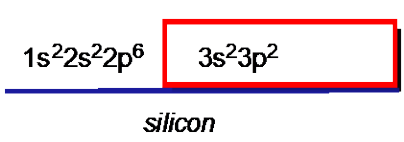
In Atoms



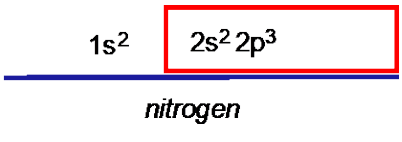
neon



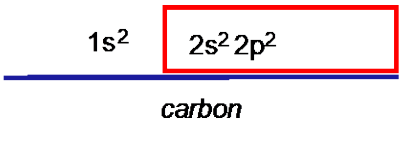
potassium



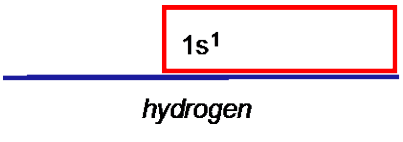
silicon



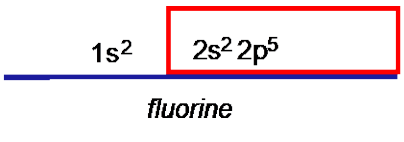
nitrogen



carbon

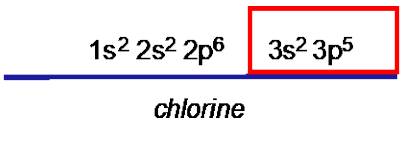


hydrogen

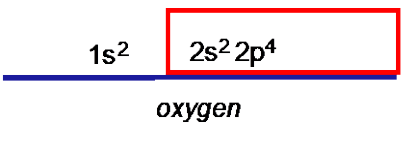


fluorine

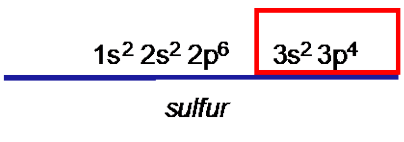
bromine



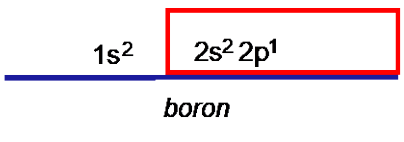
chlorine



oxygen



sulfur



boron

In Molecules: Valency

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

are formed when atoms *share* to form stable
ionic bonds are formed when atoms *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*

The electronic structure of *He*

C 4 *N* 3 *O* 2 *F* 1 *Cl* 1 *Br* 1 *S* 2

hydrogen atom may only bring *1* electron(s)
hydrogen in common molecules is *1*.

C CH_4 *N* NH_3 *O* H_2O *F* HF *Cl* HCl *Br* HBr S H_2S

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*

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*

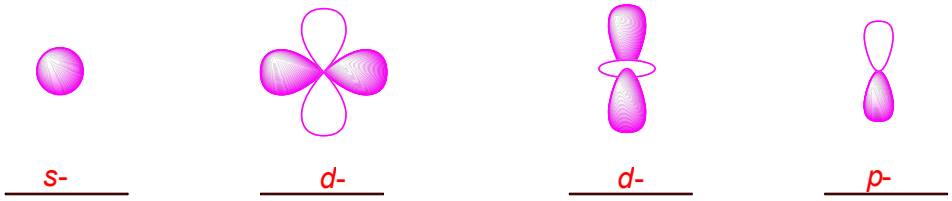
atomic origin of electrons *is* lost

C. Hybdridization: Mixing Atomic Orbitals To Maximize Bonding

Combining *s*- and *p*-Orbitals

refer to where some electrons *have maximum probability of being*.

have *different* shapes as atomic orbitals.



s- *d-* *d-* *p-*

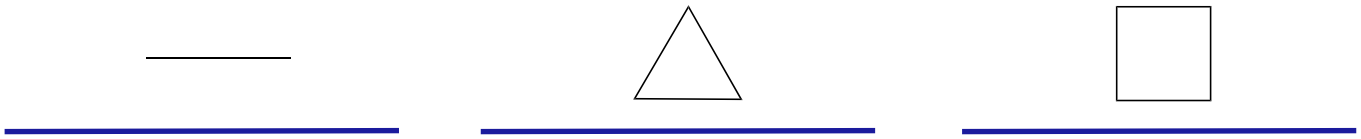
atomic orbitals that are mixed or *hybridized* to make them.

2 molecular orbitals, of three gives *3*, and of *n* gives *n*.

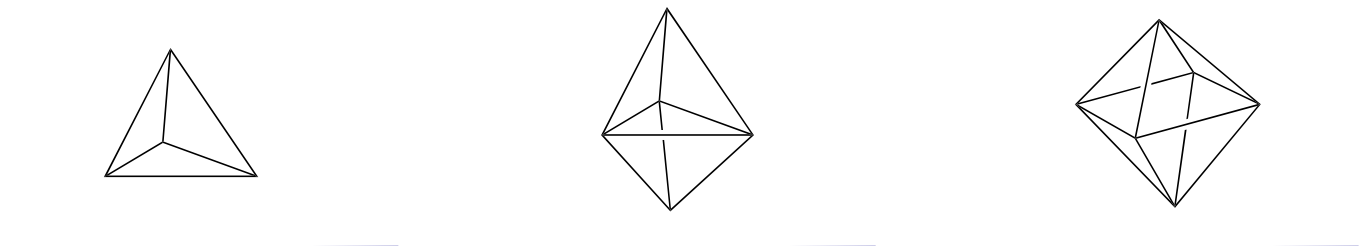
one *s*- and one *p*-orbital gives a *sp*-hybrid, whereas sp^2-orbitals are formed if *two* *p*-orbitals are mixed with one *s*-.

three *p*- and one *s*-orbitals gives a ___sp^3___-hybrid.

Geometric Shapes



straight line connecting three dots *a triangle* *a square*



a tetrahedron *a trigonal bipyramid* *an octahedron*

a line with the boy *in the middle*.

girl-boy-girl angle is *180°*
this is called the *ideal bond* angle.

herself in the middle of a *triangle* with
then *120°*.

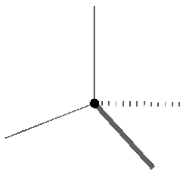
with the point in the middle of a *tetrahedron*,
then the bond angle is *109°*.

Molecular Shapes

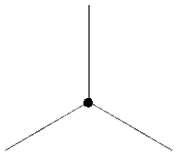
one *s*- and one *p*- atomic orbitals gives *2* *sp*-hybrid orbitals.

one *s*- and two *p*-orbitals give *3* hybrid orbitals
and *4* arise from one *s*- and three *p*-orbitals

Bold lines mean “emerges from the plane of the paper” and *dashed* lines indicate “projects behind the plane”.



sp^3



sp^2

sp

central atom will be sp^2-hybridized.

A tetrahedron of sp^3-hybrids will be formed if *4* bonds and/or lone pairs
is generated from two *sp*-hybrid orbitals.

it has *0* lone pairs
therefore it is *tetrahedral*.

and it has *6* electrons that it did not share, *ie 3* lone pairs.

that fluoride has *4* entities

hydrogen fluoride is approximately *tetrahedral*.

Water, *oxygen* is surrounded by *4* objects
O-geometry is *tetrahedral*

hydrogen chloride, *chlorine* is surrounded by *4* objects
Cl-geometry is *tetrahedral*

ammonia, *nitrogen* is surrounded by *4* objects
N-geometry is *tetrahedral*

hydrogen sulfide, *sulfur* is surrounded by 4 objects
S-atom is at the center of a *tetrahedral* arrangement

borane, *boron* is surrounded by *3* objects
B-atom is at the center of a *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°*

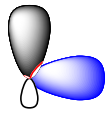
S in H_2S is *tetrahedral* with a dihedral angle of *109°*

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

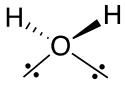
sp-hybrid consisting of *2* MOs in a *linear* arrangement with a dihedral angle of *180°*

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

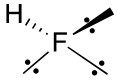
4 sp^3 MOs, and these arrange in a *tetrahedral* arrangement with a dihedral angle of *109°*



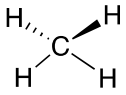
eg



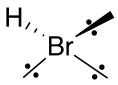
water



hydrogen fluoride

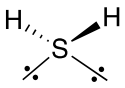


methane

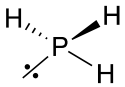


HBr

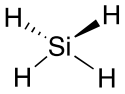
BH_3



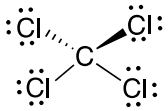
hydrogen sulfide



PH_3



SiH_4

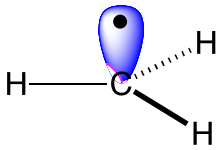


CCl_4

D. Hybridization In Ethane

the *C*-atom after sharing has *8* electrons in its second shell
the *C*-atom shares *7* electrons in its second shell; this *is not* a particularly favorable
why methyl radicals *are* relatively reactive.

Methyl radicals could be *sp^3*-hybridized



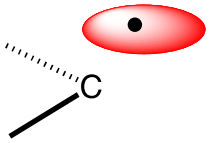
p^2

σ-bonds are formed between two orbitals that *point directly at each other*.
π-bonds are formed between two orbitals that *are parallel*.

E. Hybridization In Multiple Bonds

Ethene

σ-bonded sp^2-hybridized *C*-atoms



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

new MO in ethene contains *2* electrons.

combining sp^n-hybrids (*n* = 1 – 3) at each other are σ.

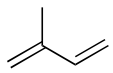
p-orbitals mix they form a π-orbital.

p-orbitals when they are *aligned*.
Perpendicular *p*-orbitals *do not* interact because the signs of the wave equations *cancel* in regions

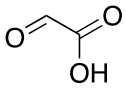
sp^2-hybridization is stabilized by formation of a π-bond.

Other Types Of Double Bonds

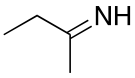
σ-bonds are represented by *1* line(s),
both one σ- and one π-bond are represented by *2* parallel line(s), so they are called *double bonds*.



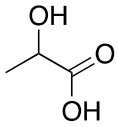
__2__
isoprene



__2__
pyruvic acid

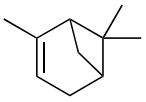


__1__
an imine



__1__
lactic acid

_3___
benzene



__1__
β-pinene

Electrons in hybridized atoms *can* occupy hybrid orbitals

Atoms in molecules *can* selectively

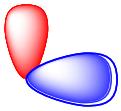
Ethyne

highly reactive species because it has only *6* electrons

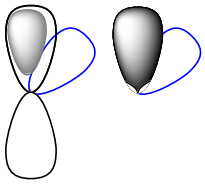
this is called the *singlet* state.

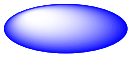
this is a *triplet* state.

Another possibility is a *sp*-hybridized



σ-bonded *sp*-hybridized *C*-atoms

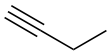




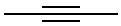
two π bonds surrounding the σ bond
called a *triple* bond.

Other Types Of Triple Bonds

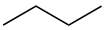
__1__
propyne



__1__
1-butyne

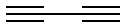


__1__
2-butyne



__0__
butane

__1__
acetonitrile

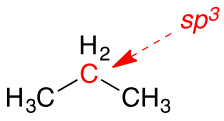


__2__
1,3-butadiyne

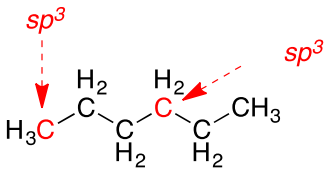
it *does not* matter if multiple or single

F. Assigning Hybridization States

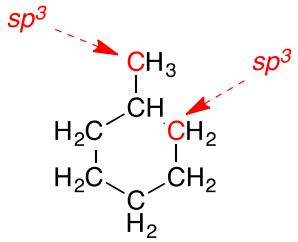
are *sp*-hybridized, three sp^2, and four sp^3.



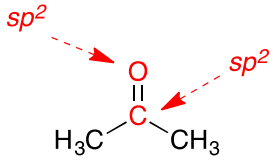
propane



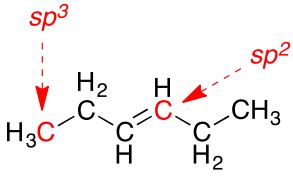
hexane



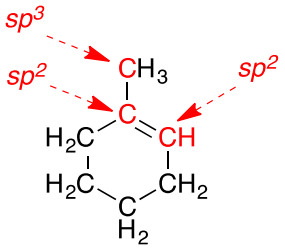
methylcyclohexane



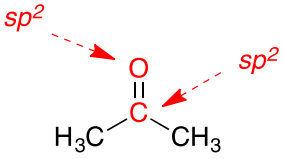
acetone



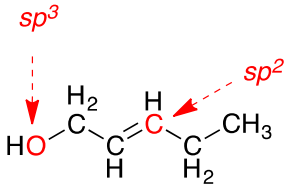
1-pentene



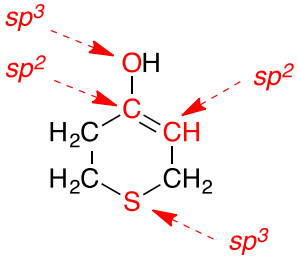
1-methylcyclohexene

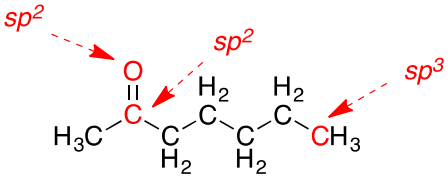


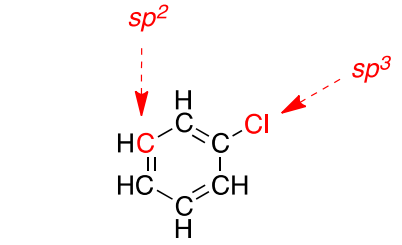
acetic acid

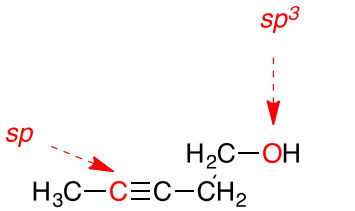


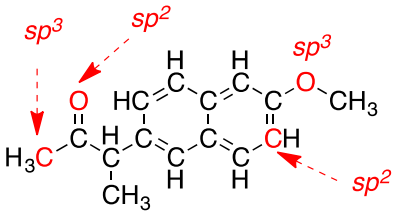
cis-1-hydroxy-2-butene



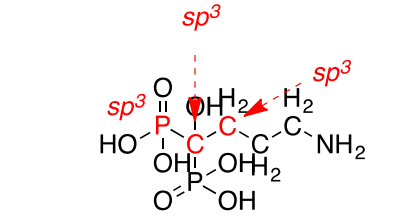




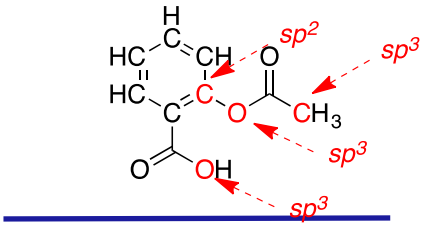




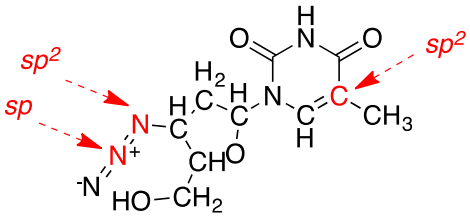
naproxen



alendronate



aspirin



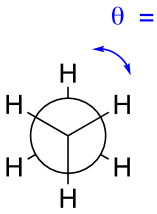
zidovudine (AZT)

2. Saturated Acyclic Hydrocarbons

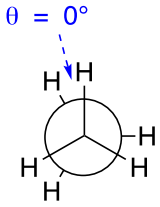
A. Introduction

B. Newman Projections

Ethane

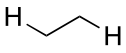


staggered

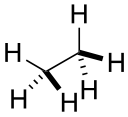


shown slightly offset but direct allignment is assumed

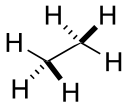
eclipsed



staggered



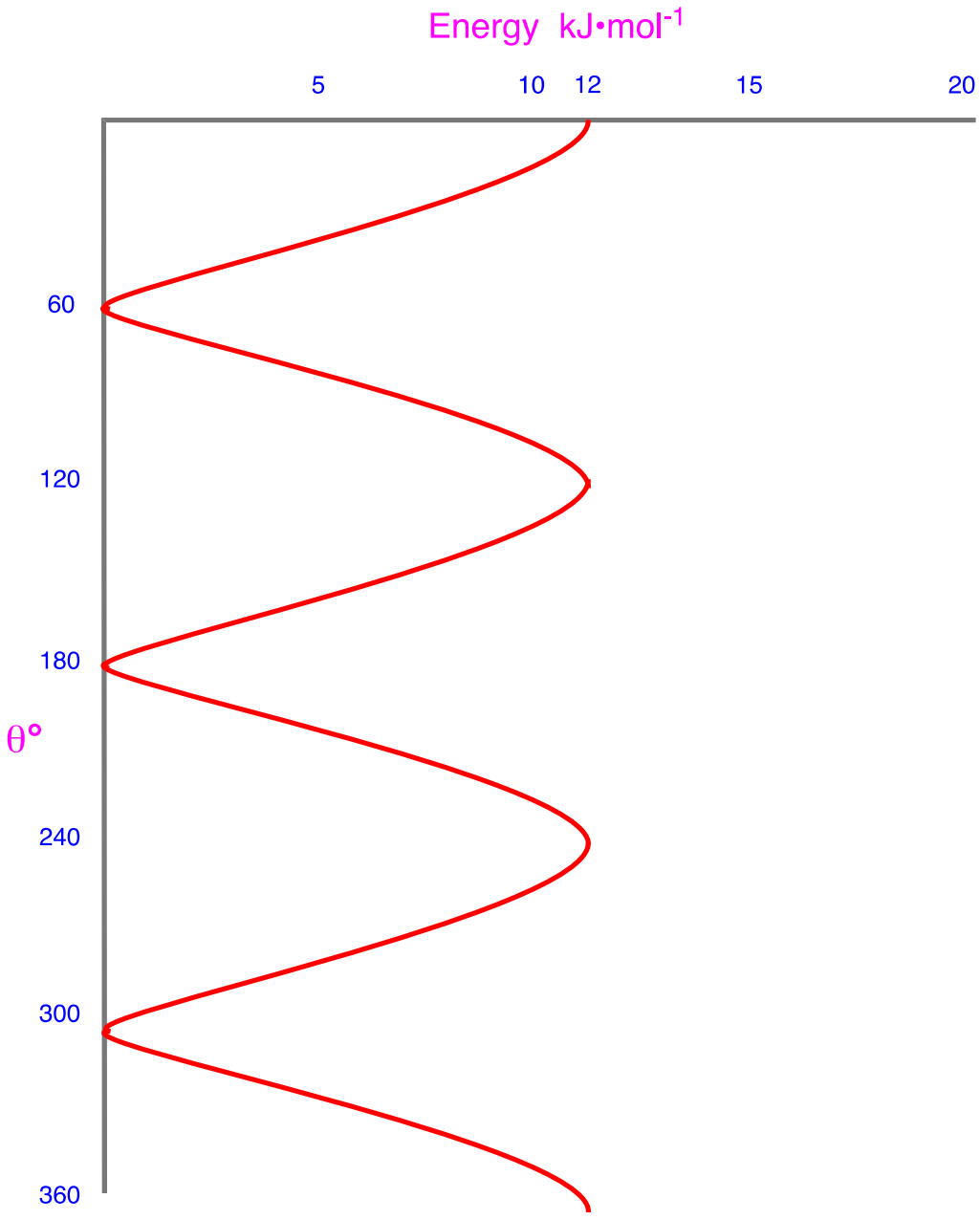
eclipsed

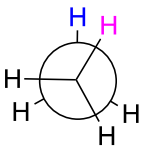


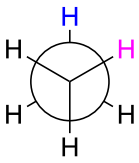
staggered

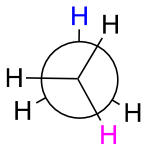
eclipsed

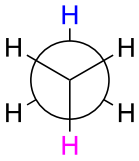
The *staggered* ethane conformer is more stable

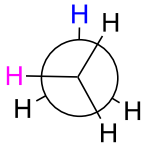



e


s


e


s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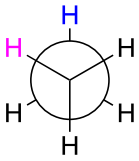
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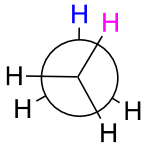
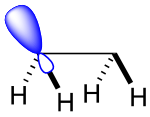

e

that repulsion is called *torsional* strain.

molecular orbital diagrams to indicate *destabilizing* interactions
and *stabilizing* interactions

σ-orbital contributes *2* e
an empty one donates *0* e

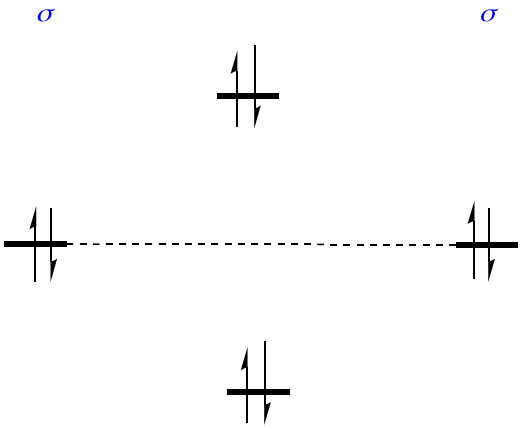
sive



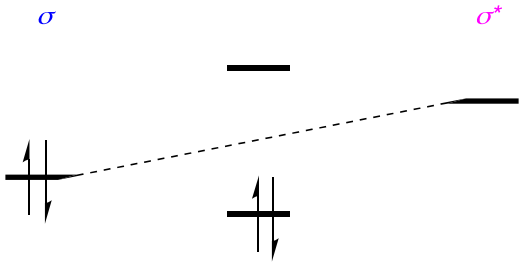
torsional strain

attractive

add electrons to the diagrams below and indicate bond orders:

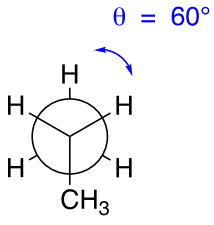


non-bonding

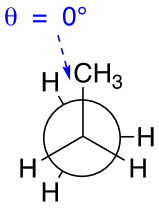


bonding

Propane

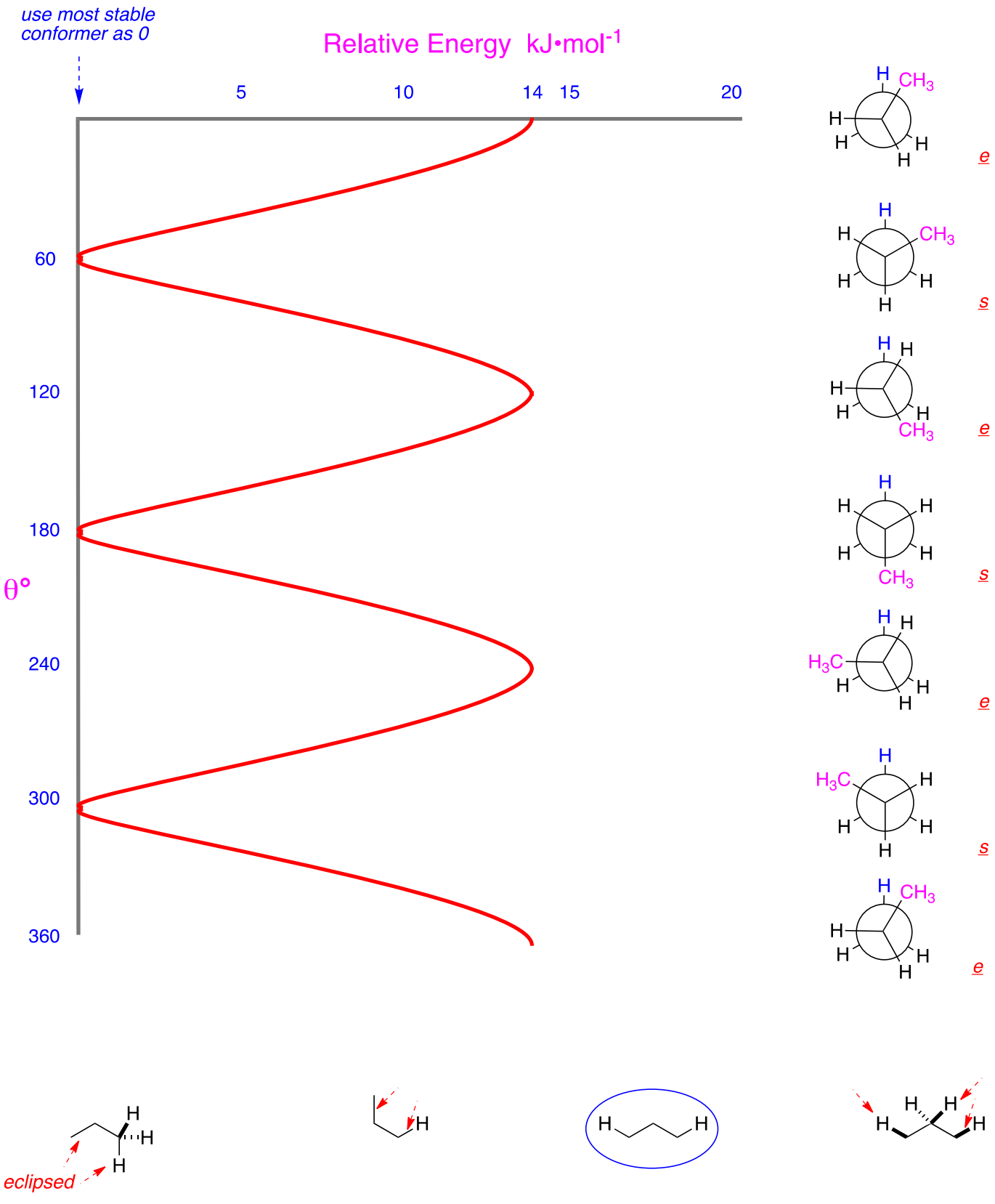


staggered

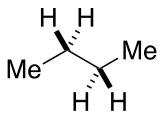


shown slightly offset but direct allignment is assumed

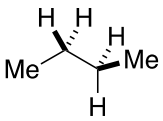
eclipsed


use most stable conformer as 0
Relative Energy kJ•mol-1
5
10
14
15
20
60
120
180
240
300
360
θ°
CH3
H3C
e
s
e
s
e
s
e
eclipsed

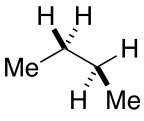
Butane



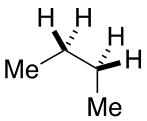
very low



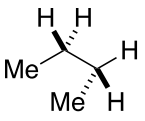
high



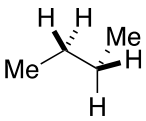
low



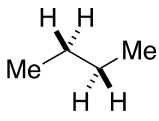
very high



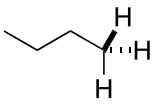
low

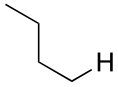


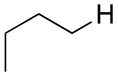
high

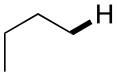


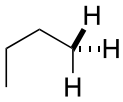
very low

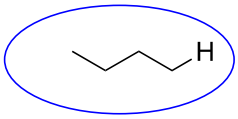


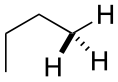


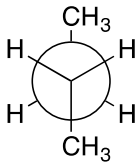












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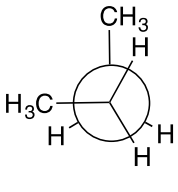
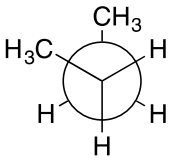
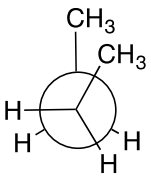


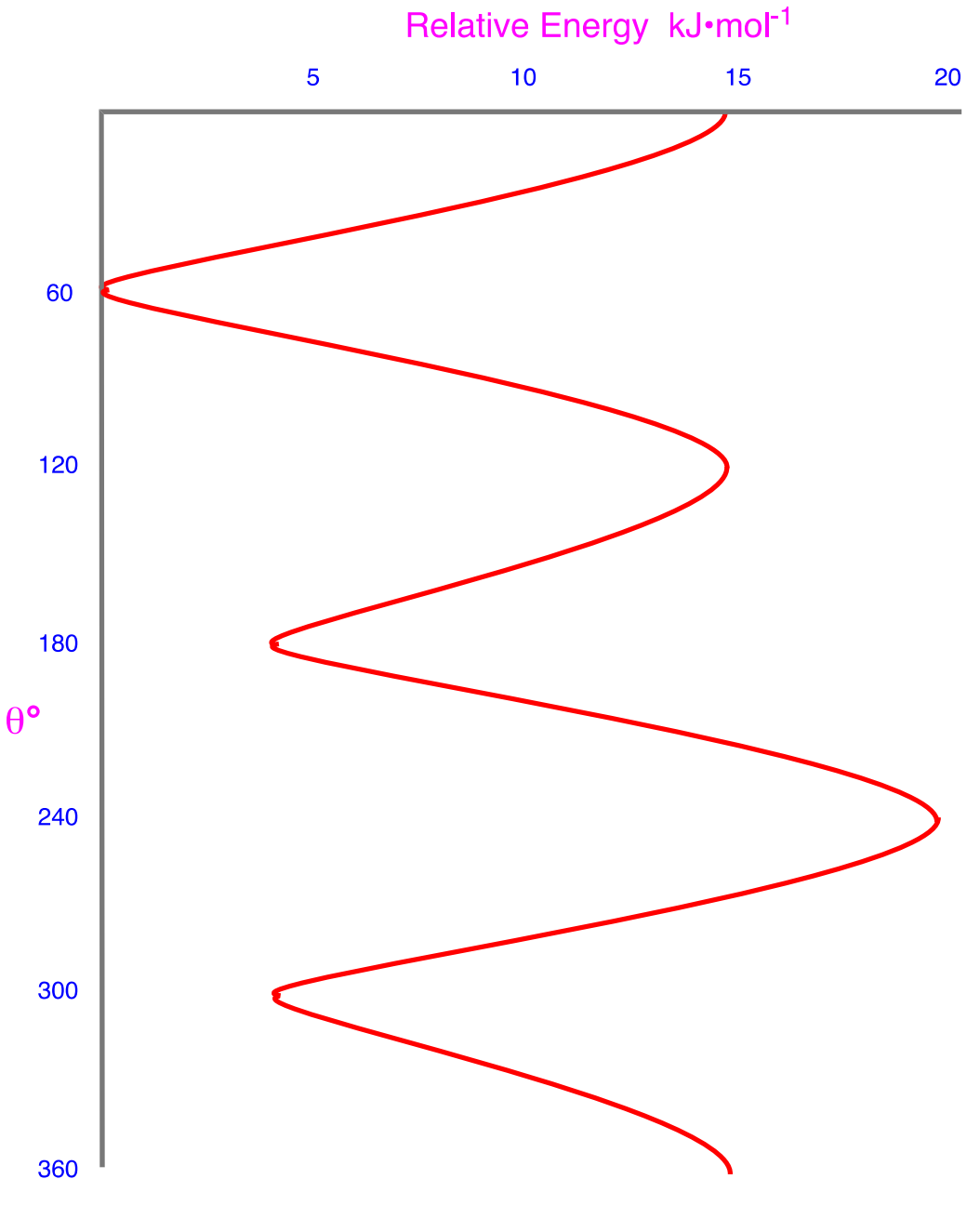
pe



g



fe



Destabilization of butane in the totally eclipsed conformation is a result of combinations of *torsional / steric* strain.

Steric strain between the methyl groups in butane is that which results when atoms compete for the same region of space.

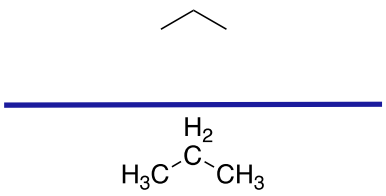
C. How To Draw Organic Structures

is one bond to an apex that {terminal point} represents *CH_3*
two bonds to an apex means it is a *CH_2*
three bonds to a branch point represent *CH*.
this means there are *0* hydrogen atoms on that carbon.

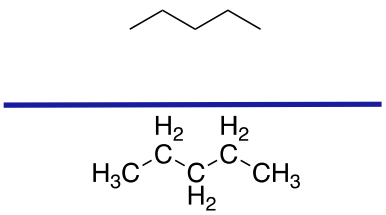
Zigzag conformations represent *staggered* conformers

it *does not* matter if the chains zigzag

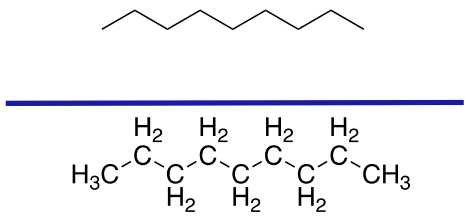
propane



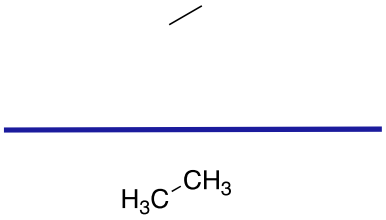
pentane



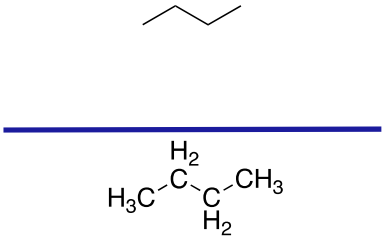
nonane



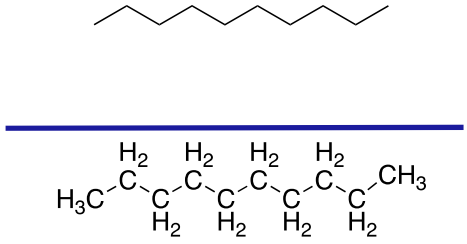
ethane



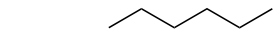
butane

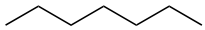


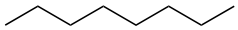
decane

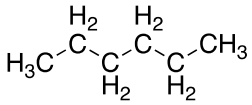


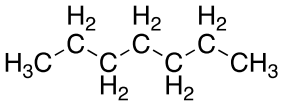
hexane *heptane* *octane*

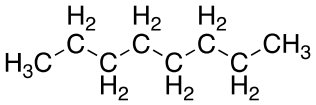












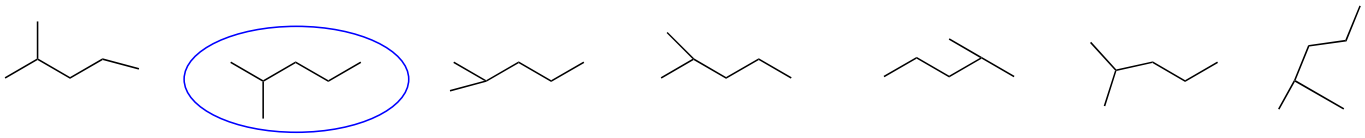
ideal bond (*H*-*C*-*H*) angles for sp^3-hybridized carbons ~*109°*

has *4* bonds to other atoms.

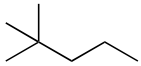
carbon atoms in organic structures *always* have
C-atoms in common organic molecules *never*

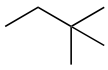
hybridization state of the carbons in the above molecules is *sp^3* *because* they have *4* atoms attached.

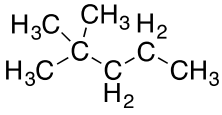
corners of a *tetrahedral* shape
ideally about *109°*

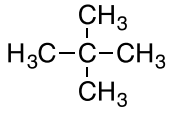


2,2-dimethylpentane *2,2-dimethylpropane* *2,2-dimethylbutane*

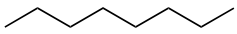






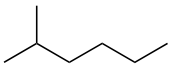


$CH_3CH_2C(CH_3)_2CH_3$



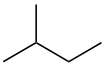
octane

heptane

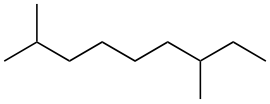


2-methylhexane

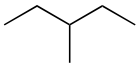
methylpropane



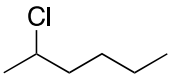
2-methylbutane



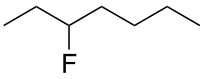
2,7-dimethylnonane



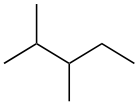
3-methylpentane



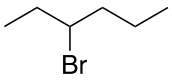
2-chlorohexane



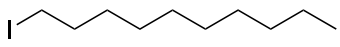
3-fluoroheptane



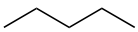
2,3-dimethylpentane



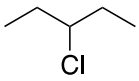
3-bromohexane



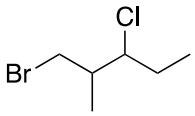
1-iododecanane



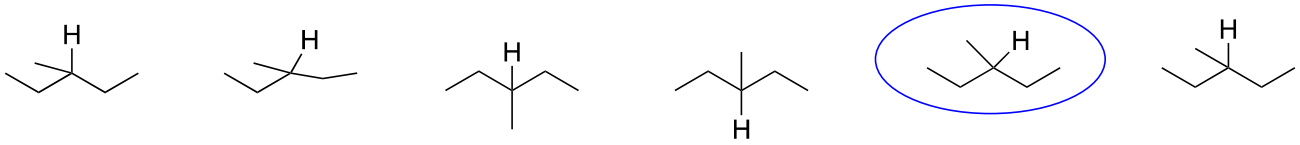
$CH_3CH_2CH_2CH_2CH_3$



$CH_3CH_2CHClCH_2CH_3$



$BrCH_2CH(CH_3)CHClCH_2CH_3$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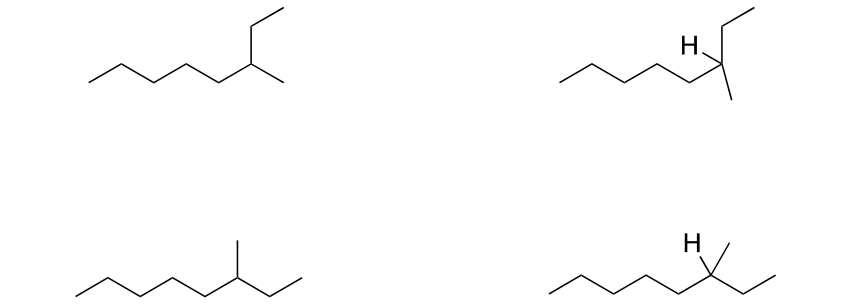
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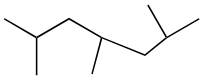

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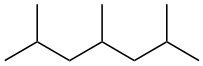

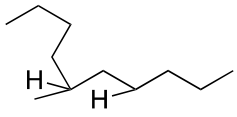
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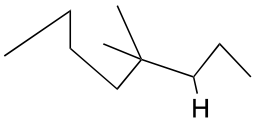
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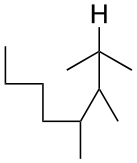
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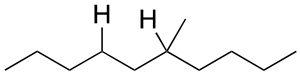
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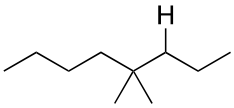
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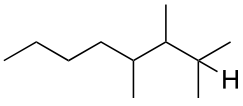
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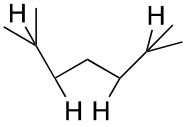
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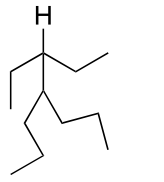
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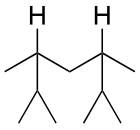
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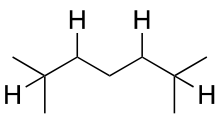
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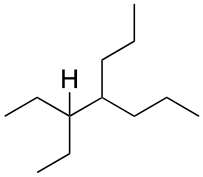
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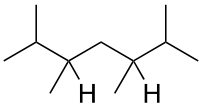
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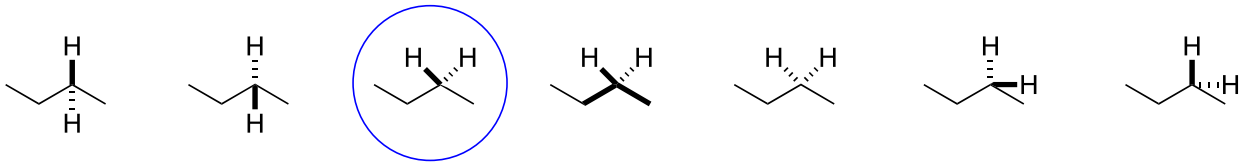
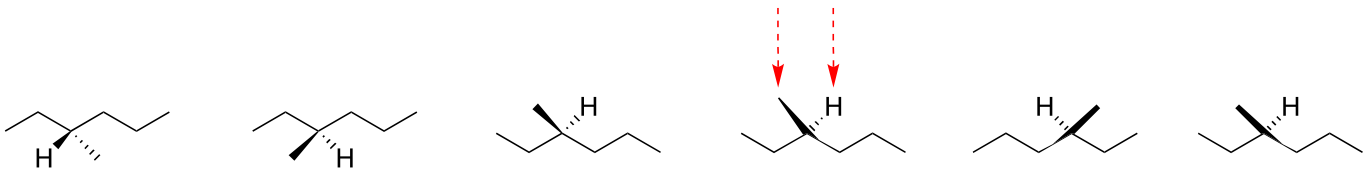
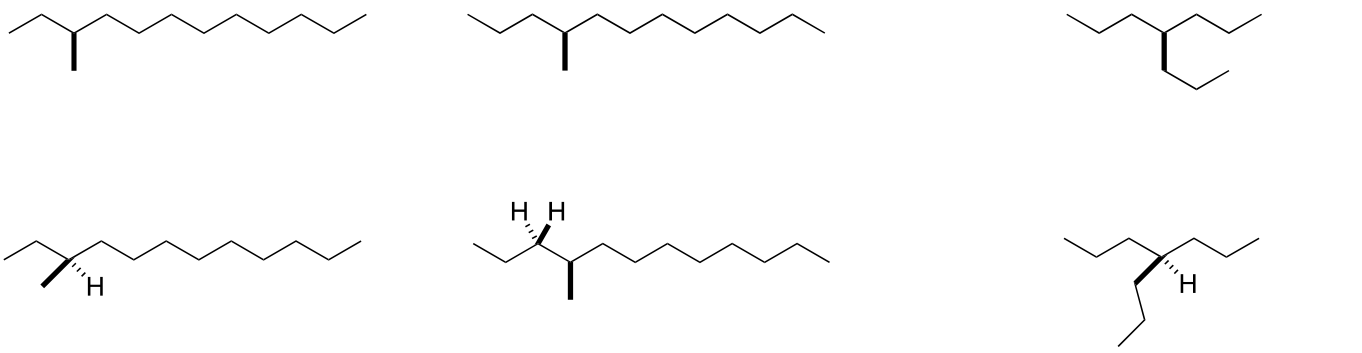
D. How To Show 3D In Organic Structures

Projecting From Linear Hydrocarbon Chains



wedges wrong way around





.... the C^3 hydrogen

.... both hydrogens on C^3

.... the H on unique C

E. Alkyl Group Abbreviations

In Acyclic Hydrocarbons

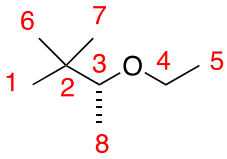
carbon connected to three hydrogens is called a *methyl*

Methylene fragments (of molecules) are those that have CH_2 connected

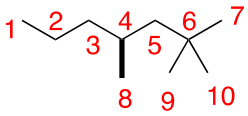
Methine is the name given to *CH* fragments

CH_3 connected to anything is called a *methyl*

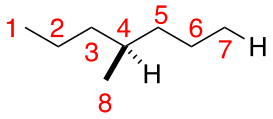
A quaternary *C* has *0* hydrogen



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

removed and replaced with something else *ie* *substituted*

represented as *CH_3, Me*

represented as *CH_3CH_2, Et*

ethyl group *cannot* be isolated and put in a bottle; it *is not* a discrete compound, but it *is* a molecular fragment

the fragment *is* attached to something else

Propane contains *2* types of

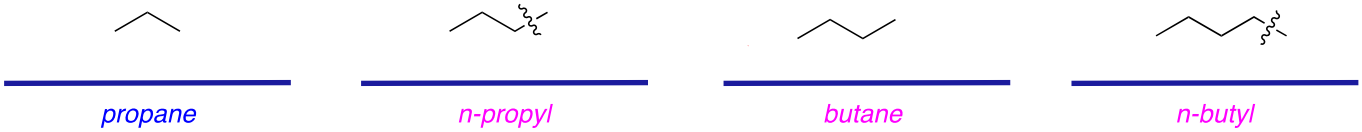
gives *different* outcomes

chain gives *a normal* propyl

represented as *$MeCH_2CH_2$, $EtCH_2$, ^nPr*

a(n) *iso-* propyl group

can be represented as *^iPr, $(CH_3)_2CH$*



propane *n-propyl* *butane* *n-butyl*

3 types of hydrogen

butyl chain gives a *normal* butyl group

represented as *$MeCH_2CH_2CH_2$, $^nPrCH_2$, $CH_3CH_2CH_2CH_2$*

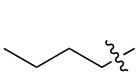
a(n) *sec* butyl group

represented as *$CH_3CH_2CHCH_3$*

2-Methylpropane is an *isomer* of butane: it has __2__ chemically inequivalent hydrogen

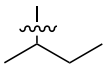
ie a *^iBu* group.

ie ^{t}*Bu*.

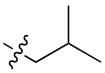


n-butyl

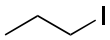
tert-butyl



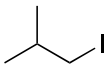
sec-butyl



iso-butyl

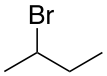


^{n}PrI



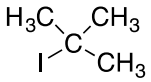
^{i}BuI

^{i}PrCl

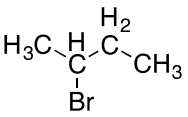


^{s}BuBr

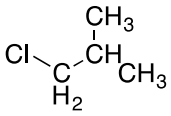
MeBr



^{t}BuI

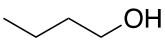


^{s}BuBr

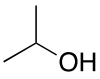


^{i}BuCl

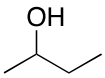
^{t}BuOH



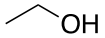
^{n}BuOH



^{i}PrOH

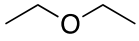


^{s}BuOH

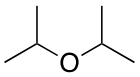


EtOH

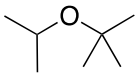
^{t}BuOMe



EtOEt
an anesthetic



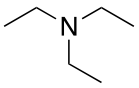
^{i}PrO^{i}Pr



^{t}BuO^{i}Pr

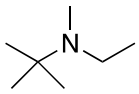
MeOMe

^{t}BuNHMe



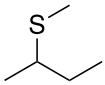
Et_3N

^{i}PrNH$_2$

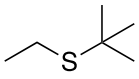


^{t}BuNMeEt

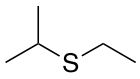
MeNH$_2$



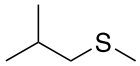
^{s}BuSMe



EtS^{t}Bu

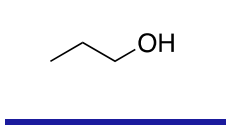


^{i}PrSEt



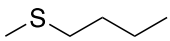
^{i}BuSMe

Me_2S



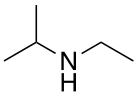
HO^{n}Pr

alcohol



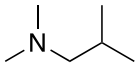
MeS^{n}Bu

thioether



^{i}PrNHEt

amine



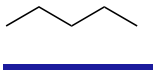
^{i}BuNMe$_2$

amine

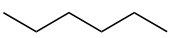
name functional groups as alcohol, amine, ether, or thioether on the dashed lines

D Conclusion

These *are* zigzag conformations.



pentane



hexane

heptane

decane

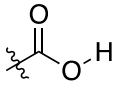
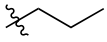
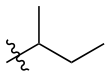
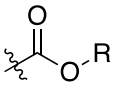
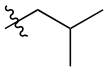
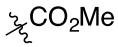
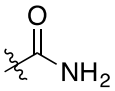
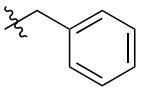
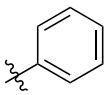
linear hydrocarbons *can* be represented

3. Fragments And Functional Groups

A. Introduction

B. Fragments

a *molecular fragment* connected to something else and *cannot* be isolated.

			
carboxyl	*n*-propyl	carboxyl	*s*-butyl
name of fragment		carboxylic acid	
			
carboxyalkyl	*i*-butyl	carboxymethyl	*i*-propyl
ester		ester	
			
carboxamide	*t*-butyl	carboxamide	ethyl
amide		amide	
			
acyl	benzyl	acyl	phenyl

acyl

vinyl

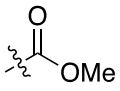
acyl

amine

acyl

carbonyl chloride

acid chloride



carboxyalkyl

ester

methoxy

$-CO_2Et$

carboxyethyl

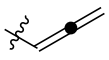
Ac

acyl

Bn

benzyl

nitro



allene

$-CH_2C_6H_5$

benzyl

-Ph

phenyl

-COEt

acyl

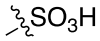
-C_6H_5

phenyl

-OMe

methoxy

cyano or nitrile



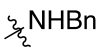
sulfonic acid

epoxide

sulfonyl chloride

acetyl

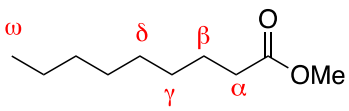
phenoxy

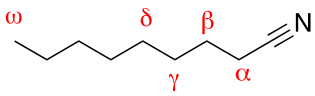


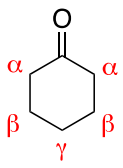
benzylamine

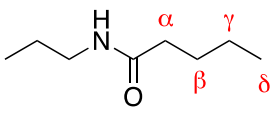
acyl

benzoyl





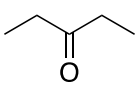




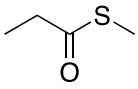
ω is last, δ is more specfic

In Greek, ω means *last*.

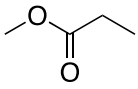
C. Functional Groups Shown With Bonds



ketone

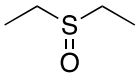


thioester

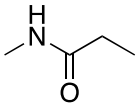


ester

aldehyde

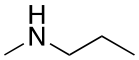


sulfoxide

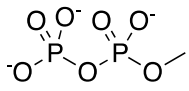


amide

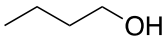
ester



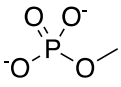
amine



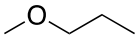
diphosphate



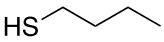
alcohol



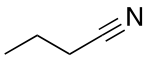
monophosphate



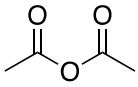
ether



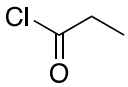
thiol



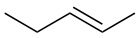
nitrile



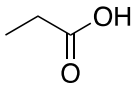
carboxylic acid anhydride



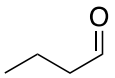
acid chloride



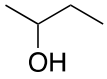
alkene



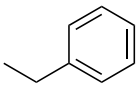
carboxylic acid



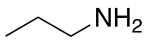
aldehyde



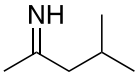
alcohol



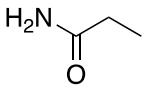
arene



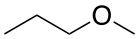
amine



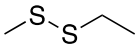
imine



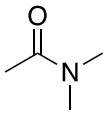
amide



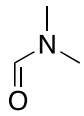
ether



disulfide

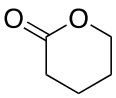


amide



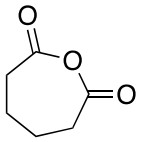
amide

incidentally this is DMF



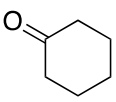
lactone

alkene



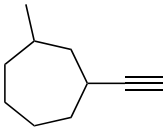
carboxylic acid anhydride

lactam

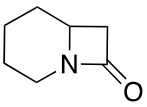


ketone

disulfide



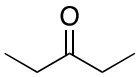
alkyne



lactam

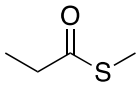
D. Functional Groups Represented Without Bonds

EtCOEt



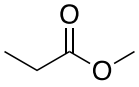
name of functional group
ketone

EtCO(SMe)



name of functional group
thioester

$EtCO_2Me$

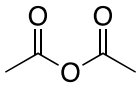


name of functional group
ester

EtCOH

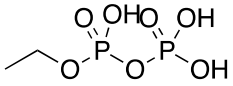
name of functional group
aldehyde

$MeCO_2COMe$



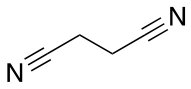
name of functional group
carboxylic acid anhydride

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



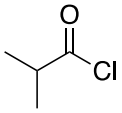
name of functional group
diphosphate

$NCCH_2CH_2CN$



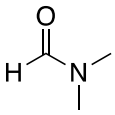
name of functional group
nitrile

$(CH_3)_2CHCOCl$



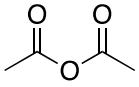
name of functional group
acid chloride

$HCONMe_2$



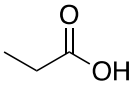
name of functional group
amide

MeCOOCOMe



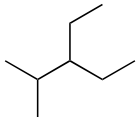
name of functional group
carboxylic acid anhydride

$CH_3CH_2CO_2H$



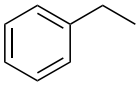
name of functional group
carboxylic acid

$(CH_3)_2CHCH(CH_2CH_3)_2$



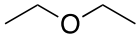
name of functional group
alkane

$C_6H_5CH_2CH_3$



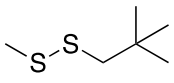
name of functional group
arene

$CH_3CH_2OCH_2CH_3$



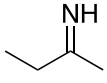
name of functional group
ether

$CH_3S_2CH_2C(CH_3)_3$



name of functional group
disulfide

$CH_3CH_2CNHCH_3$

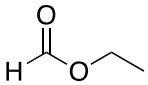


name of functional group
imine

Me_2SO

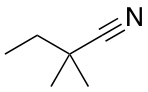
name of functional group
_____sulfoxide_____

HCO_2Et



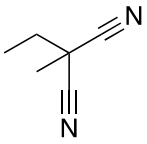
name of functional group
_____ester_____

$CH_3CH_2C(CH_3)_2CN$



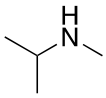
name of functional group
_____nitrile_____

$CH_3CH_2C(CN)_2CH_3$



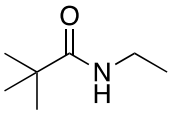
name of functional group
_____nitrile_____

$^{i}PrNHMe$



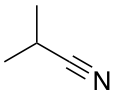
name of functional group
_____amine_____

$^{t}BuCONHEt$



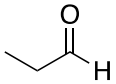
name of functional group
_____amide_____

$(CH_3)_2CN$



name of functional group
_____nitrile_____

CH_3CH_2COH

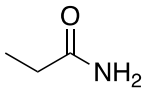


name of functional group
_____aldehyde_____

$EtNH_2$

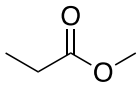
name of functional group
_____amine_____

$EtCONH_2$



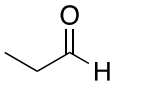
name of functional group
_____amide_____

EtCOOMe



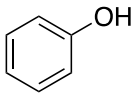
name of functional group
_____ester_____

CH_3CH_2COH



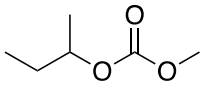
name of functional group
____aldehyde___

C_6H_5OH



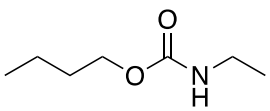
name of functional group
____phenol_____

$^{s}BuOCOOMe$



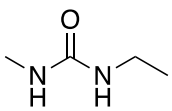
name of functional group
_____carbonate_____

$^{n}BuOCONHEt$



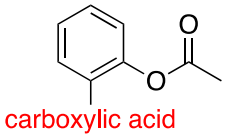
name of functional group
_____carbamate_____

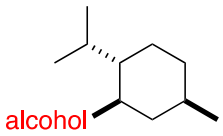
$CH_3HNCONHCH_2CH_3$

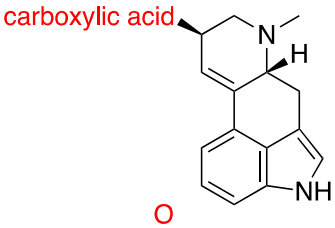


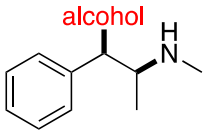
name of functional group
_____urea_____

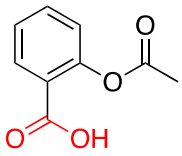
Find this question hard? Remember: go to the web and to figure out the answers for the maximum benefit (do not look at a key!).



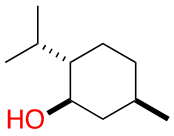




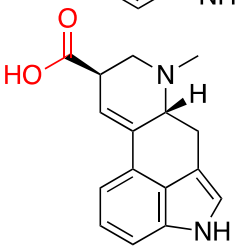




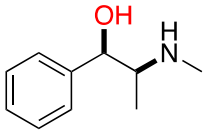
aspirin



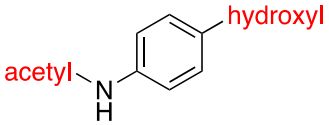
menthol

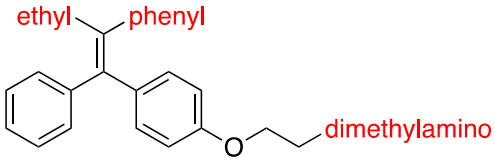


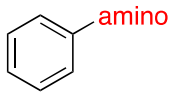
lysergic acid (LSD)

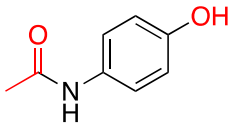


ephedrine

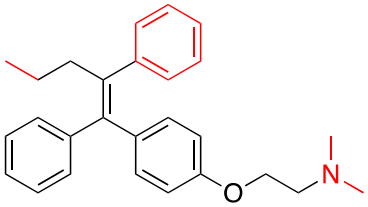




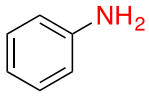




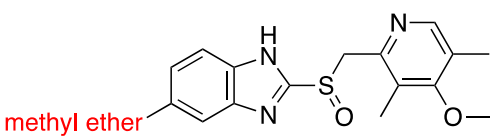
acetaminophen (tylenol)

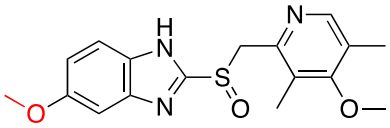


tamoxifen

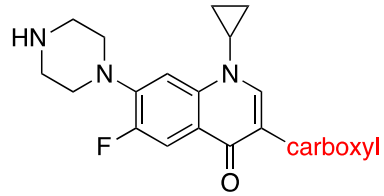


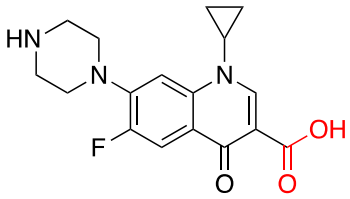
aniline



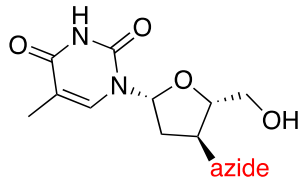


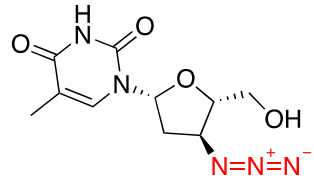
omeprazol



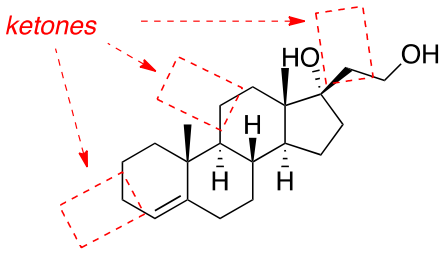


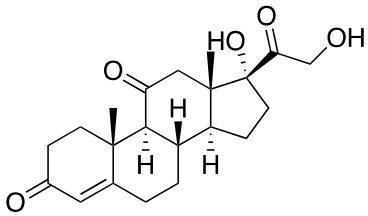
ciprofloxacin "cipro"



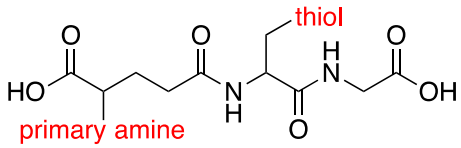


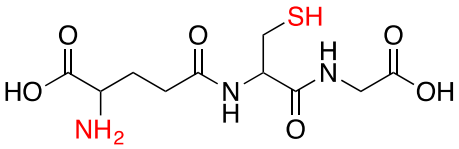
azidothymidine



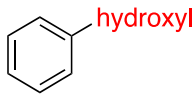


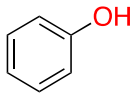
cortisone



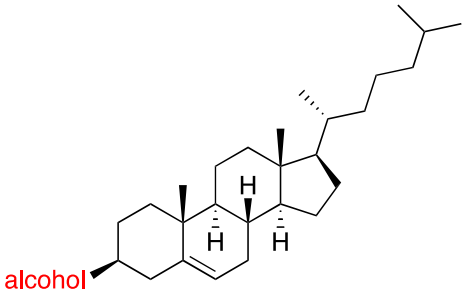


glutathione

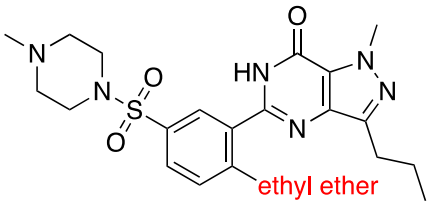




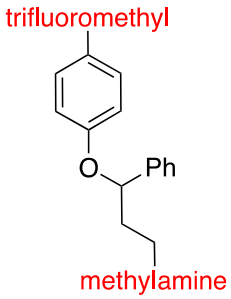
phenol



cholesterol

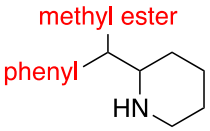


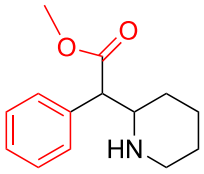
viagra



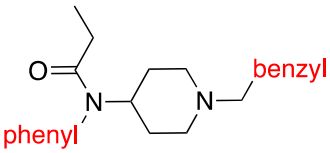
prozac

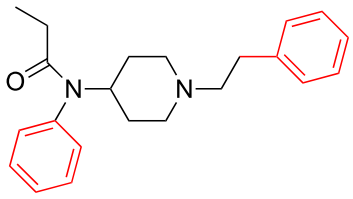
My chemistry instructor might like me to take methylphenidate (other name: Retalin) to improve my *attention.*





methylphenidate

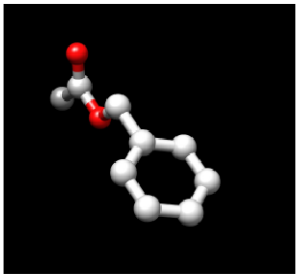




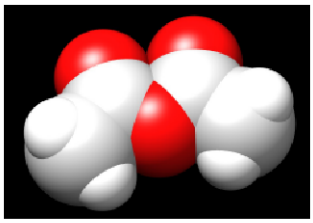
fentanyl

E. Identifying Functional Groups From Models

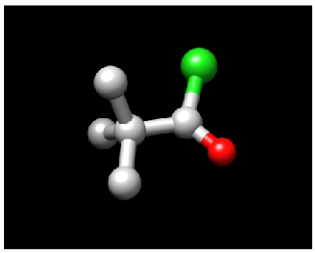
Use molecular models to construct: cyclohexane, cyclopentene, ethyl acetate, acetone, toluene, ethanol, diethyl ether, acetonitrile, ethanal, 2-butyne. Look them up on the web (*eg* Google images or Wiki) if you do not know the structures of these molecules. Pay attention to the hybridization state of each atom and make sure the geometries in your model correspond. In models, carbon is black, hydrogen is white, oxygen is red, nitrogen is blue, halogens are green, and sulfur is yellow.Make models of the following compounds and draw their structures below without using C or H. Some of the structures are labeled so you can do a web-search if you need help. Can you name any of the functional groups?



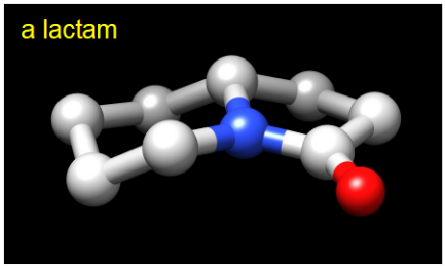
ester, phenyl



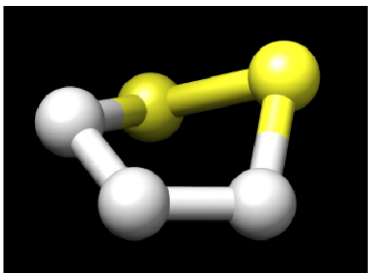
carboxylic acid anhydride



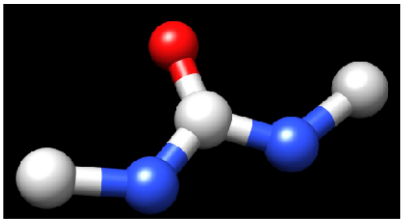
acid halide



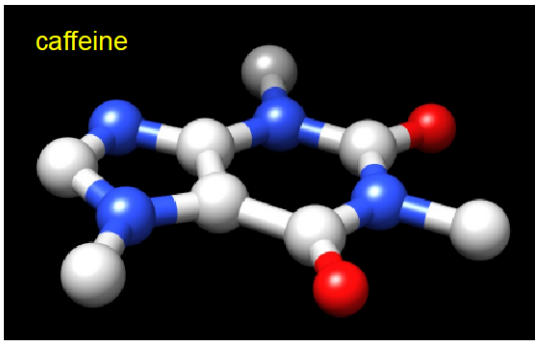
lactam (amide)



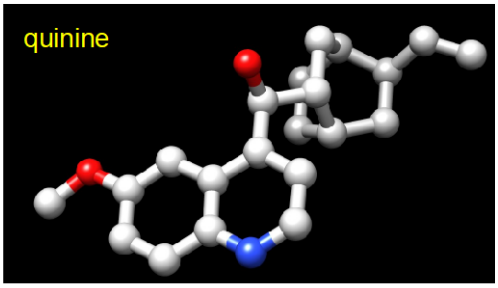
disulfide



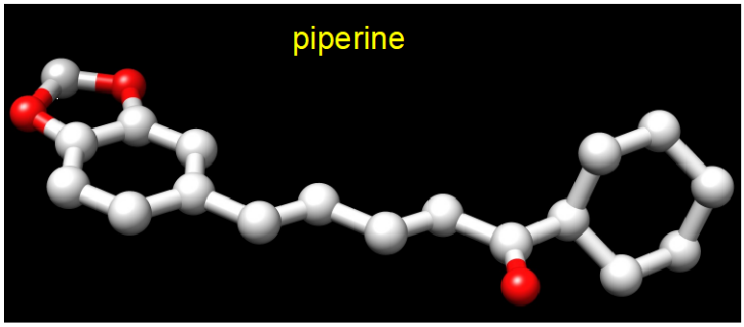
amide (urea)



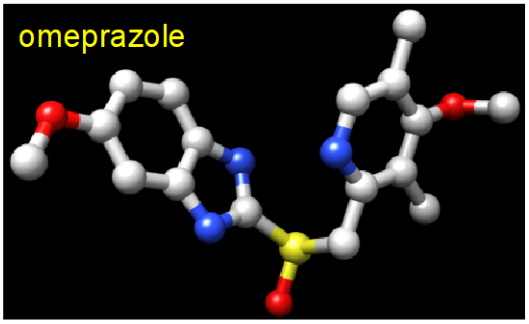
amide, arene (aromatic)



ether, arene, alcohol, alkene



ether, arene, alkene, amide

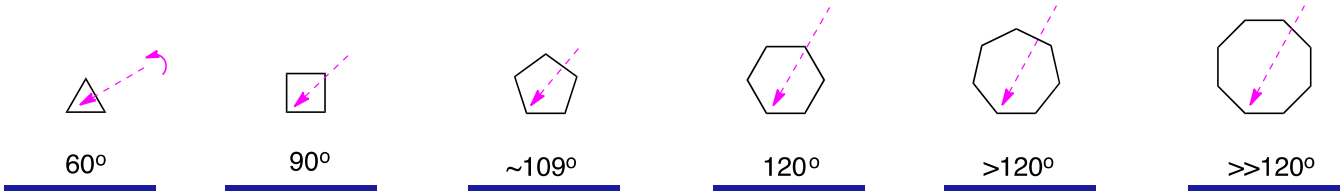


ether, arene, sulfoxide

4. Cyclic Hydrocarbon Conformations

A. Introduction

B. Angle Strain



sp^3 hybrid orbitals is around *109°*.

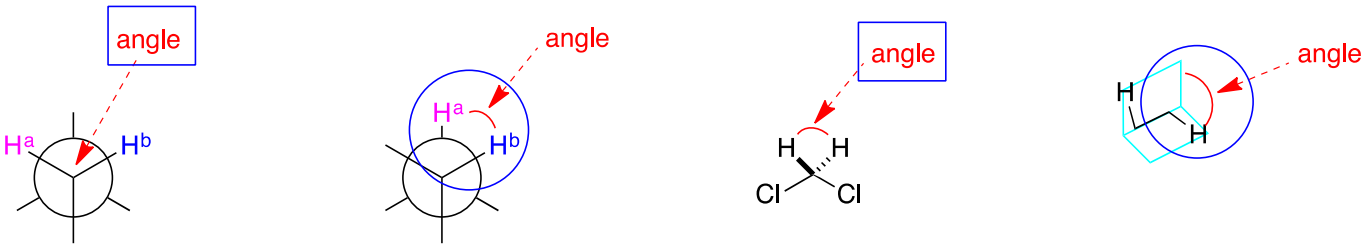
ideal bond angles the molecule has *angle* strain.

relative to the ideal value for sp^3-hybridization: *cyclopropane / cyclobutane*.

wider than the ideal value for sp^3-hybridization *if they were flat* *cyclohexane / cycloheptane / cyclooctane*.

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

C. Torsional Strain



Valence bond angles involve *3* atoms, whereas torsional angles involve *4*.

involves interactions between *e⁻ in bonds* and is *minimized* as

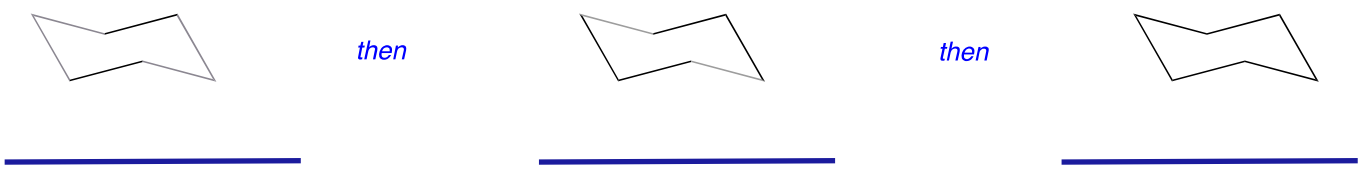
Eclipsed conformations involve high *torsional* strain.

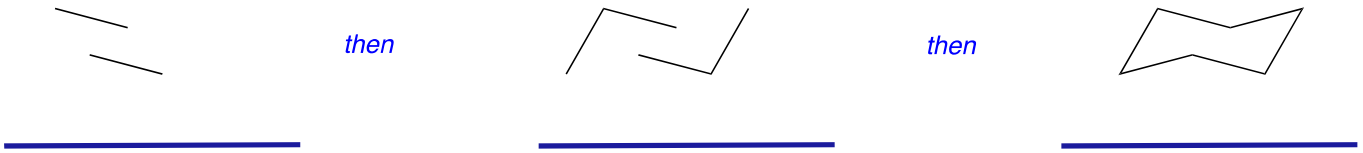
D. Cyclohexanes

Unsubstituted

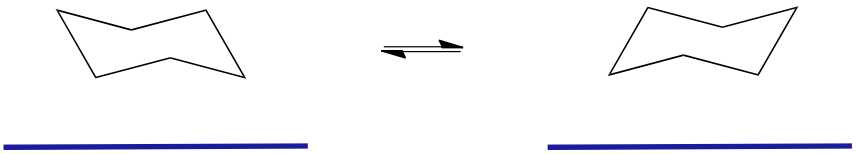
cyclopentane would have *less* angle strain because the internal angle is *closer to* the ideal sp^3 angle.

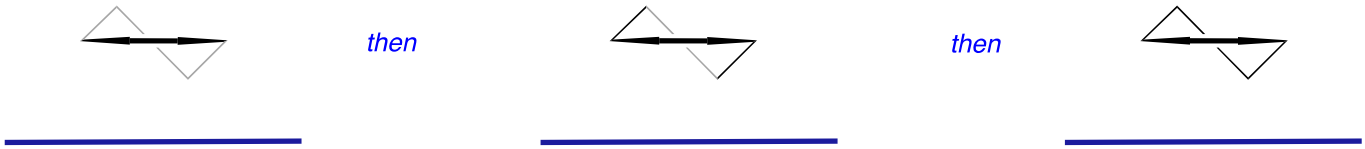
are *not* flat due to *torsional* strain.

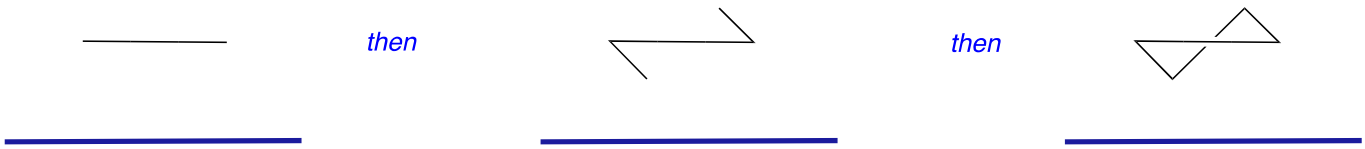




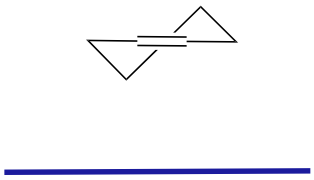
The two conformers have *exactly the same* energies.





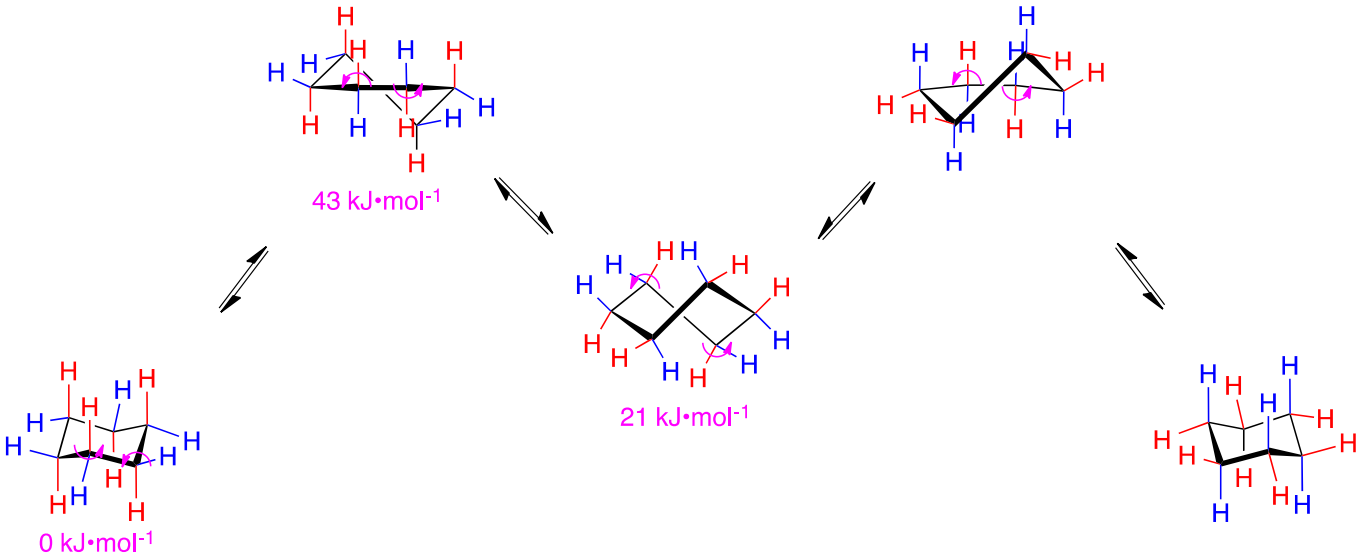


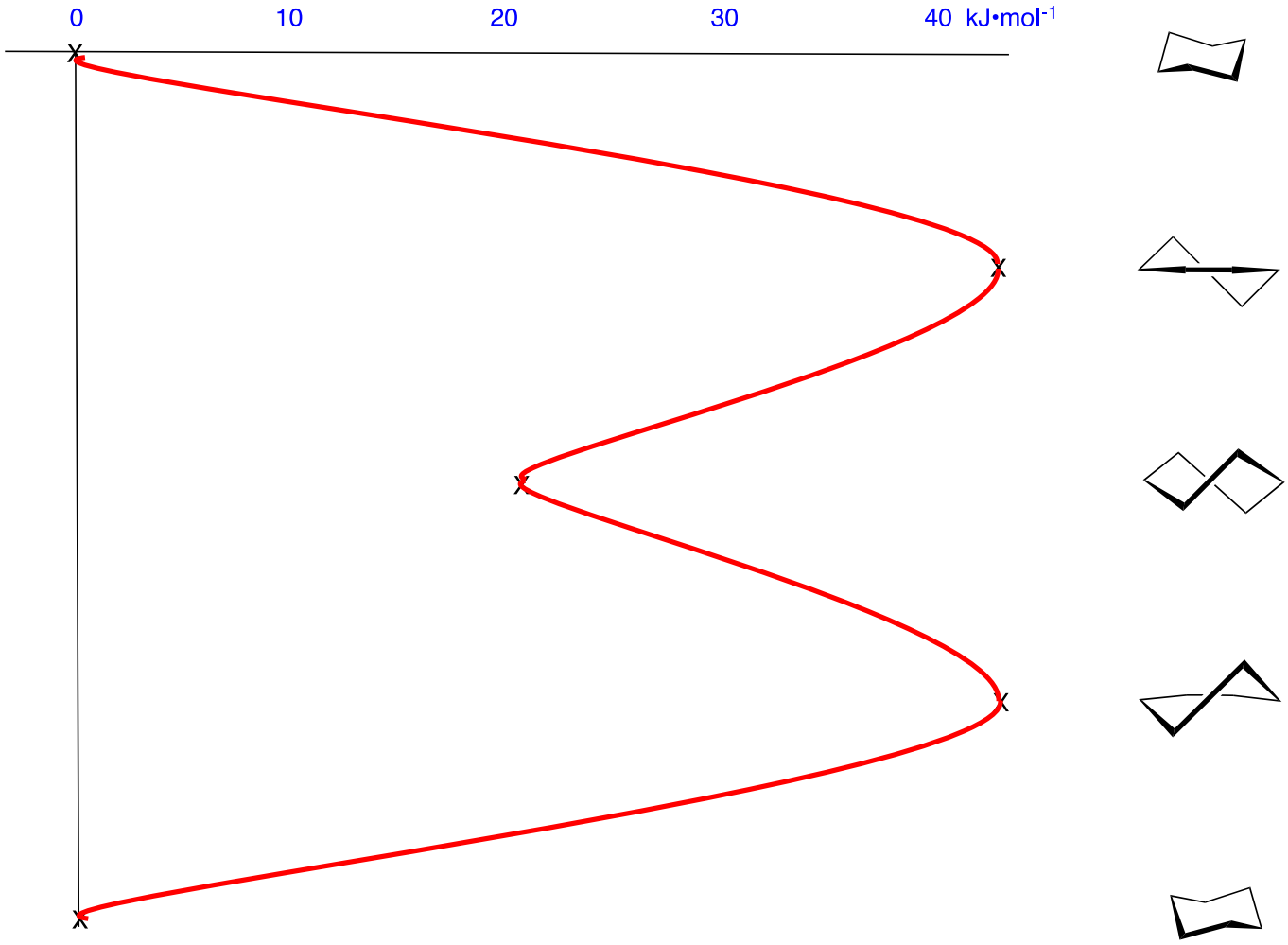
Cyclohexene with a double bond at the front:



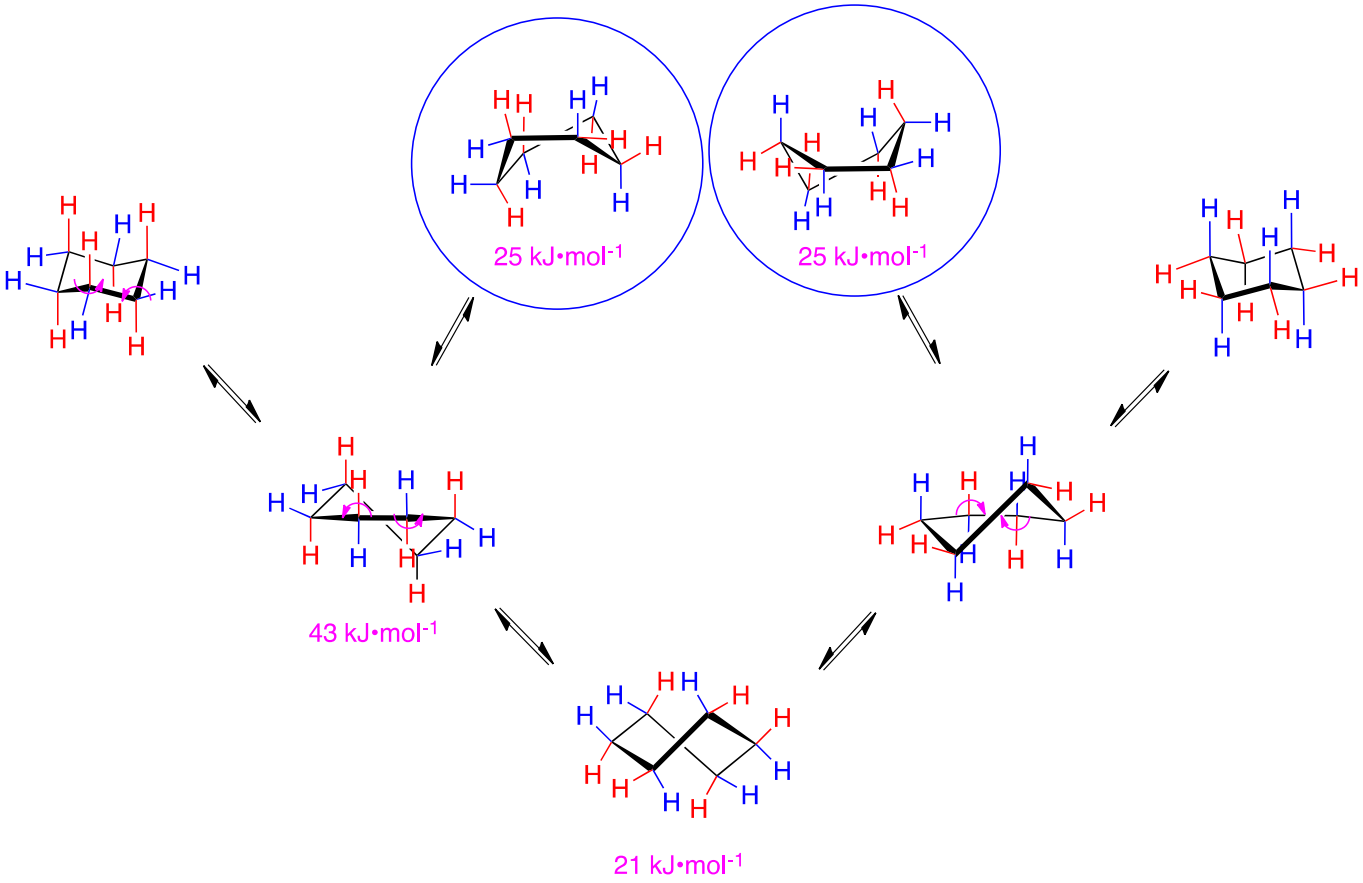
Boats And Twist-Boats

Flipping between chairs involves half-chair transition states and twist-boat intermediates *(Not a solution-understand this diagram and the relationship between conformations and energy levels)*:




0
10
20
30
40 kJ•mol-1

Boat conformers *are not necessarily* intermediates in flipping

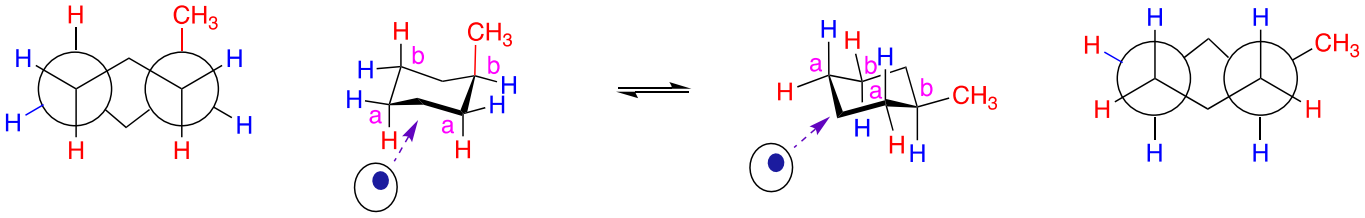


describe interconversion of two chair conformers are *three*-dimensional.

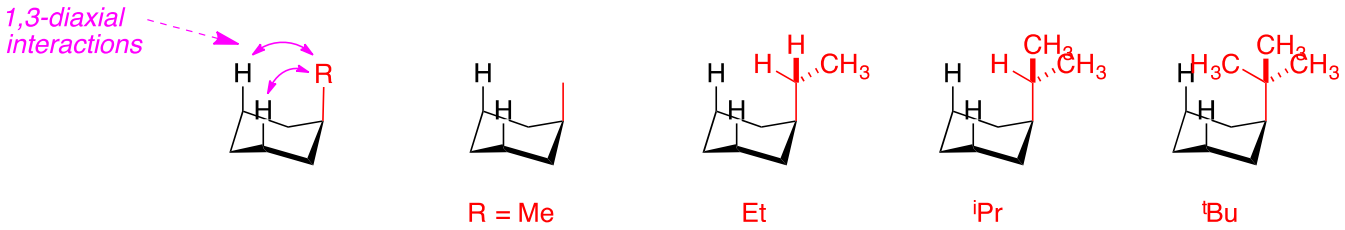
chair *boat*

the bonds around C^a – C^b are aligned like the *antiperiplanar* conformation of butane, whereas in the boat form they are like the *gauche* conformer.

Monosubstituted



methyl group is axial has 2 H-to-Me gauche interactions, whereas there are *0* similar interactions



The axial conformer of *tert*-butylcyclohexane is much less stable than the other members of this series because, unlike for the other substituents, no rotamer (rotation about the σ-bond) around the *C*-^{t}Bu group allows the methyls to avoid the axial hydrogens.

equilibrium so much that only the *equatorial* conformer is observed.

NMR *does* give distinct peaks for the monosubstituted

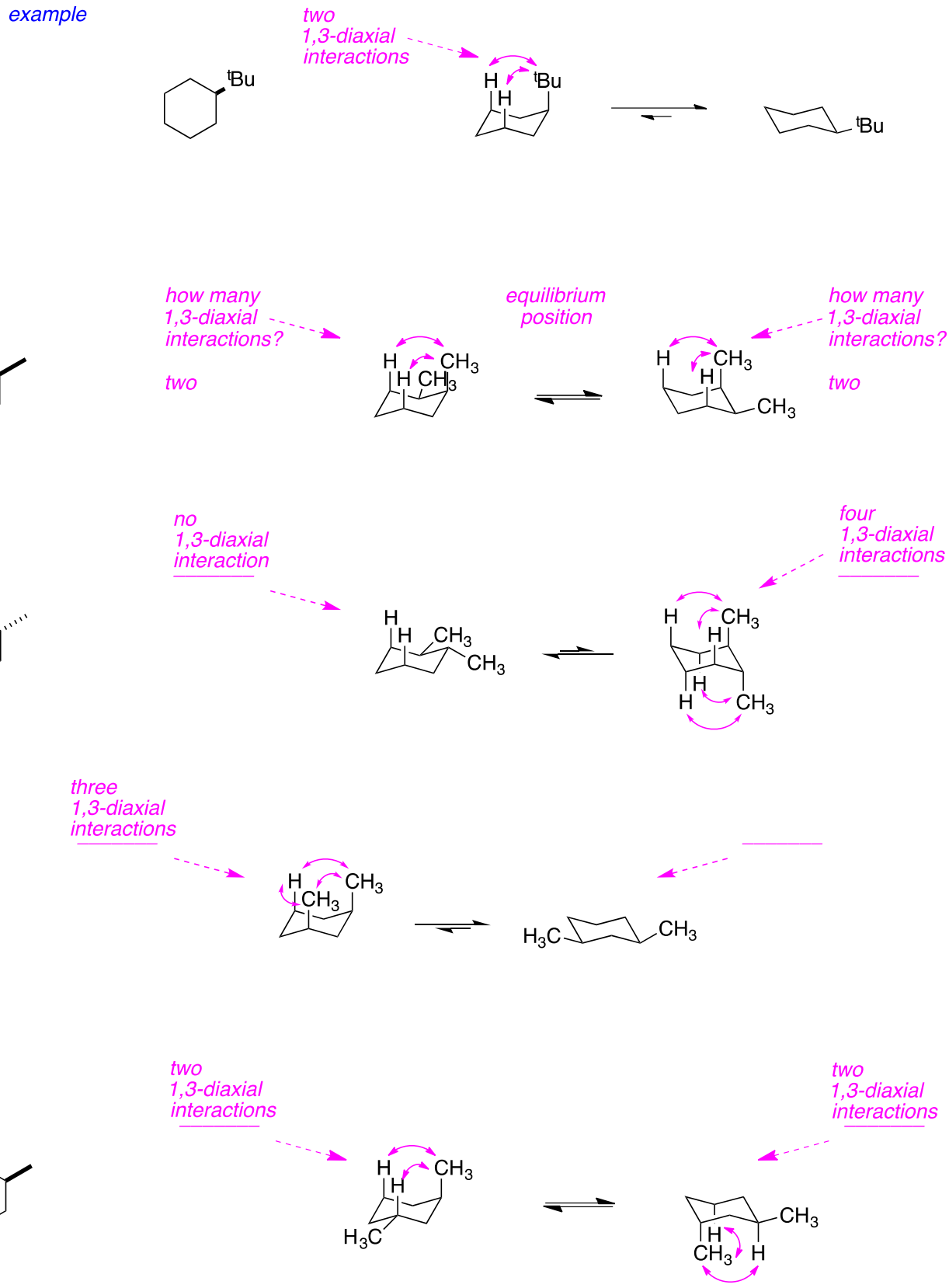
equilibrate faster than about *1,000* times per second.

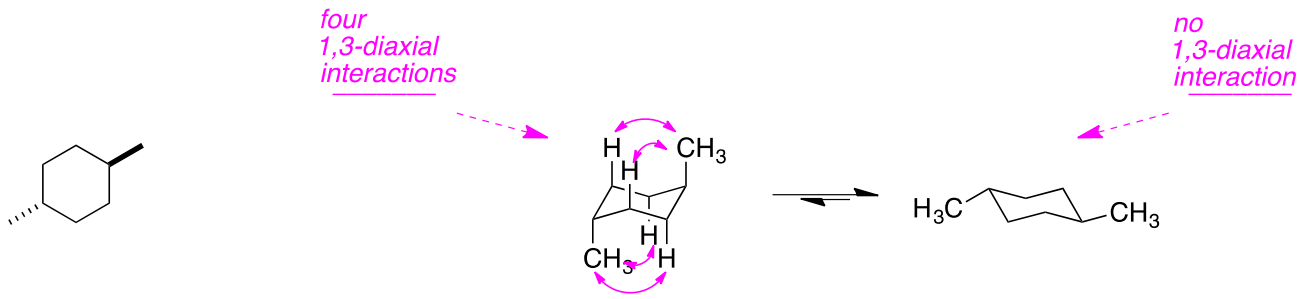
C – *O* bonds have *lower* σ- and σ*-orbitals

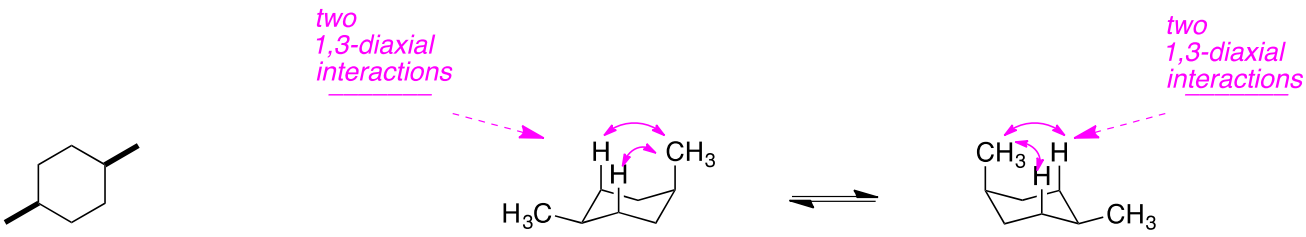
involve *less*
σ-to-σ* is *less*

The axial conformer of methoxycyclohexane is slightly more stable than ethylcyclohexane because *C* – *O* bonds have lower σ*-orbitals, thus the energy gap between this and the *C* – *H* σ-orbital is less and this stabilizes σ-to-σ* interaction.

Disubstituted

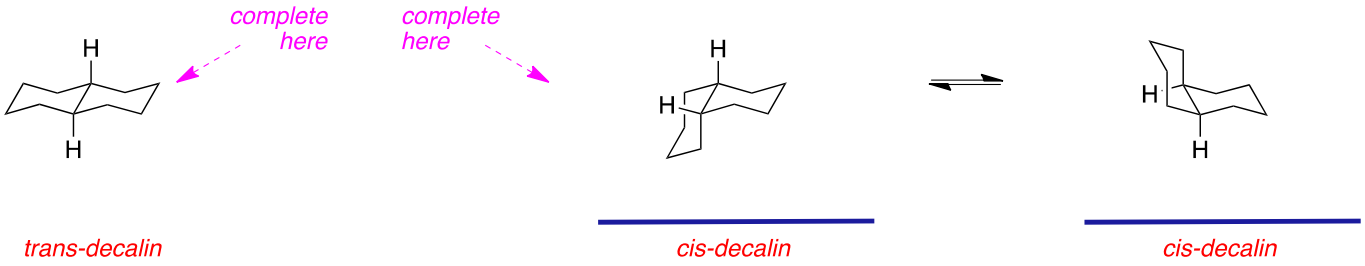


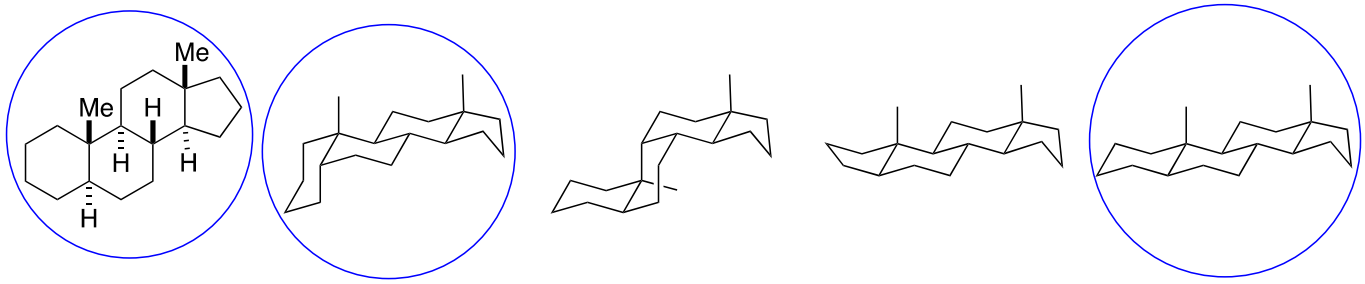




Decalins

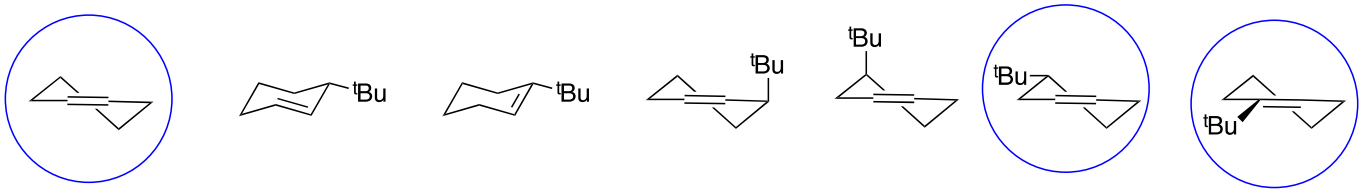
Decalins feature two cyclohexane rings sharing *a bond*; look up the structure in Wiki.

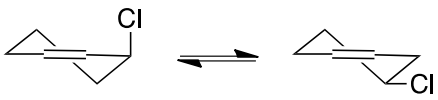


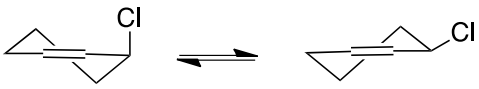


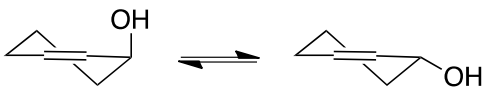
None of the above structures can undergo a ring flip. If ring **A** were flipped, ring **B** would have to flip too, but it cannot because **B**/**C** is a *trans*-decalin, and *trans*-decalins cannot flip.

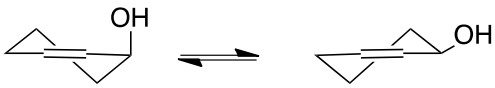
Cyclohexenes: Unsaturated Cyclohexenes

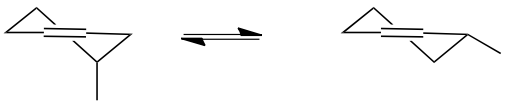


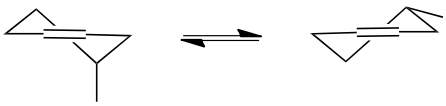












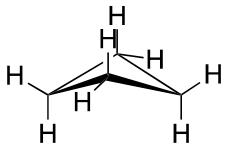
E. Other Ring Sizes

Cyclopropanes

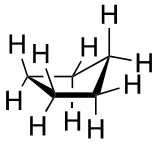
rigid and flat

Cyclopropane substituents are *eclipsed* relative to each other.

Cyclobutanes And Cyclopentane



cyclobutane



cyclopentane

In solution these molecules *do* rapidly interchange (on the NMR time-scale)

Three membered rings in cyclopropanes are *rigid and flat*.

5. Curly Arrows

A. Introduction

B. Electron Flow Types

Affecting Only One Bond

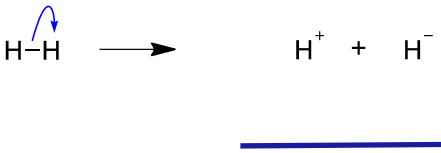
of electrons is illustrated using a *full* arrow.

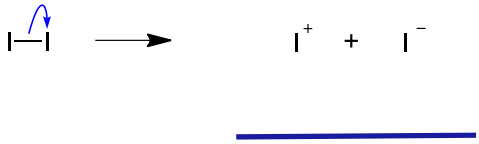
electrons *are*, ie at the site of relatively *high* electron density.

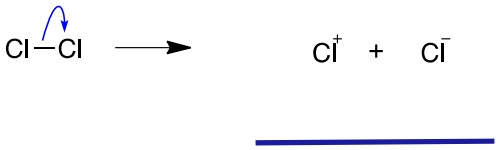
energetically *uphill*

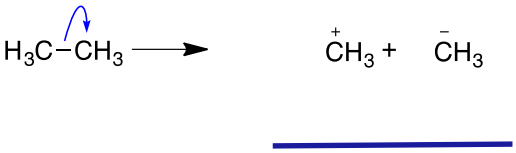
Affecting Only One Bond

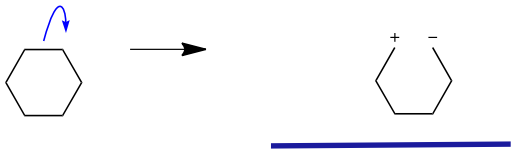
the following *heterolytic* bond fission reactions









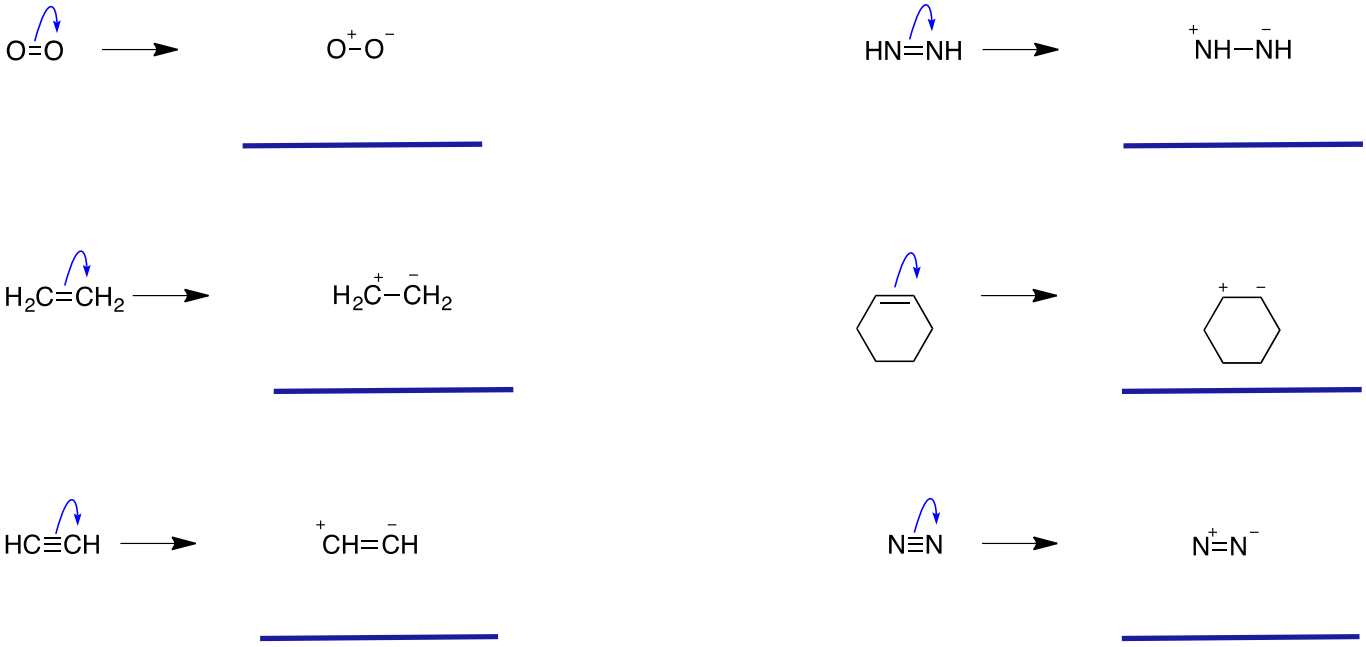


precise English *need not be* absolutely true; it is *possible* to tell lies

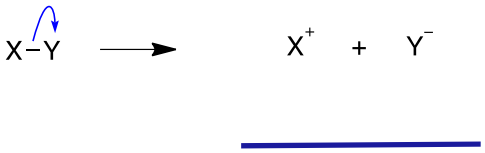
if the arrows are accurate that *does not* mean the movement

number of cations formed *must* equal the number of anions.

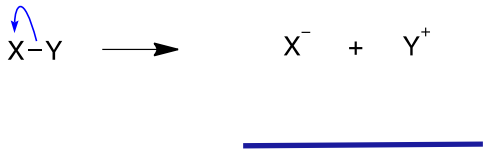
full arrow represents movement of *2 e*; this *sometimes* severs the link between



a



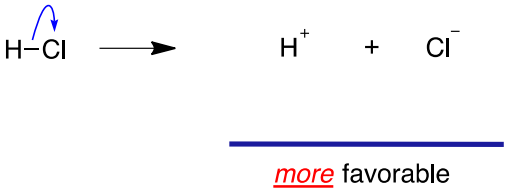
b



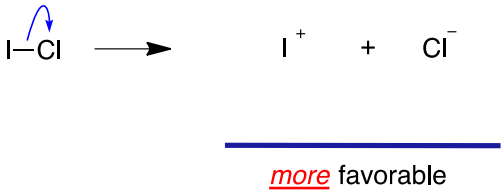
then this implies X is *less* electronegative than Y

than X then electrons would tend to move *towards* Y.

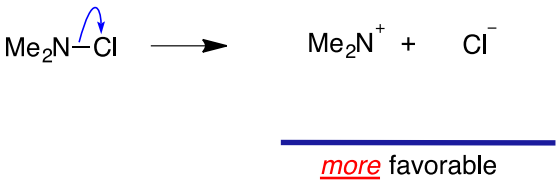
pathway 1



more favorable



more favorable

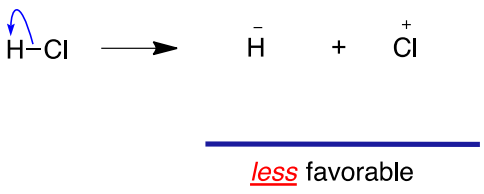


more favorable

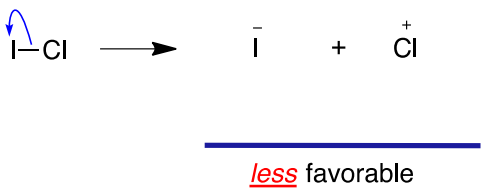
less favorable

less favorable

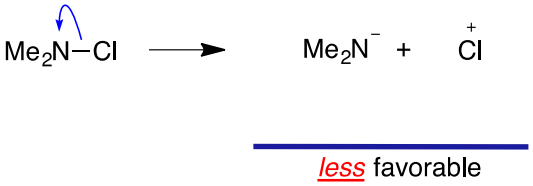
pathway 2



less favorable



less favorable



less favorable

more favorable

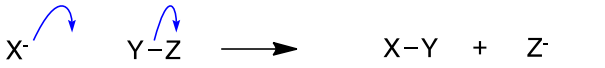
more favorable

more favorable

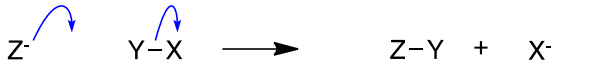
less favorable

Affecting Two Bonds

a



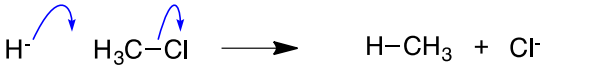
b



Pathway **a** tends to be *disfavored* if X is more electronegative than Z.

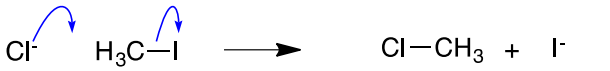
pathway 1

more favorable

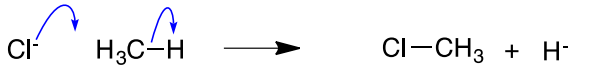


more favorable

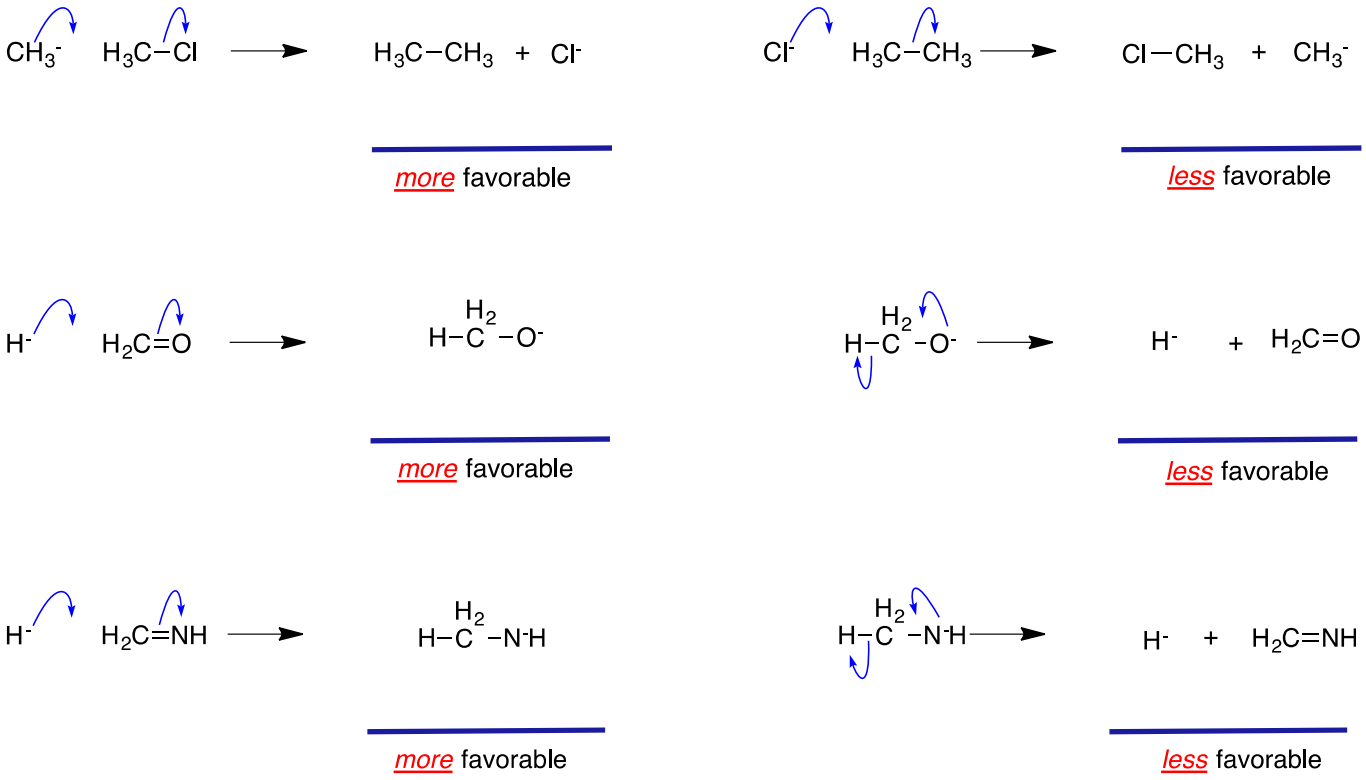
pathway 2



less favorable

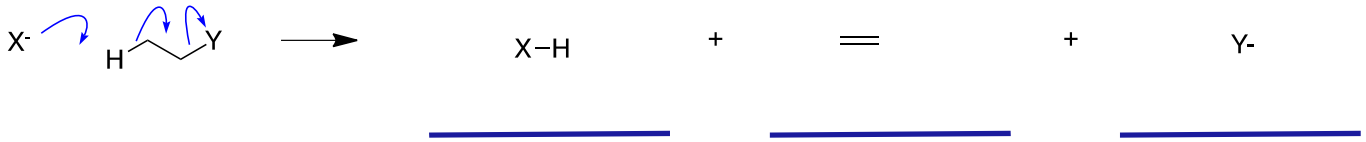


less favorable

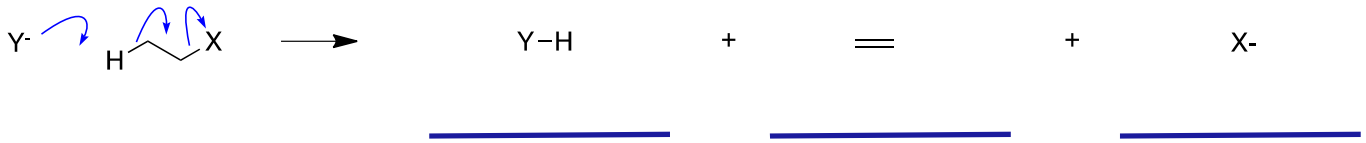


Affecting Four Bonds

a



b



Pathway **a** tends to be *favored* if X is more basic than Y

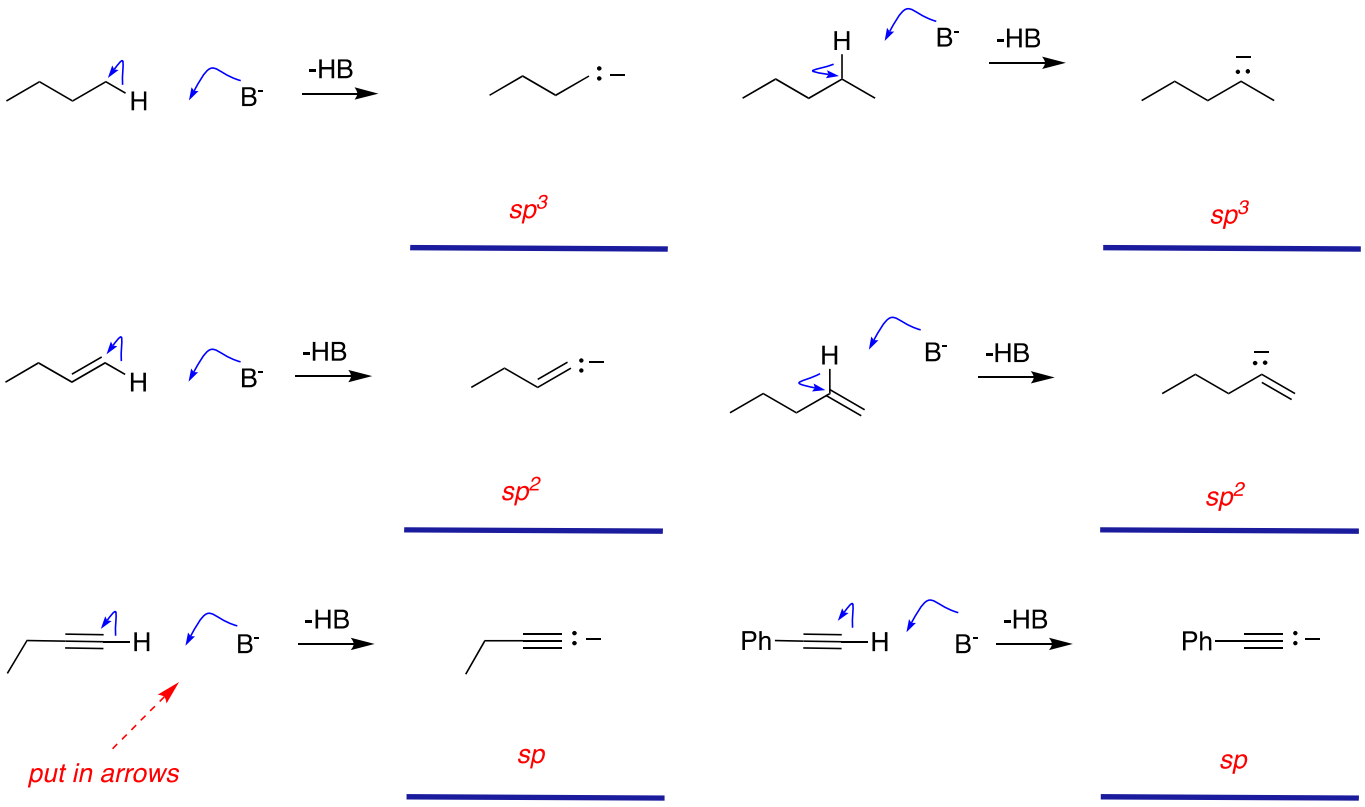
C. Electron Flow To Form Anions

the way they pronounce "*unionized*".

from a sp^3-hybridized carbon the resulting anion is sp^3-hybridized.

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

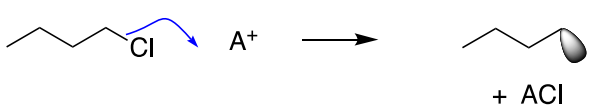
sp-Hybridized carbanions are formed from *sp*-hybridized

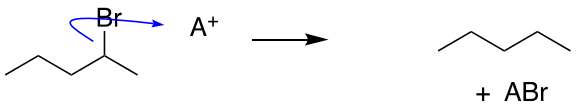


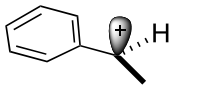
A sp^3-hybridized carbon has __4__ groups around it.

D. Cabocations Via Electron Flow

carbocations formed from sp^3-hybridized atoms tend to be sp^2-hybridized.



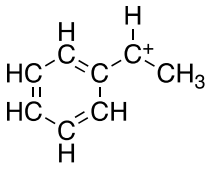


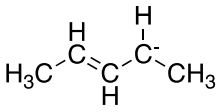


igonal planar

pyramidal

pyramidal



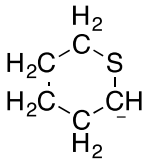


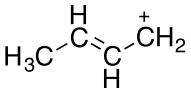
$^{t}BuSeCH_2^-$

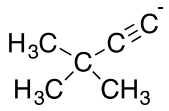
Carbocations of the type C^+R_3 tend to be sp^2-hybridized, and carbanions C^-R_3 are sp^3-hybridized.

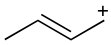
Explain why this is so by considering the number of electrons around carbon in C^+H_3 and in C^-H_3.

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.



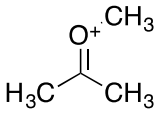






$H_2\dot{C}-N^+\equiv N$

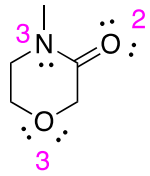
$H_2C=N^+=N^-$

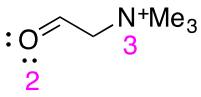


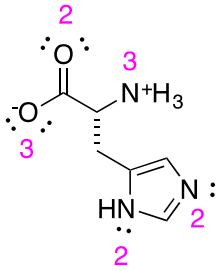
$\dot{-}-N^+\equiv N$

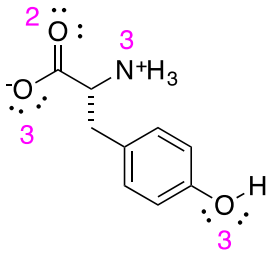
$=N^+=N^-$

E. Electron Flow Involving Lone Pairs On Heteroatoms







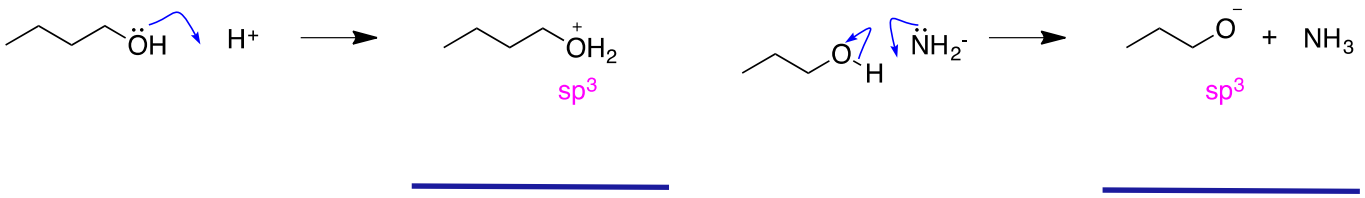


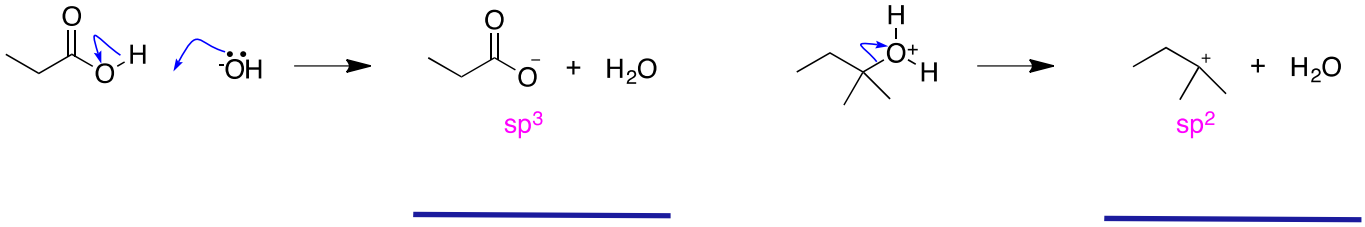
These answers are for the form shown in the diagram (of course resonance makes the O atoms equivalent)

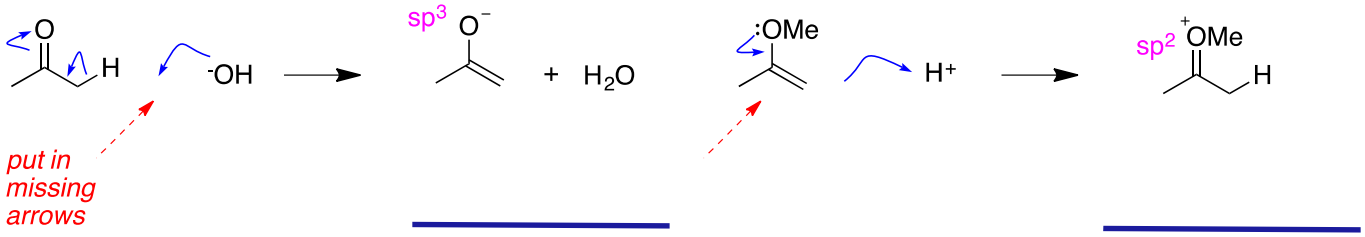
There *is not* a change in the number of groups
sp^3-hybridized heteroatoms gives *sp*^{3}-hybridized protonated

sp^2-hybridized heteroatoms become *sp*^{2}-hybridized protonated heteroatoms, and *sp*-hybridized heteroatoms become *sp*-hybridized protonated heteroatoms.

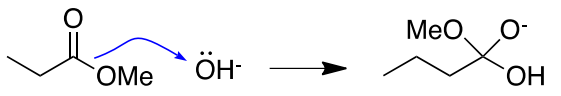
Conversely, there *can* be a change in hybridization state when electrons shift to atoms without protonation (*eg* between the oxygens of carbonyl groups).



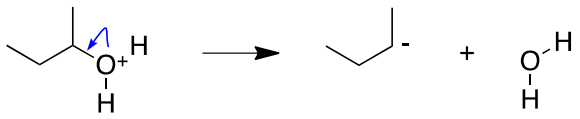


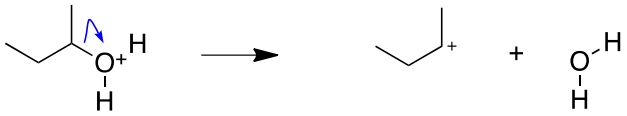


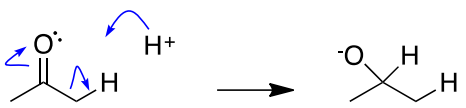
it is *usually* advisable to put the pen on the electron density and push

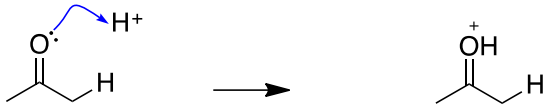

O
OMe
OH-
MeO
O-
OH


O
OMe
OH-
MeO
O-
OH

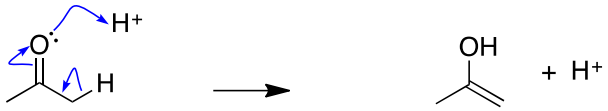

H
O+
H
-
+
O
H
H

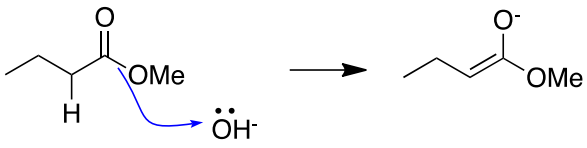

H
O+
H
+
+
O
H
H

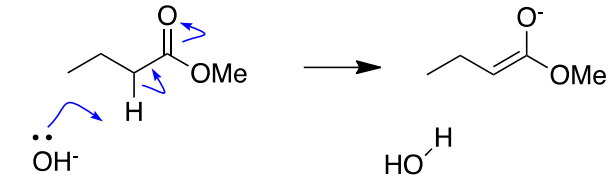

O
H+
H
-O
H
H

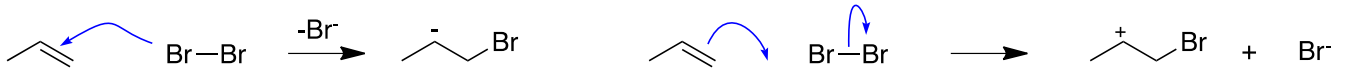

O
H+
H
OH
+
H
H

OR


O
H+
H
OH
+ H+

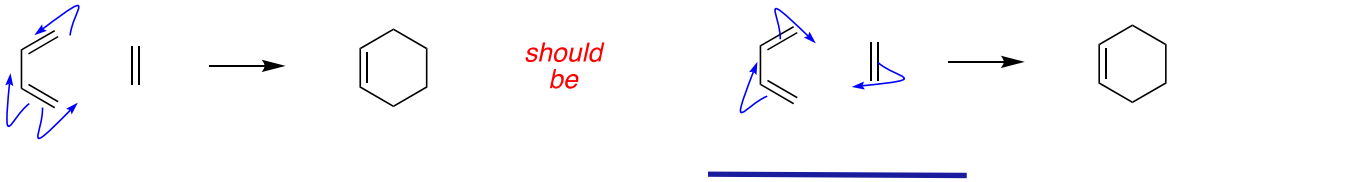

O
OMe
H
OH-
O-
OMe


O
OMe
H
OH-
O-
OMe
H
HO

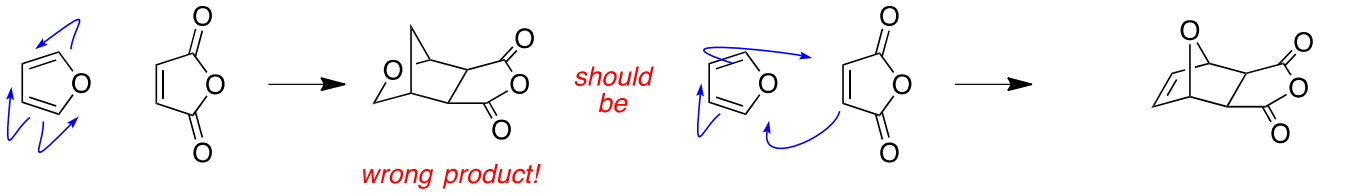


put in missing arrows

F. Cycloadditions: Apparently Not Charge Driven



show all arrows



wrong product!

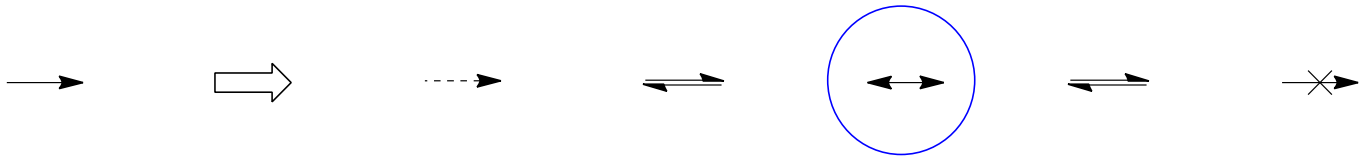
show all arrows

6. Resonance

A. Introduction

B. Resonance: Ground Rules And Generalities

Electrons move *much faster than* atoms in a molecule

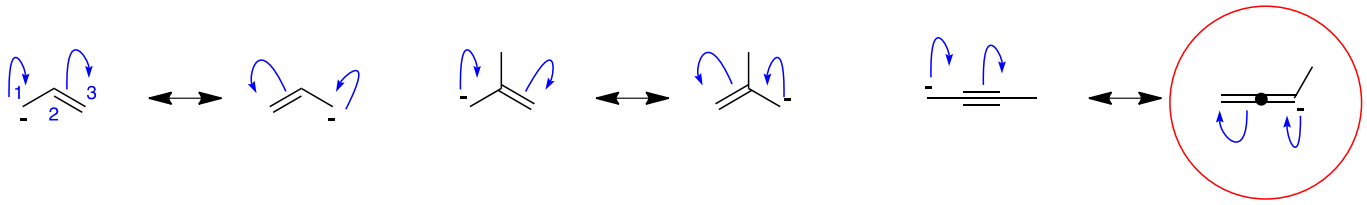


It is *absolutely wrong* to use the other descriptors shown above.

to depict movement of *electrons*.

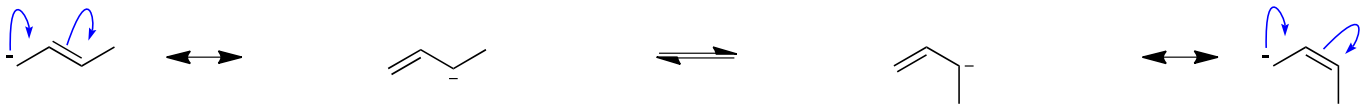
C. Resonance Stabilized Anions

Monoenes



allene

Electron flow *does not* allow the negative charge
The same *is* true for the methyl allyl

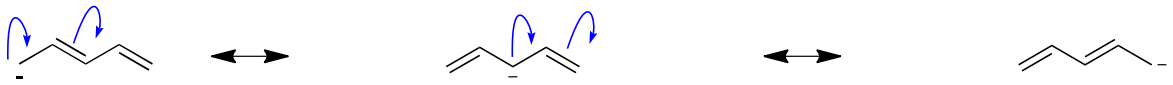


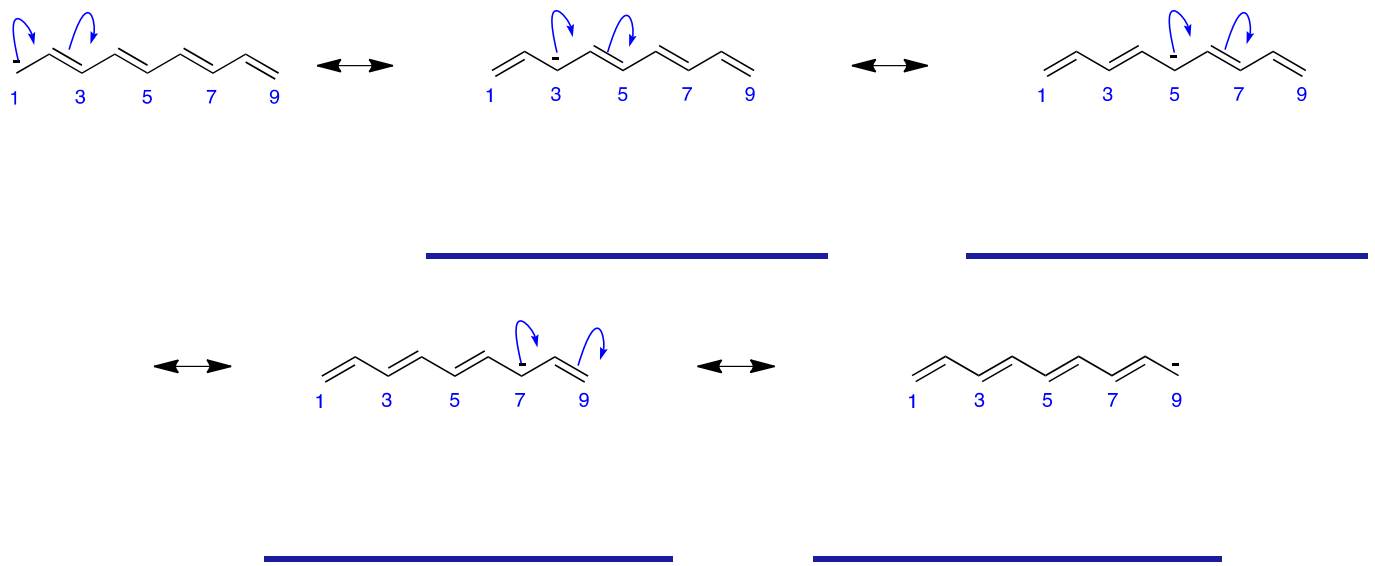
E- *Z*-

It is possible for *Z*-butenyl anions to equilibrate

It is *possible* for a molecule to have more than one resonance structure.

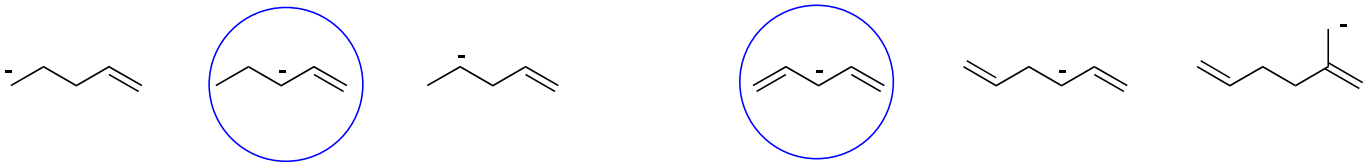
Conjugated Dienes





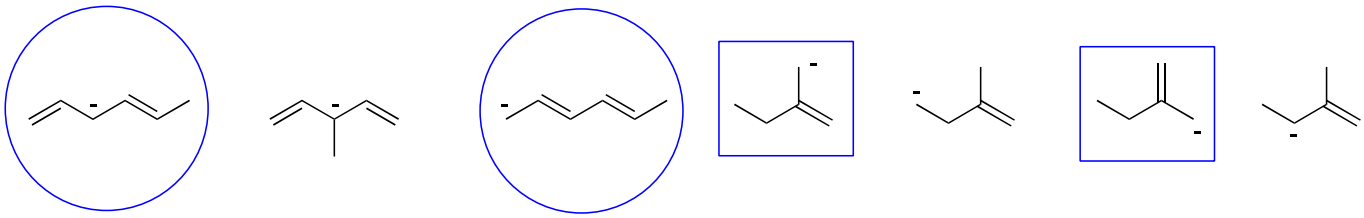
It *is* possible for the negative charge on the nonatetraenyl anion to reside on the 1,3,5,7,9-carbon atoms.
The negative charge in that anion *never* can be found on C^2, C^4, C^6
it *does* appear that the negative charge hops

drawn is likely to be *more* stable



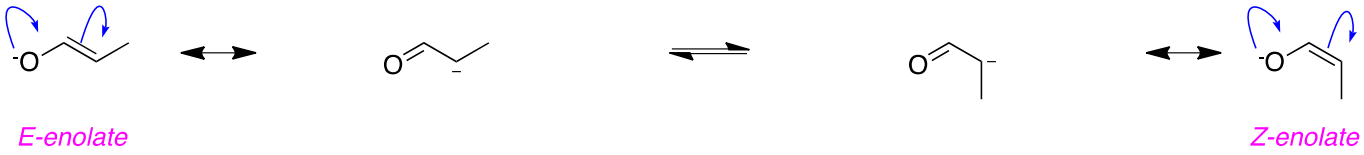
Anions that have several resonance structures are said to be *delocalized / resonance stabilized* relative to ones that do not

The allyl anion *less* stable than the pentadienyl anion

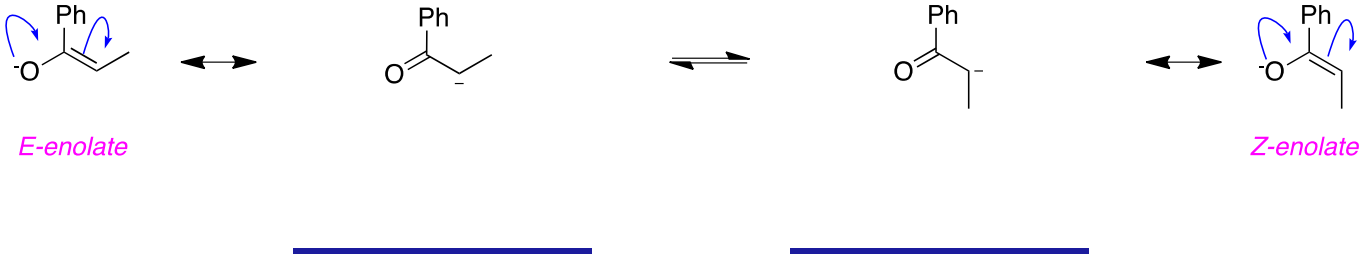


It *is* possible for the negative charge to hop

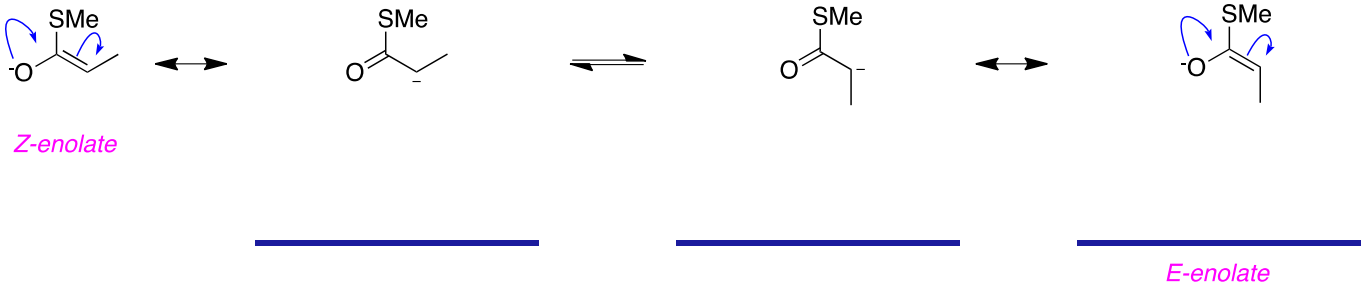
Systems With Heteroatoms



E-enolate *Z-enolate*

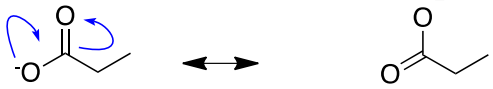


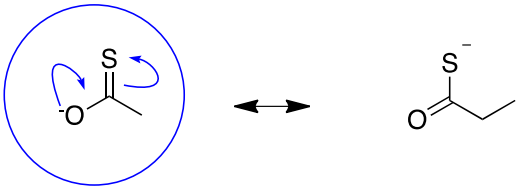
E-enolate *Z-enolate*



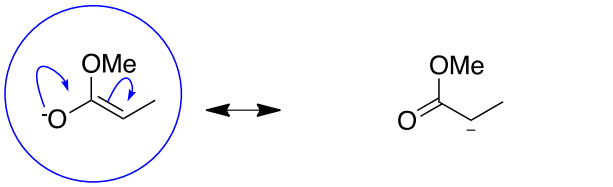
Z-enolate *E-enolate*

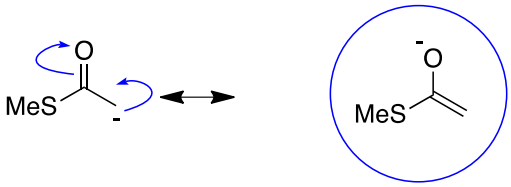
has the charge on the most *electronegative* atom.

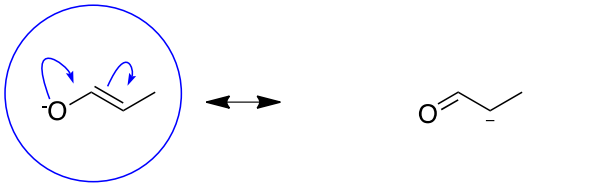


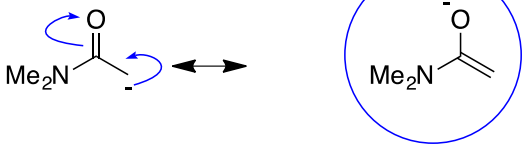


(^Equal Stability^)

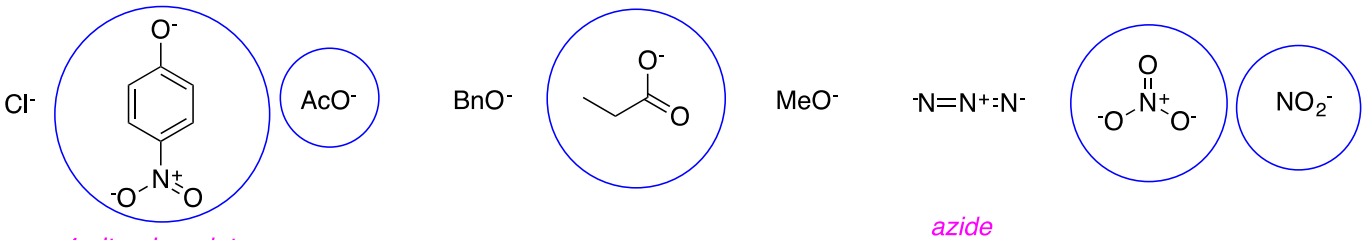








Resonance Stabilization Of Anions Influences Acidities



4-nitrophenolate

azide anion

-ve charge localized on electronegative atom

many contributing resonance forms

highly localized charge

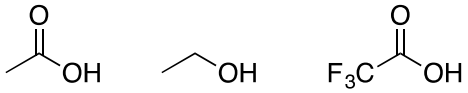
electron delocalization

-ve charge localized on electropositive atom

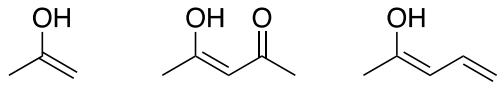
How Resonance Stabilization Of Anions Influences Acidity

The following equilibrium favors *product* if the anion A^- is resonance stabilized

Higher concentrations of protons correspond to *low* pK_a and *low* pH values for the acid HA.

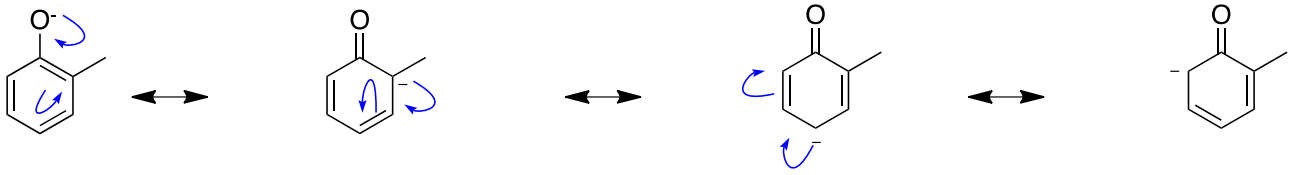


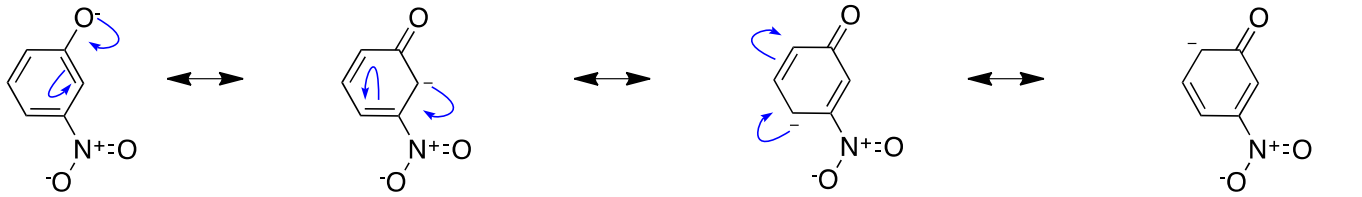
3 1



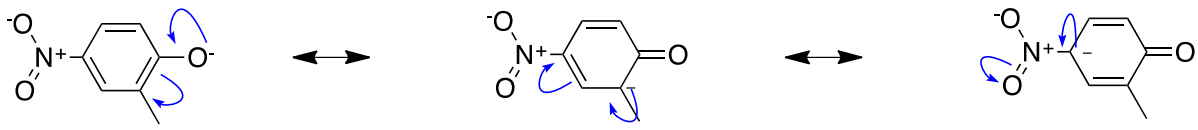
3 1

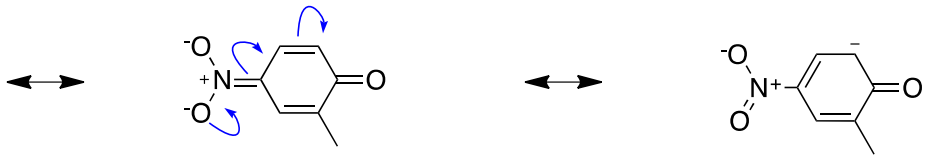
Aromatic Anions





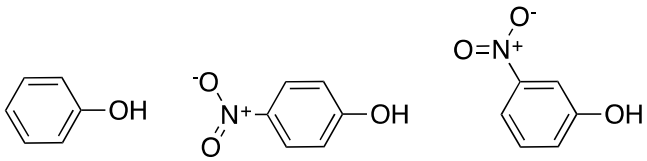
it *is not* possible for both the *O*-atoms



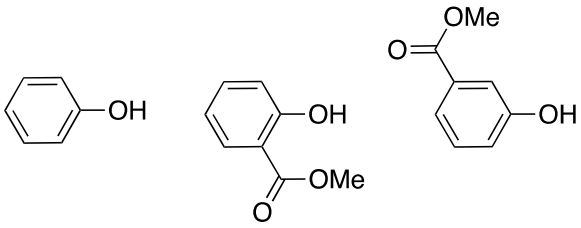


it *is* possible for both the *O*-atoms

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

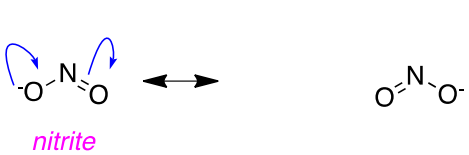


3 1

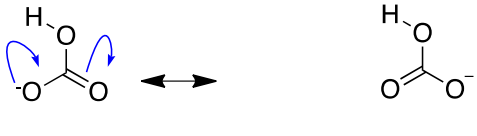


3 1

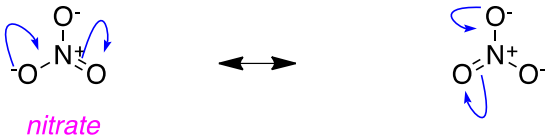
Inorganic Anions



nitrite



hydrogen carbonate



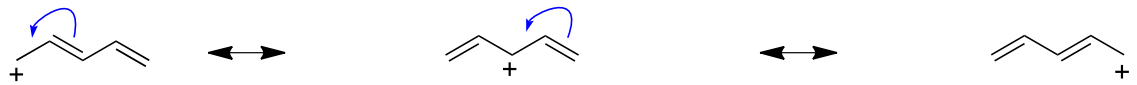
nitrate

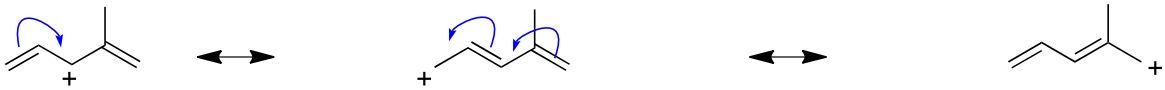
nitric acid should be a *stronger* acid than nitrous and carbonic acid.
strongest acid in the series is HNO_3.

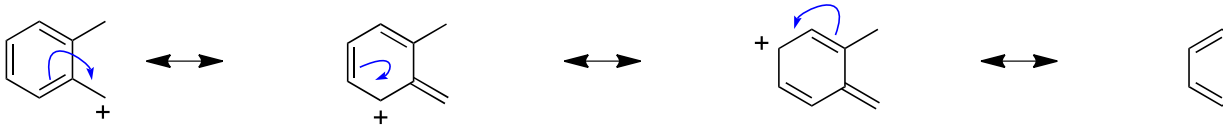
D. Resonance Stabilized Cations

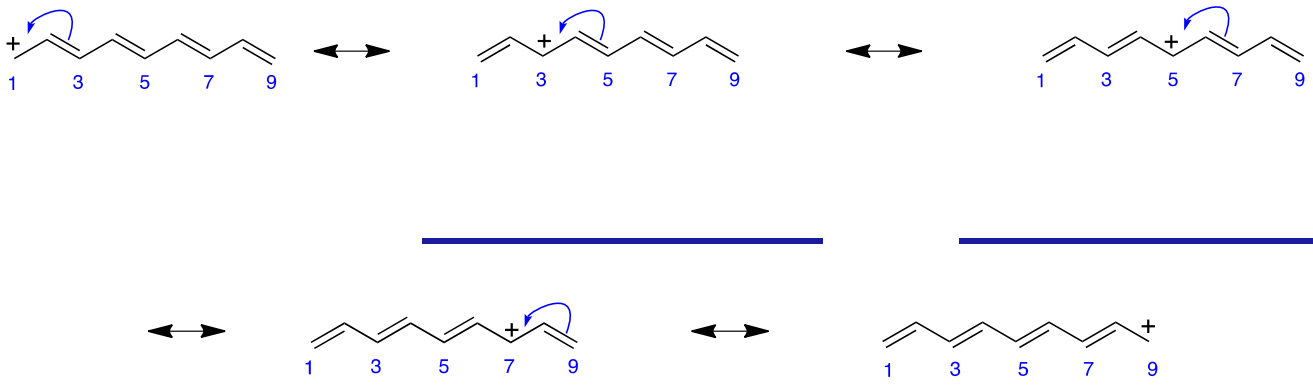
Conjugated Alkenes And Aromatics

represent flow of electrons *towards* positive charges and rarely the reverse.



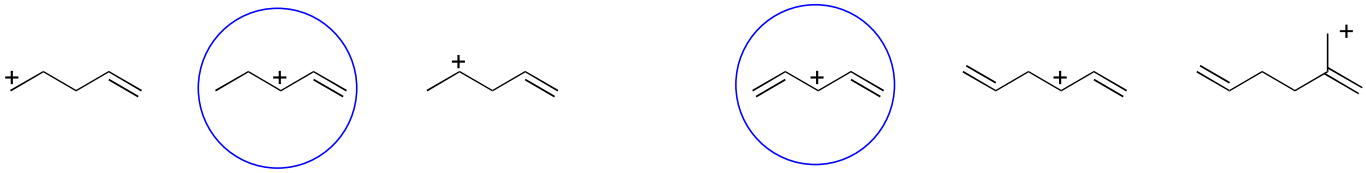




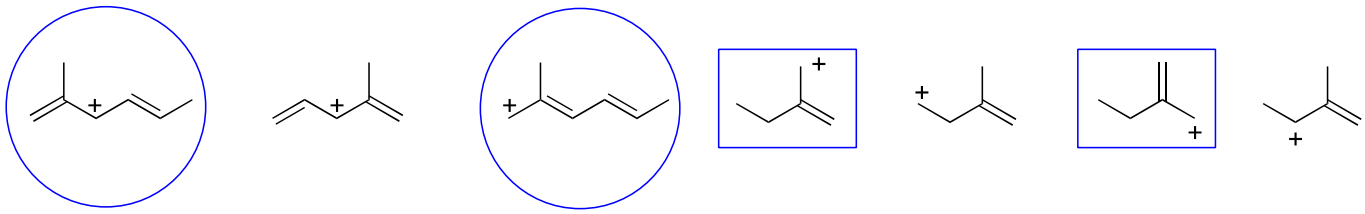


nonatetraenyl cation *can* reside on the 1,3,5,7,9-carbon atoms and it is *never* found on C^2, C^4, C^6, and C^8; consequently, it *does* appear to hop

drawn is likely to be *more* stable



resonance structures are said to be *more delocalized* than ones that do not.
Allyl cations are *less* stable than pentadienyl ones



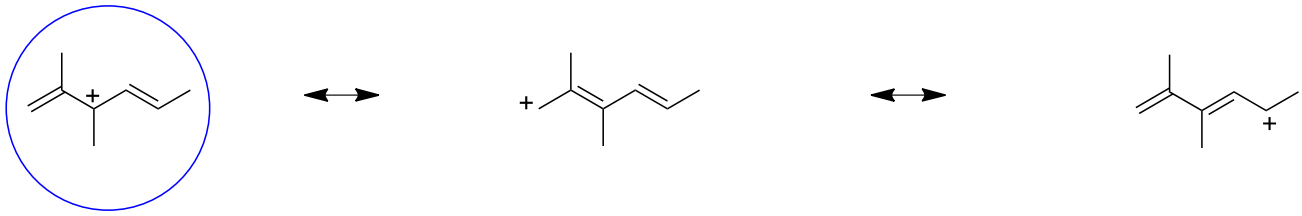
It *is* possible for the positive charge to hop between atoms

the charge on the most *electropositive* atom.

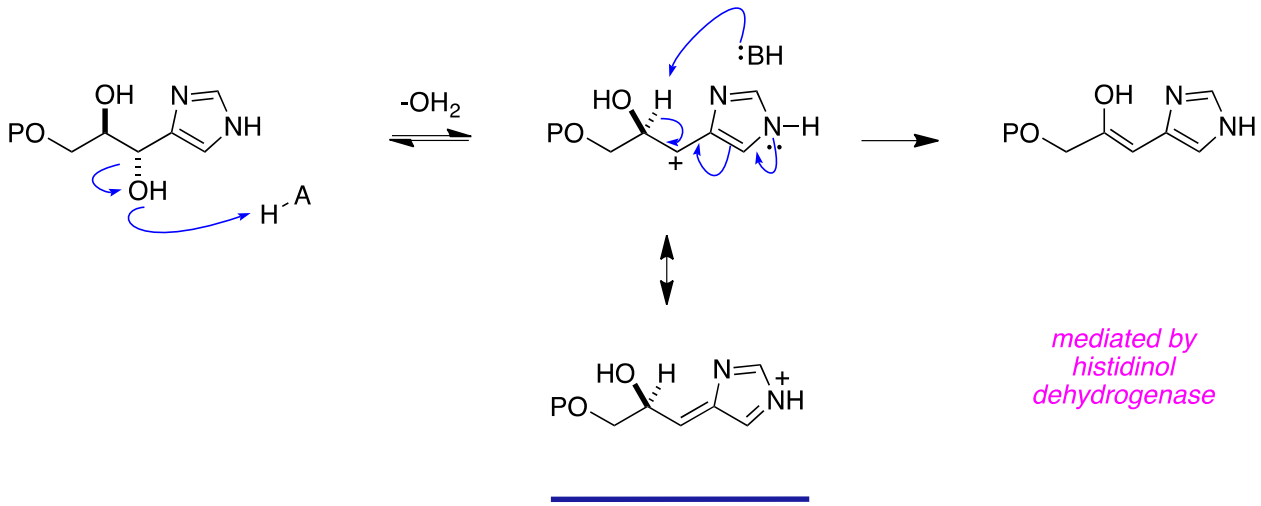
Cations with a positive charge on carbon, *ie carbocations*, tend to be *more* stable when the carbon is more substituted with other carbons

A carbocation that has one substituent is *primary (1°)*.

It *is not* possible possible to make a quaternary carbocation.



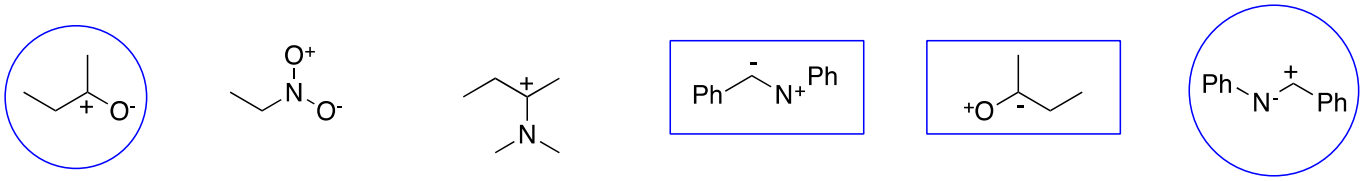
A Biochemical System



E. Resonance In Neutral Molecules

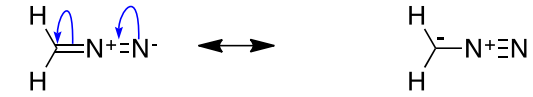
Unfavorable Charge Speration

tend to be significantly *less* stable

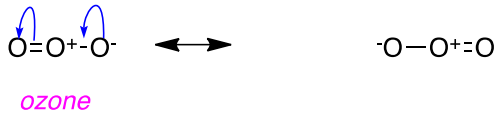


Enforced Charge Seperations In Dipolar Molecules

Some molecules that have a net neutral charge can only be represented as *zwitterions*.



diazomethane

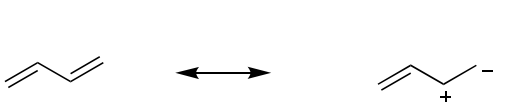


ozone

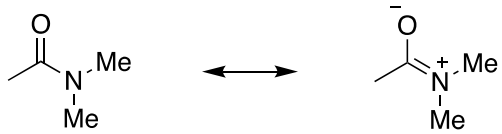
methyl azide

nitrous oxide

F. Resonance Stabilizes Some Conformations

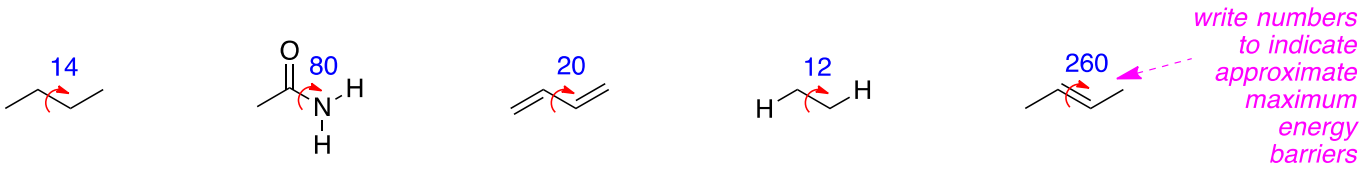


charge separated form
less stable



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}

7. Acids And Bases

A. Introduction

B. Proton Dissociation On Log Scales

Equilibria That Generate Protons: pKa's

hats not worn at any moment is a *constant*, because an equilibrium

of hats worn at equilibrium in *different* games will be *variable*; therefore, it *is not* a good parameter

the *ratio* of *people wearing hats* to *people not wearing hats will not* change significantly

This *is* effectively the same as the statement:

protons in acid base equilibria *may* be represented as:

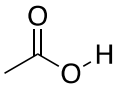
to generate protons for *all* organic

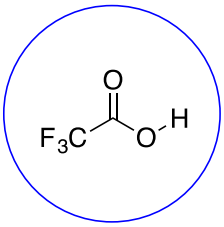
Weak acids dissociate to give a *small* fraction

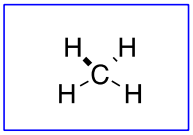
compound is a *strong* acid and the equilibrium constant is *high*.

methane is therefore a *weak* acid.

therefore a significantly *stronger* acid than methane.

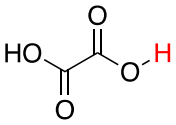






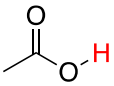
the number of moles of CH_3^- *does* equal the concentration of protons

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



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

1



1.8×10^{-5}

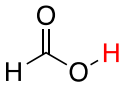
4

1.1×10^{-7}

5

1.0×10^{-14}

6



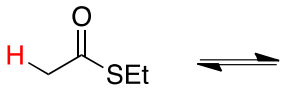
2.4×10^{-4}

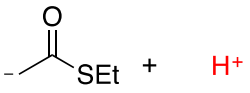
3

6.6×10^{-4}

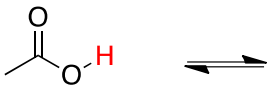
2

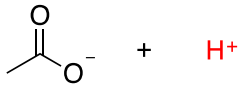
with a K_a of 1 would be a *strong* acid.



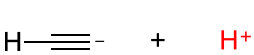


and $[H^+] = \frac{K_a\ [CH_3COSEt]}{[^-CH_2COSEt]}$

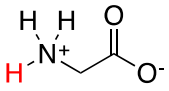


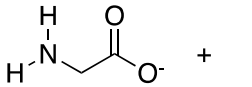


and $[H^+] = \frac{K_a\ [CH_3CO_2H]}{[CH_3CO_2^-]}$

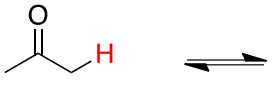


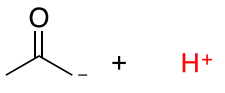
and $[H^+] = \frac{K_a\ [CHCH]}{[CHC^-]}$





and $[H^+] = \frac{K_a\ [^+NH_3CH_2CO_2^-]}{[NH_2CH_2CO_2^-]}$

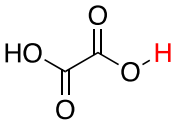




and $[H^+] = \frac{K_a\ [CH_3COCH_3]}{[CH_3COCH_2^-]}$

pKa's Simplify Ka Comparisons

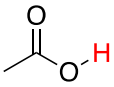
condenses



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

$\log K_a = -1.27$

$-\log K_a = 1.27$



1.8×10^{-5}

$\log K_a = -4.74$

$-\log K_a = 4.74$

1.1×10^{-7}

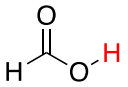
$\log K_a = -6.95$

$-\log K_a = 6.95$

1.0×10^{-14}

$\log K_a = -14$

$-\log K_a = 14$



2.4×10^{-4}

$\log K_a = -3.74$

$-\log K_a = 3.74$

6.6×10^{-4}

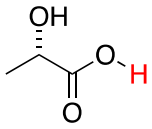
$\log K_a = -3.18$

$-\log K_a = 3.18$

diagram above the values for $-\log K_a$, *ie* the *pK_a* value.

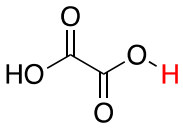
have K_a values less than one, meaning *only a small amount* of the compound
using negative logs of K_a values is they are *positive* for most organic compounds.

Strong acids have *larger* K_a values than weak acids, *less* $-\log K_a$ values, and *smaller* pK_a values.



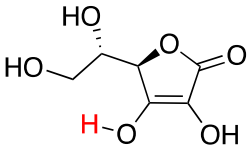
lactic acid
$pK_a = 3.86$

2



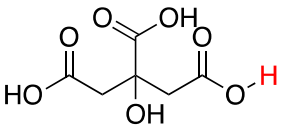
oxalic acid
4.19

4



ascorbic acid
4.10

3



citric acid
3.08

1

one pK_a unit means that it is *10* times easier

10 pK_a units means that it is *10,000,000,000* times easier

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

it is about 10^{29} times *more* likely that an ammonium ion

it is about 10^{17} times *less* likely that water will dissociate

C. Acid-Base Equilibria

Deductions Based On Quantitative Ka And pKa Data

following equilibrium favors the *starting materials*

NH_4^+	+	H_2O	⇌	NH_3	+	H_3O^+
acid		*base*		*base*		*acid*

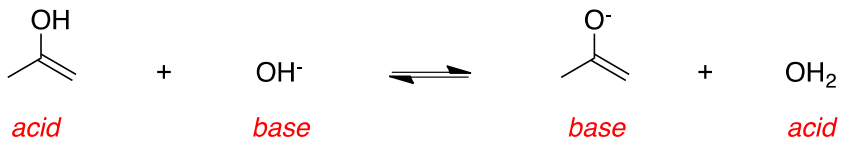
favor the side with the *weakest* acid because

Weak acids have *higher* pK_a values than stronger acids.

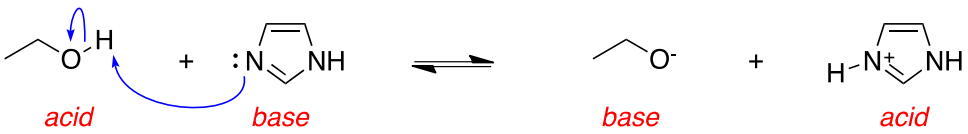
EtO^-	+	H_2O	⇌	EtOH	+	OH^-
base		*acid*		*acid*		*base*

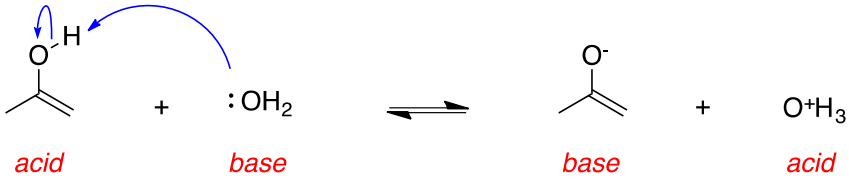
MeOH	+	Me_3NH^+	⇌	$MeOH_2^+$	+	Me_3N
base		*acid*		*acid*		*base*

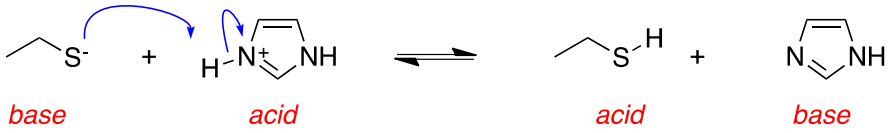
	+	H_2O	⇌		+	H_3O^+
acid		*base*		*base*		*acid*

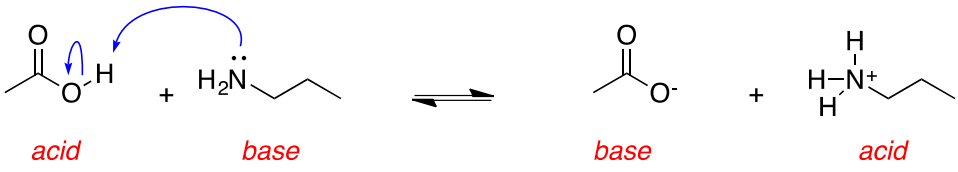


It *is* possible for the same compound to be an acid in some reactions and a base in others.







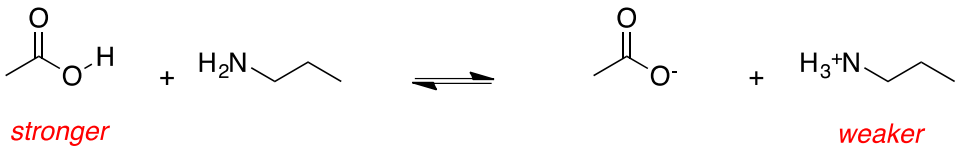


deprotonating an acid can be called its *conjugate base*.

given to the substance formed by *protonating a base*.

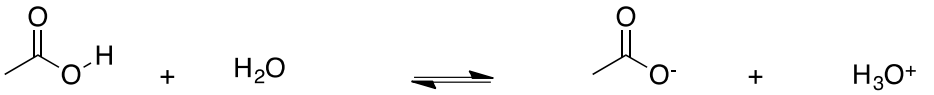
Ammonium, NH_4^+, is the conjugate *acid* of ammonia.

Hydroxonium is the conjugate *acid* of water.



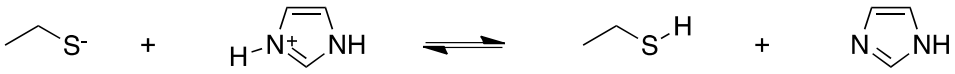
stronger *weaker*

favors *products*



weaker *stronger*

favors *starting materials*



stronger *weaker*

favors *products*

stronger *weaker*

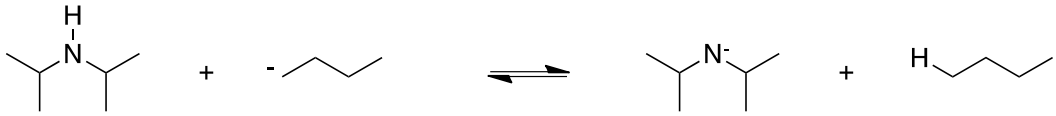
favors *products*

guanidine *stronger* *weaker*

favors *products*

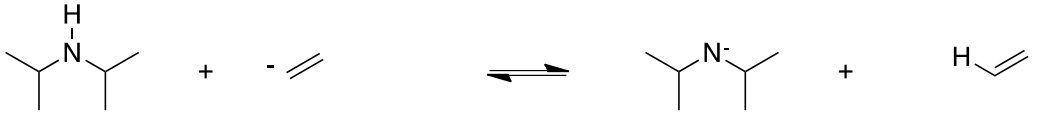
stronger *weaker*

favors *products*



stronger *weaker*

favors *products*



stronger *weaker*

favors *products*

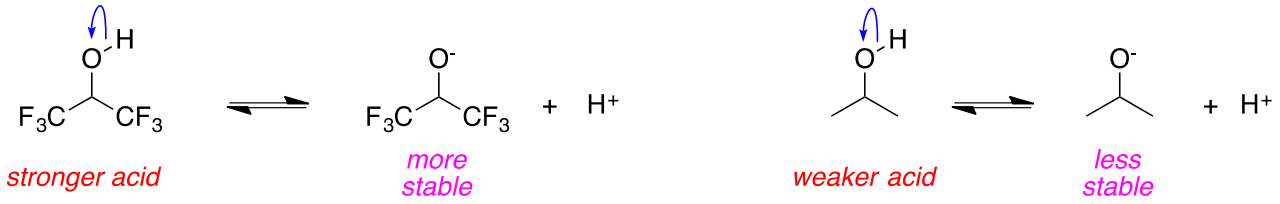
weaker *stronger*

favors *starting materials*

Relative Acidities

Ethanoic acid is a *weaker* acid than trifluoroethanoic acid.

stabilized by *electronegativity* effects.

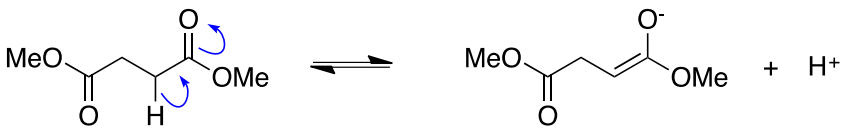


1,1,1,3,3,3-Hexafluoropropan-2-ol has a lower pK_a than propan-2-ol; therefore, it is a stronger acid.

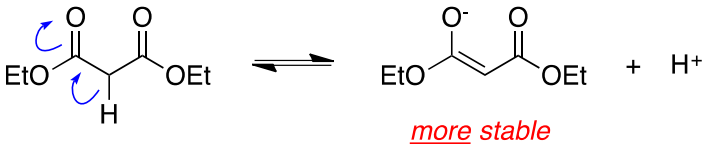
The alkoxide from 1,1,1,3,3,3-hexafluoropropan-2-ol is *more* stable than that from propan-2-ol because of *electronegativity* effects.

Allyl anions are *more* stable than propyl anions due to *resonance* effects, hence propene is a *stronger* acid than propane.

The enolate from ethanal is *more* stable than allyl anions due to *electronegativity* effects, so ethanal has a *lower* pK_a than propene.



less stable

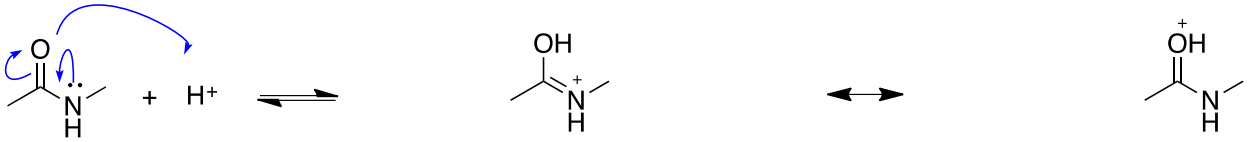


more stable

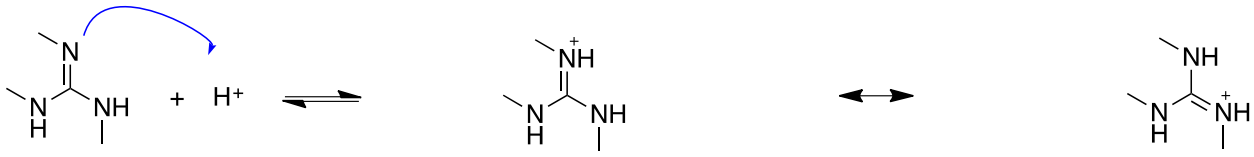
Dimethyl succinate has a *higher* pK_a than diethyl malonate, mainly due to *resonance* effects.

D. Basic Atoms In Molecules Protonate

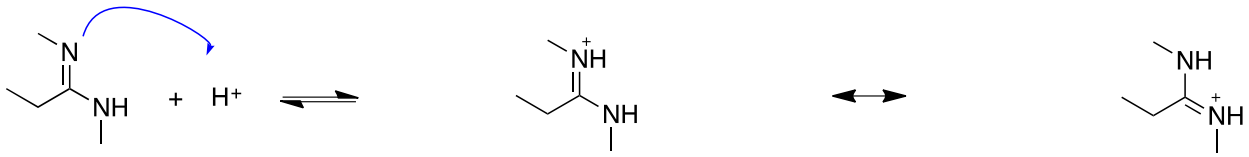
protonated form *protonated form*



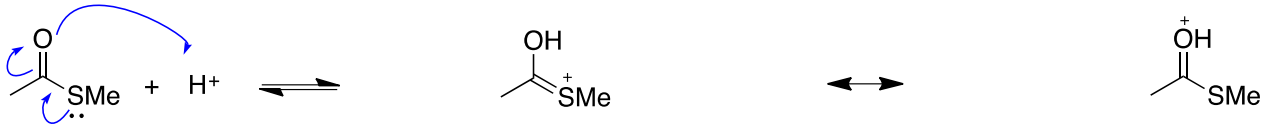
protonated form *protonated form*



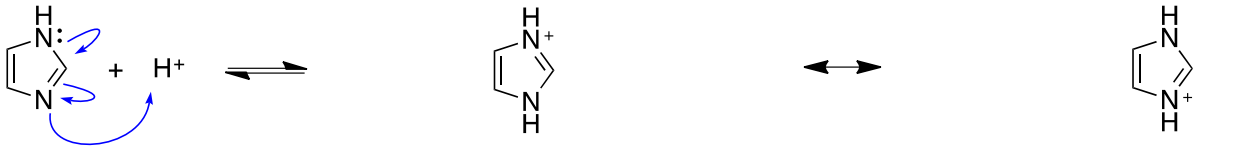
protonated form *protonated form*



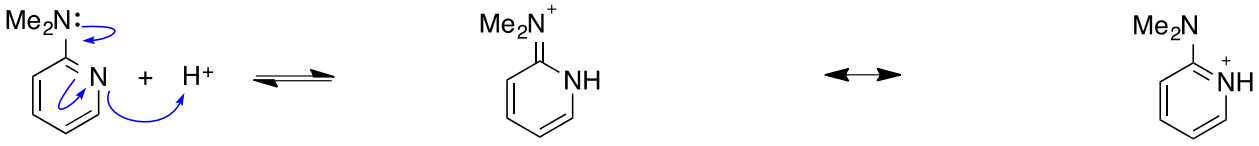
protonated form *protonated form*



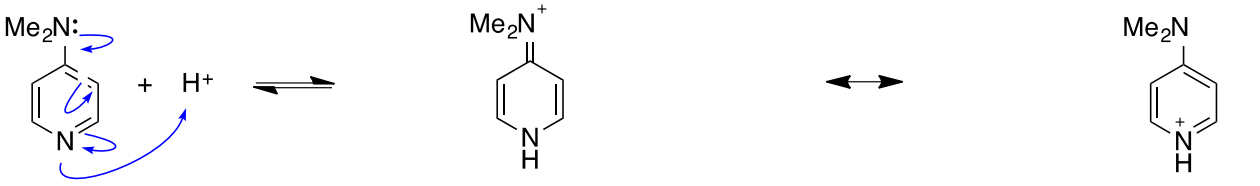
protonated form *protonated form*



protonated form *protonated form*

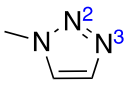


protonated form *protonated form*



protonated form *protonated form*

most likely to be protonated selectively at *N*^{3}.



explanation:

because of resonance, electrons can move from *N*^{1} to *N*^{3} another

E. Lewis Acids And Bases

Protons feature in *some* acids.

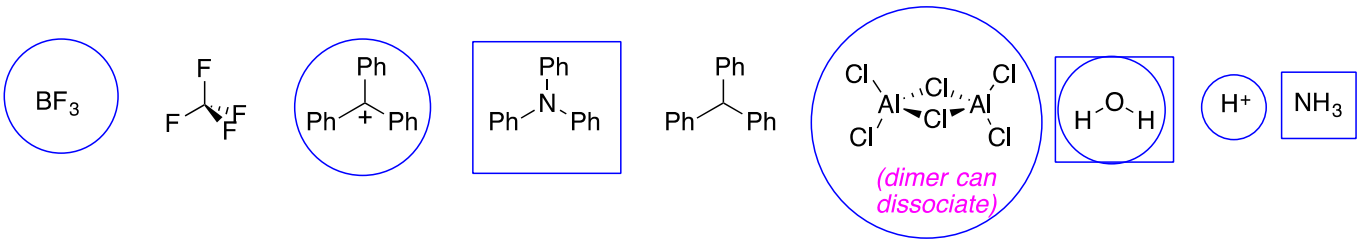
eg an empty p-orbital.

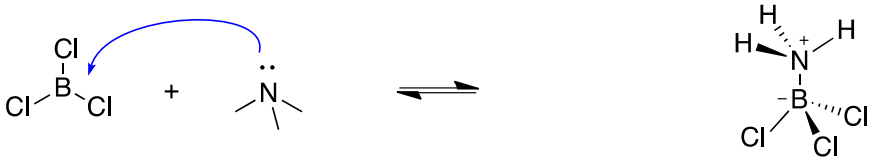
Lewis *acids*

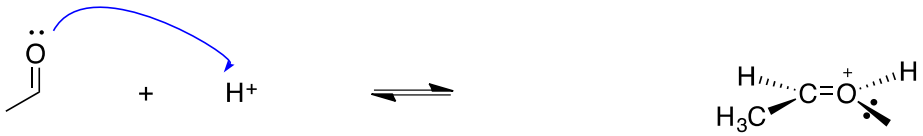
acids because they have *6* electrons in their valence shell and *an empty*

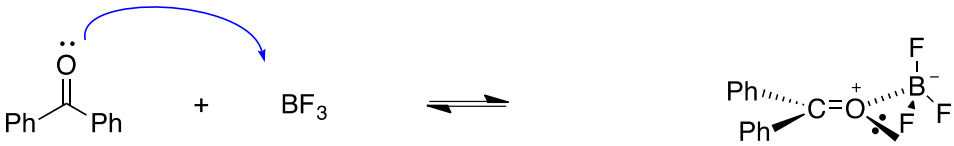
can fit the definition of a Lewis acid.

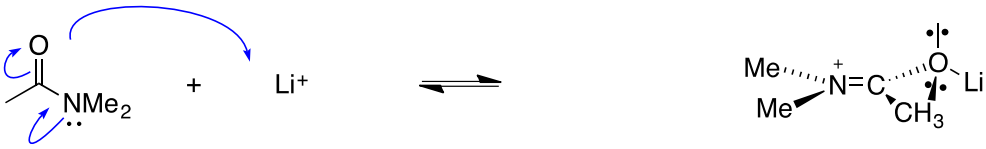
Protons *do* fit

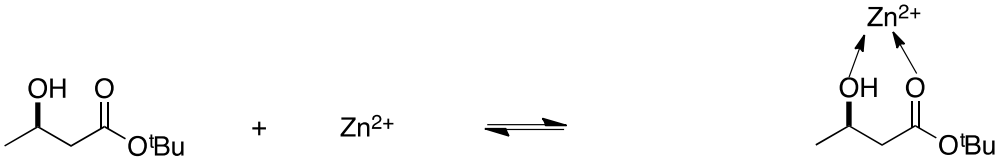

BF3
F
F
F
Ph
Ph
+
Ph
Ph
N
Ph
Ph
Ph
Cl
Al
Cl
Cl
Al
Cl
Cl
Cl
(dimer can
dissociate)
H
O
H
H+
NH3


Cl
B
Cl
Cl
+
N
H
H
H
N
B
Cl
Cl
Cl

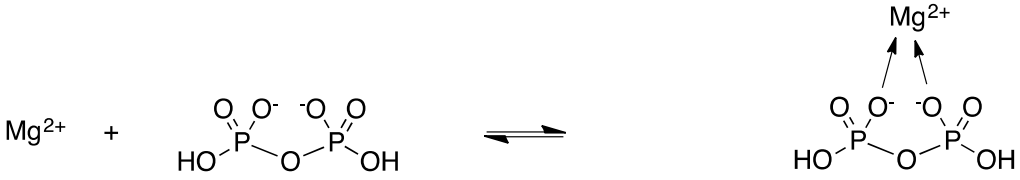

O
+
H+
H
C=O
H
H3C


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





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



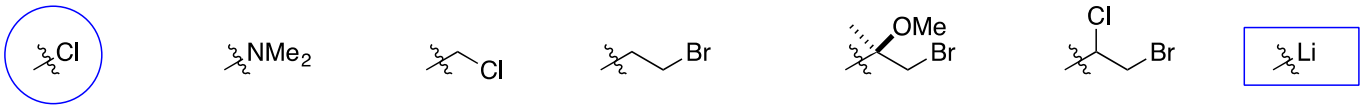
8. Priority Rules

A. Introduction

B. Priority Rules

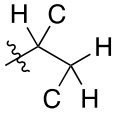
Substituents Without Multiple Bonds

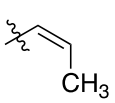
the atom with *higher* atomic mass takes priority.

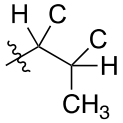


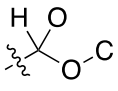
Substituents Connected Multiple Bonds

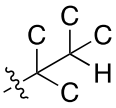
The problem is: *the first atom of the substituents is the same for every molecule*.

eg  *is equivalent to* 



is equivalent to 

is equivalent to 


is equivalent to 

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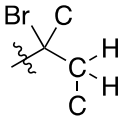

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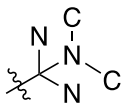

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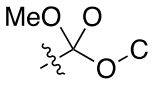

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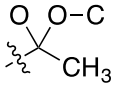

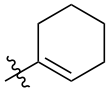

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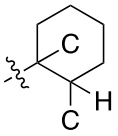

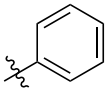

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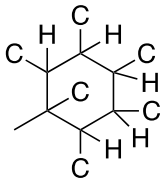

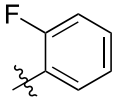

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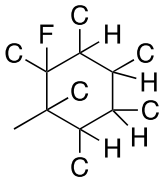

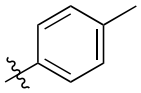

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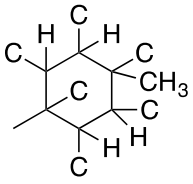

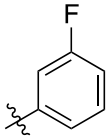

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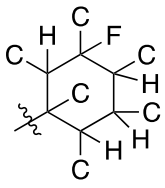

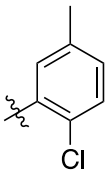

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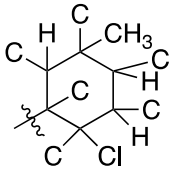
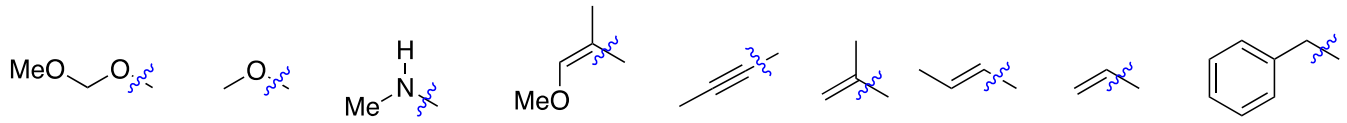
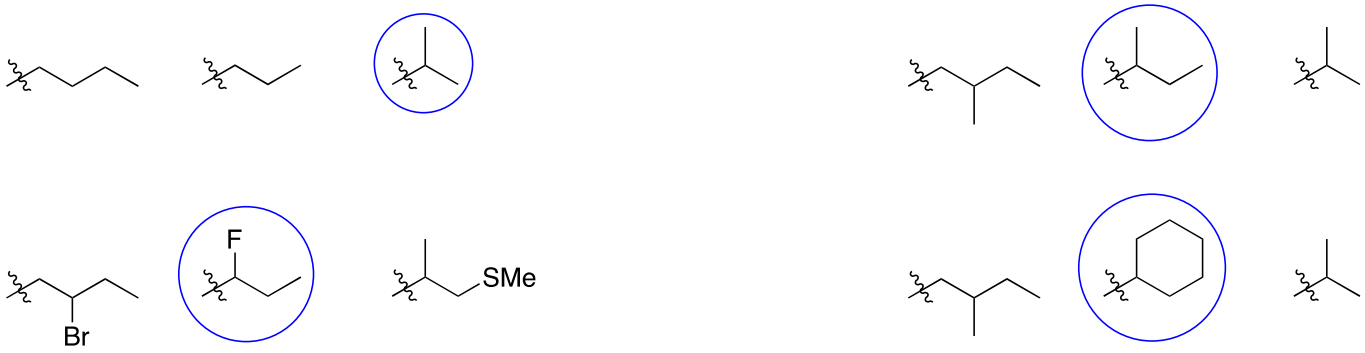


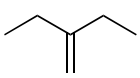


highest priority *lowest*

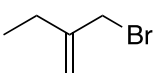


C. Classifying Alkene Geometries

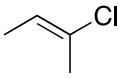
the terms *cis* / *trans* means the same as *E* / *Z*.



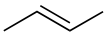
na



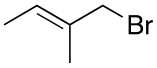
na



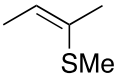
E-



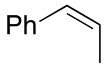
E-



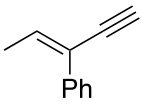
E-



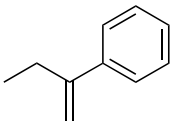
Z-



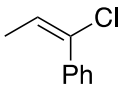
Z-



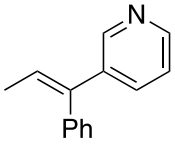
Z-



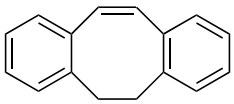
na



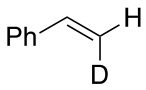
E-



E-

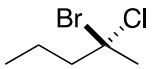


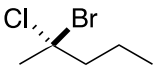
Z-



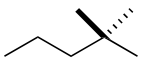
Z-

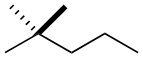
D. Chiral Centers



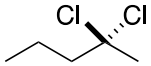


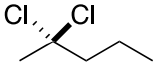
no



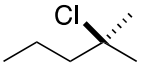


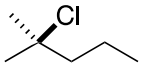
yes





yes



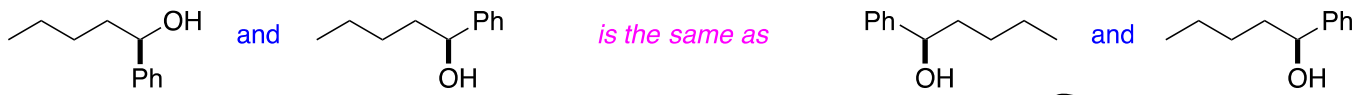


yes

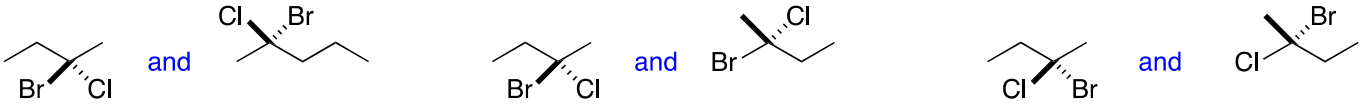
yes *no*

non-superimposable mirror images *do* require that there be four different groups on a carbon atom.

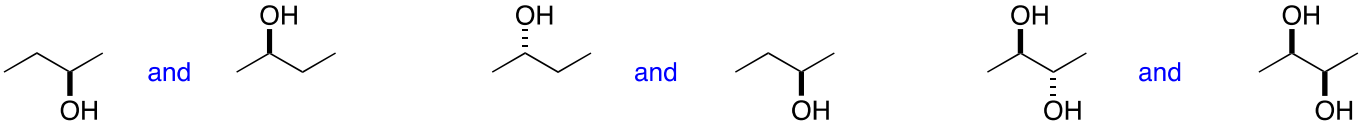
Mirror images of organic molecules are called *enantiomers*- *only if* they are non-superimposable.



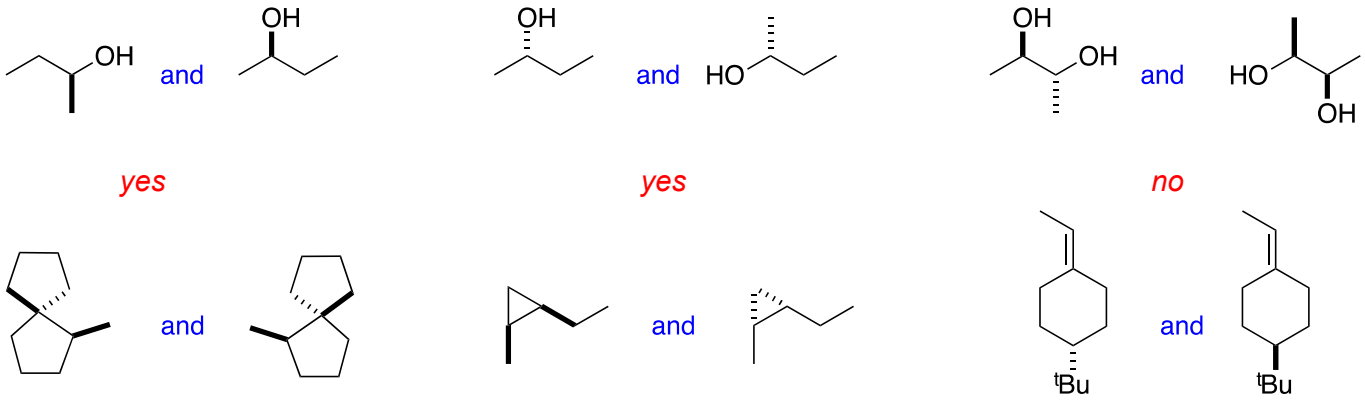
yes



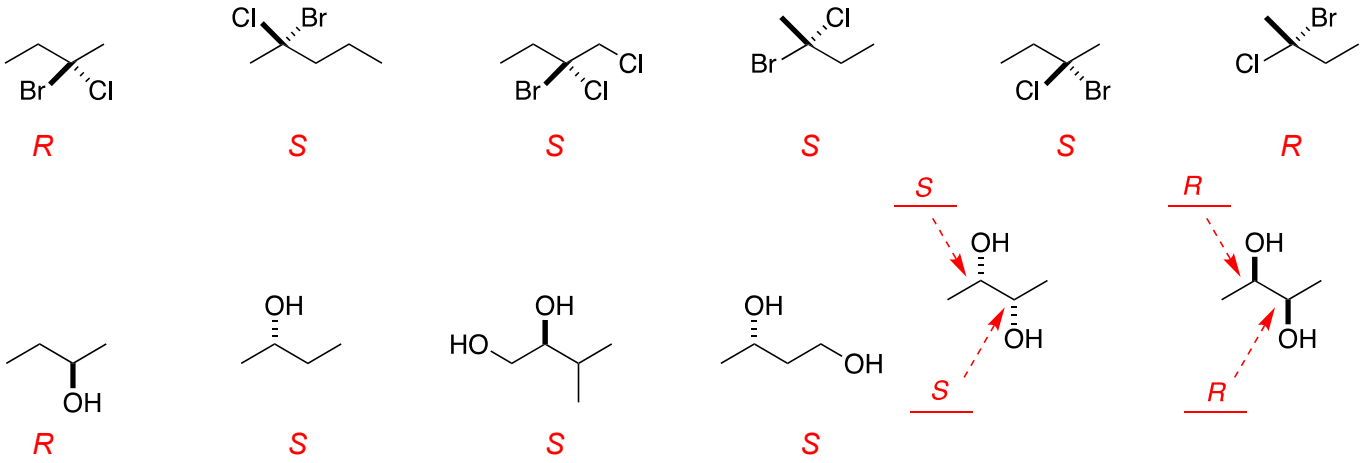
no *yes* *yes*



no *yes* *no*



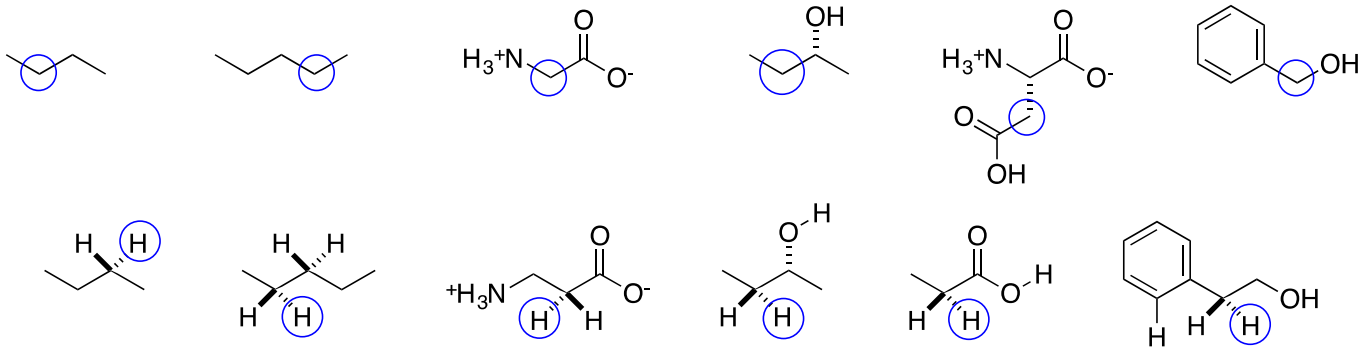
Assigning chirality like this *can* establish if molecules are mirror images.



If a compound has *R*-stereochemistry, its enantiomer is always *S*-.

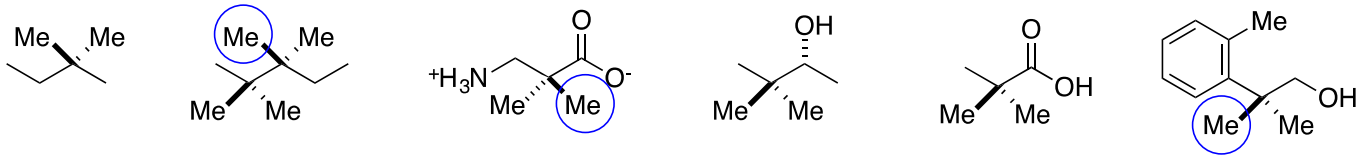
E. Prochirality

"Some prochiral compounds can be converted to chiral ones by *substituting* a group at the prochiral center" *true*

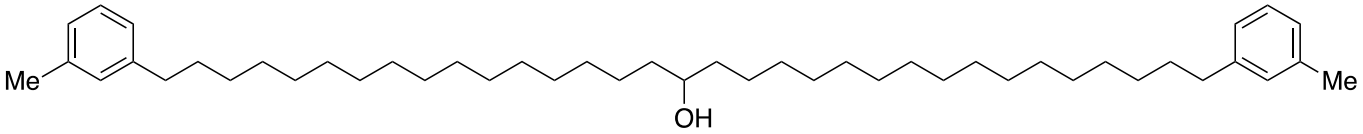


The hydrogen atoms circled in the diagram above are all *pro-R*.

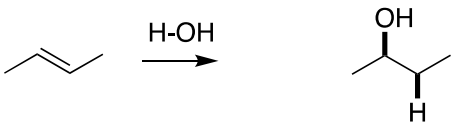
This is a *substitution* reaction.

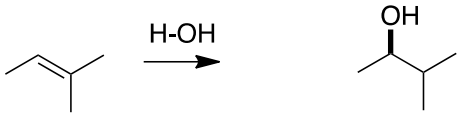


Methyl groups circled in the diagram above are all *pro-S*.



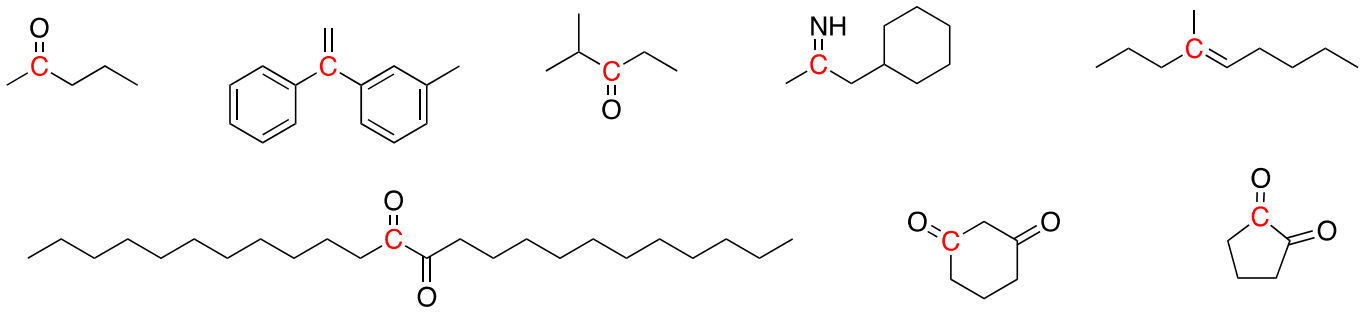
The two methyl groups in the molecule above *are* prochiral.



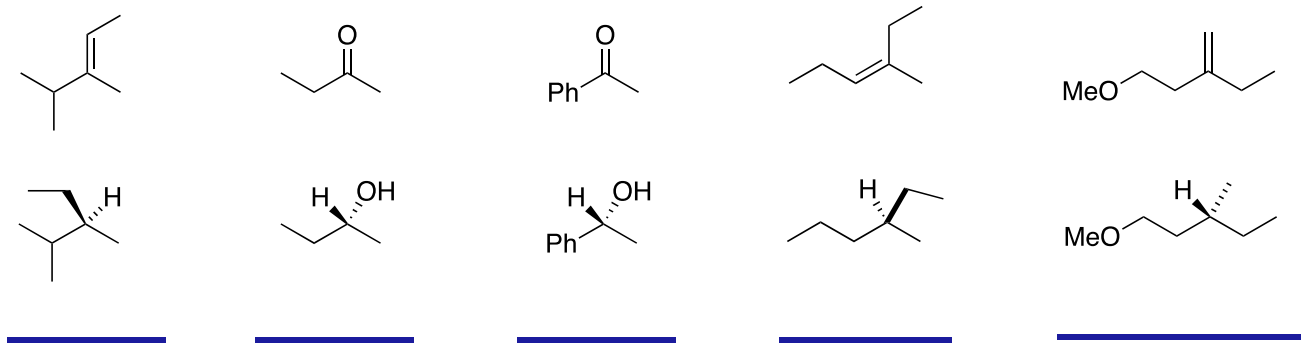


"Some prochiral compounds can be converted to chiral ones by *adding* a group to the prochiral center".
true

(looking down on the paper), the priority of the groups attached to the highlighted carbon in the following compounds are *all Re-*.



(looking up from below the paper), the priority of the groups attached to the highlighted carbon in the following compounds are *all Si-*.



Reactions from the *Re*-face *sometimes* gives the *R*-chiral
while reactions from the *Si*-face *sometimes* gives the *S*-chiral centers.

9. Chiral Molecules

A. Introduction

B. Optical Rotation and Enantiomeric Excess

Optical Rotations

excess of one enantiomer over another are optically *active*
those containing only one enantiomer are optically *active and pure*.

Optically active molecules *can* rotate the plane
Rarely, there *may* be wavelengths of that plane of polarized light

rotation for a sample is called its *observed optical rotation*; it is measured in *degrees* on an instrument called a *polarimeter*.
plane to the right is called *dextrorotatory / positive*
rotate light to the right *are not* always *R*-, and *S*-enantiomers *are not* always levorotatory.

solvent / wavelength of the plane polarized light / temperature
pathlength of the sample container (cell) /
concentration of the sample

optically active impurities *do not* lead to reproducible readings.

variables specified are called *specific* rotations.
These values *do* facilitate comparisons of data

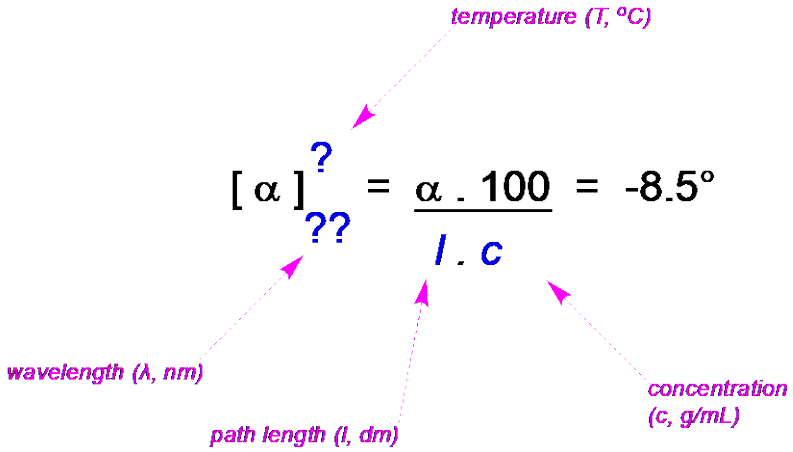
which are the temperature of the sample (in *centigrade*)

$$\alpha = -21°$$

observed optical rotation

$$[\alpha]^{?}_{??} = \frac{\alpha \cdot 100}{l \cdot c} = -8.5°$$

specific rotation



determine which enantiomer is in abundance, *and* how much it is in excess or the other.

Enantiomeric Excess

prepared *a different* enantiomer to the one made in the US, and it was *optically pure*.

the specific rotation of the mixture solution was *+8* ° (same solvent, temperature, and light wavelength).

The enantiomeric excess of the solution featured above was *33* %.

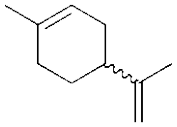
$$\text{enantiomeric excess} = \frac{[S]-[R]}{[S]+[R]} \cdot 100\ \%$$

then the enantiomeric excess would be *50* %.

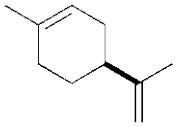
enantiomeric excess values are often abbreviated to *ee*, and they *are* proportional to the optical rotation of the sample measured using a *polarimeter*.

shown that the Jabberwock excretes *R*-bong-tree essence.

oranges (*R*-enantiomer) and lemons (*S*-), and it was given another name: *limonene*.



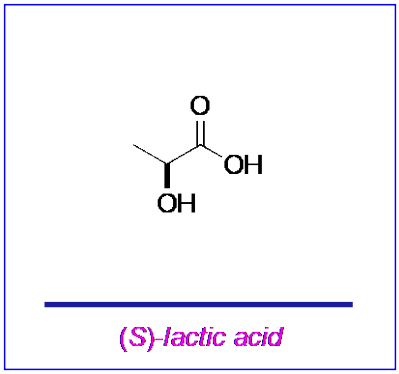
bong-tree essence (stereochemistry not defined)



bong-tree essence (stereochemistry defined)

C. Properties Of Enantiomers

(*R*)- and (*S*)-lactic acid *do* rotate plane-polarized light



(*S*)-lactic acid

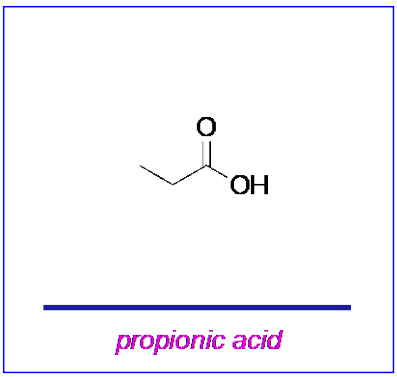
(*S*)-Lactic acid is dextrorotatory, so it rotates plane polarized light *counterclockwise*, *ie* to the *left*, otherwise denoted *(-)*.

(*S*)- and (*R*)-lactic acid have:

- *the same* boiling points
- *the same* melting points
- *the same* infra-red (IR), nuclear magnetic resonance (NMR), ultra-violet spectra (UV)
- *the same* molecular ion in mass spectrometry (MS)
- *the same* chromatographic elution rates featuring solid and liquid phases that are not chiral (*ie* are *achiral*)

These generalities would apply to *all* sets of enantiomers.

1:1 is called *racemic* mixture or a *racemate*.



propionic acid

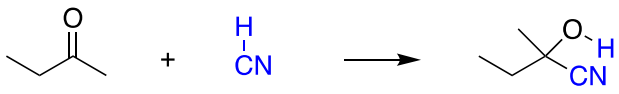
(*R*)-lactic acid by replacement of the *pro-R* this would be a *substitution* reaction.

activation energy barrier to substitute the pro-*S* and -*R* hydrogens would be *the same* and the product would be a *racemate*.

D. Combinations Of Chiral Centers

Diastereomers

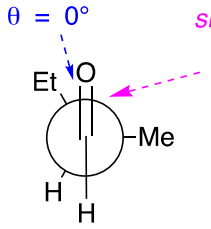
The following is an *addition* reaction.



addition
of hydrogen cyanine to 2-butanone

add to the *Si*- and *Re*- faces or the ketone would be *the same*, and a *racemate* would be produced.

implying, in this case, that a *racemate* would be produced.



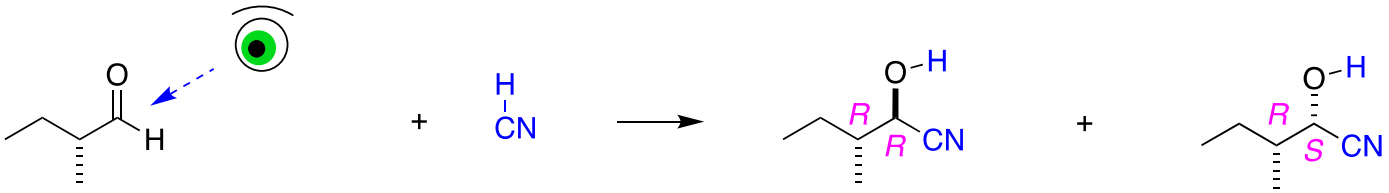
shown slightly offset but direct alignment is assumed

complete this Newman projection

addition of hydrogen cyanide to this aldehyde will be *different* as it

(*R,R*) and (*R,S*) *diastereomers* formed will be *different*.

This reaction therefore will have *diastereoselectivity*.



addition
of hydrogen cyanine to *R*-2-methylbutanal

diastereomers
eg ratio of R,R to R,S 9:1

diastereomeric excess would be: *80* %

$$\text{diastereomeric excess} = \frac{[R,S] - [R,R]}{[R,S] + [R,R]} \cdot 100\ \%$$

products formed would be *enantiomers of* those shown in the reaction above, and they would be produced in *the same* ratio.

diastereomer would be formed as *a racemate* of those shown in the reaction above.
diastereoselectivity would be *the same* as the reactions starting

Diastereoselectivity *is* a particular form of stereoselectivity.
It *is not* possible to measure the diastereoselectivity of a reaction starting with a racemic substrate.

In general, diastereomers have:

- *different* boiling points
- *different* melting points
- *different* infra-red (IR), nuclear magnetic resonance (NMR), ultra-violet spectra (UV)
- *the same* molecular ion in mass spectrometry (MS)
- *different* chromatographic elution rates featuring solid and liquid phases that are not chiral (*ie* are *achiral*)

it *is* possible to measure the diastereoselectivity

can have a *S,S-* configuration.

its enantiomer is always *S,S-*.

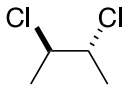
Optical rotations and enantiomeric excess *are* directly correlated

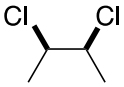
Optical rotations and diastereomeric excess *are not* directly correlated

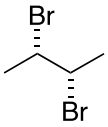
Meso Compounds

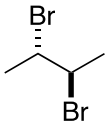
This stereoisomer of 2,3-butandiol (left) has *R* configuration at C^2 and *S* at C^3.
C^2-chiral center will *cancel* that at C^3 hence the molecule *is not* optically active.

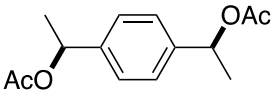
All *meso*-isomers have *a plane of symmetry* and they *do not* rotate plane polarized light.

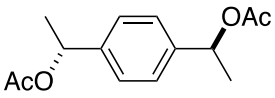


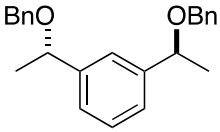


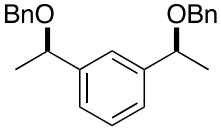


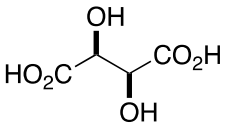




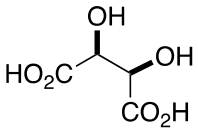


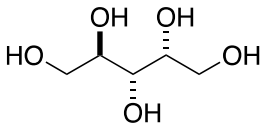


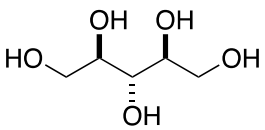


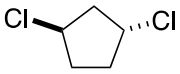


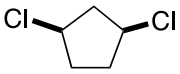
tartaric acid

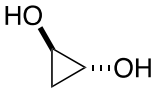


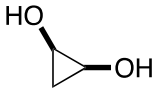


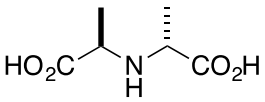


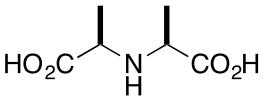


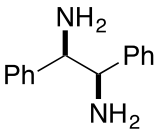


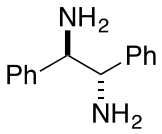


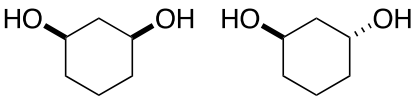


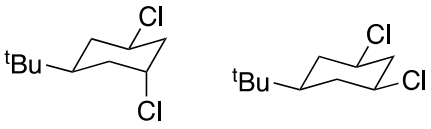

HO2C
N
H
CO2H

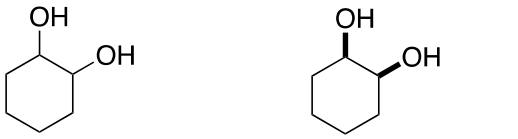

HO2C
N
H
CO2H

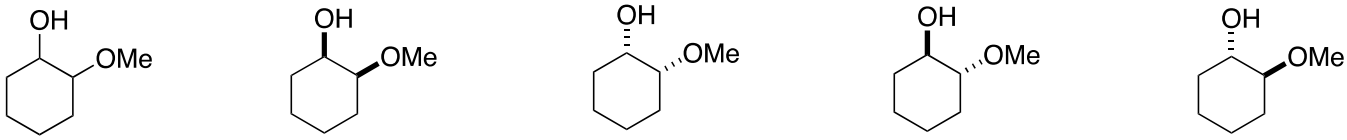

NH2
Ph
Ph
NH2


NH2
Ph
Ph
NH2

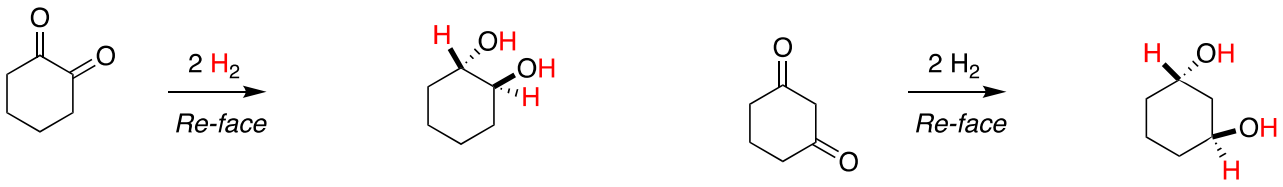

HO
OH
HO
OH


Cl
tBu
Cl
Cl
tBu
Cl
tBu
Cl
Cl


OH
OH
OH
OH
OH
OH
OH
OH


OH
OMe
OH
OMe
OH
OMe
OH
OMe
OH
OMe

In general, a compound has *n* chiral centers will have $2^n/2$ diastereomers, and $2^n/2$ enantiomers of these: *true*.



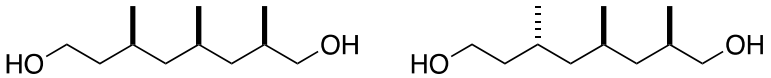
The diol products formed in the reactions above will be *optically active* stereoisomers.

Epimers

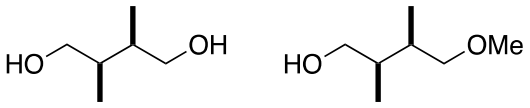
Epimers *are / are not* a sub-set of diastereomers that are configurationally different at one chiral centers. Classify the following (choose all options that are correct):

neither

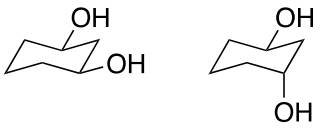
epimers



diastereomers / epimers



neither



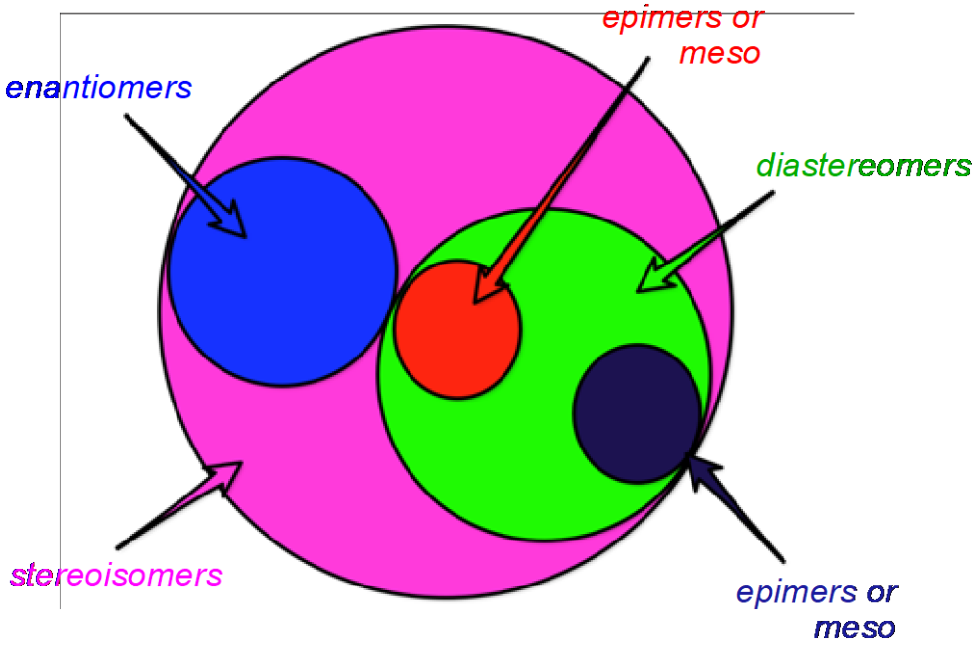
diastereomers

neither

enantiomers

diastereomers

Graphical Summary



E. Enantioselectivity In Kinetic Control

there could be some enantioselectivity in this reaction *until it reaches equilibrium*.

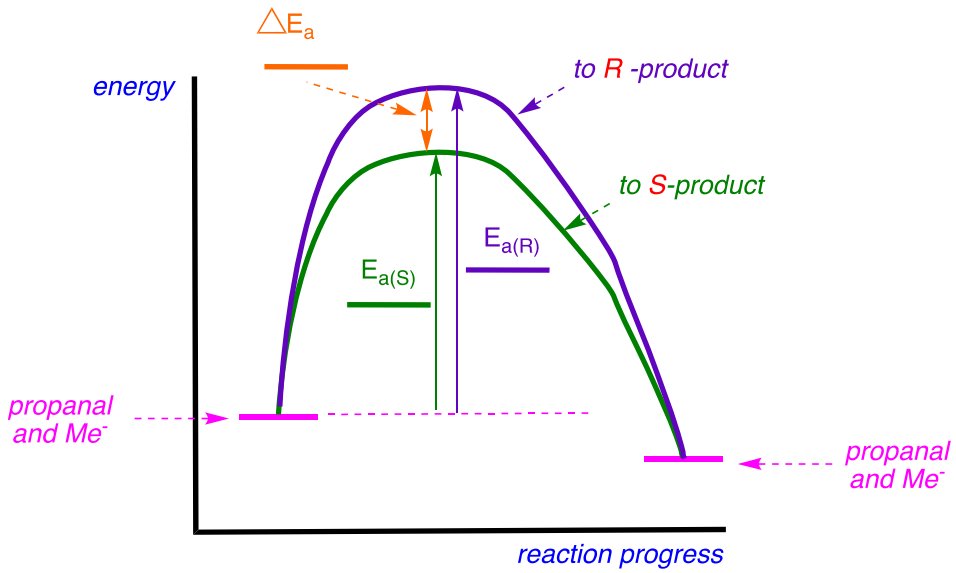
$$K_S = \frac{[S]}{[\text{propanal}][\text{HCN}]} \qquad K_R = \frac{[R]}{[\text{propanal}][\text{HCN}]}$$

$$\frac{K_S}{K_R} = \frac{[S]}{[R]} = 1$$

expressed as concentrations of products only — *numerical*

so suitable words to describe this are *thermodynamic* control.

Thermodynamically controlled reactions at equilibrium *can* be enantioselective.



transformation above, so it is *kinetically* controlled.
activation energy barrier E_a by the *Arrhenius* equation, where:

$$k = Ae^{-Ea/RT}$$

A = *pre-exponential factor* (*name*) *s -1* (*units*) E_a = *activation energy* (*name*) *J mol -1* (*units*)

R = *universal gas constant* (*name*) *8.314 J mol -1 K -1* (*numerical value (units)*) T = *temperature* (*name*) *Kelvin* (*units*)

$\ln(k_R/k_S) = -\Delta\Delta G/RT + \ln(A_r/A_S)$

but $\ln(A_r/A_S) = \ln 1 = 0$

For ee of 80 %, ratio of enantiomers is 9:1 thus $k_R/k_S = 9$.

Solve then for $-\Delta\Delta G = RT \bullet \ln 9 = 0.008314 \bullet 298 \bullet 2.197 = 5.44$