Curly Arrows And Electron Flow

A. Introduction

B. Electron Flow

double-headed arrow.

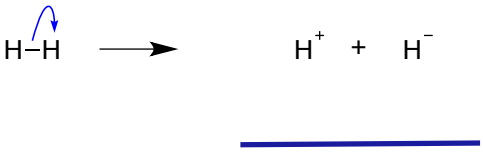
are,

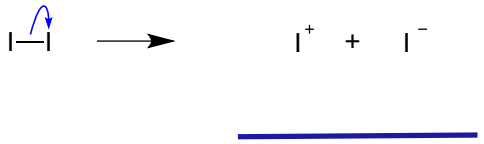
high electron density.

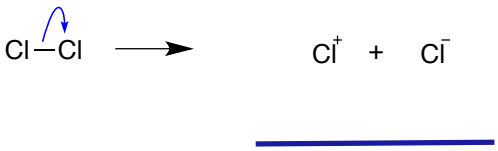
never

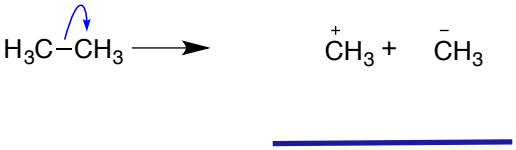
Effecting Only One Bond

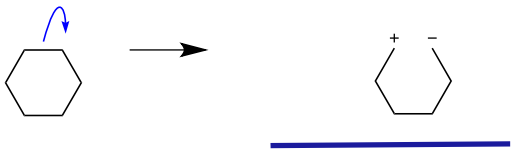
heterolytic











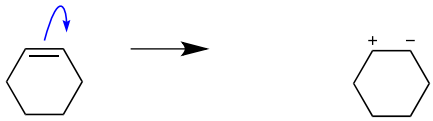
need not be

possible

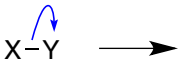
does not

must equal the number of anions.

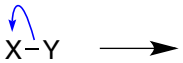
2 *e*; this *sometimes*



a

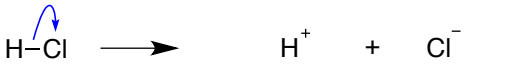


b



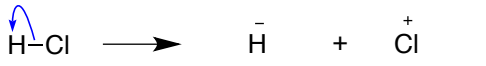
is *less*
towards Y.

pathway 1



more favorable

pathway 2



less favorable

more favorable

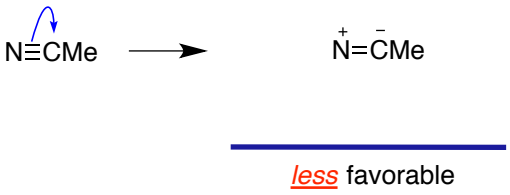
less favorable

more favorable

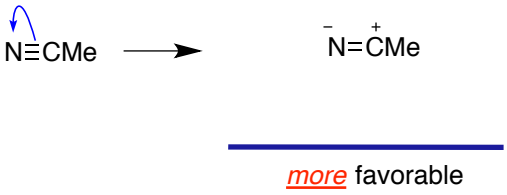
less favorable

less favorable

more favorable



less favorable



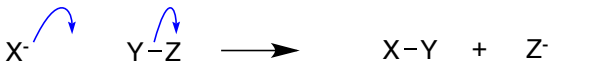
more favorable

more favorable

less favorable

Effecting Two Bonds

a



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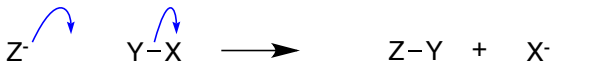
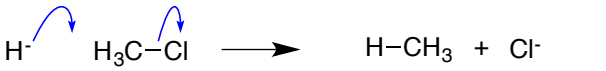


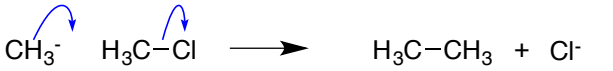
disfavored

pathway 1

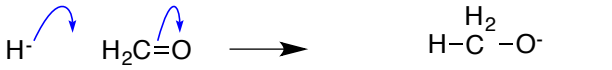
more favorable



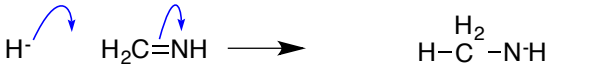
more favorable



more favorable

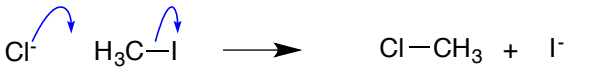


more favorable



more favorable

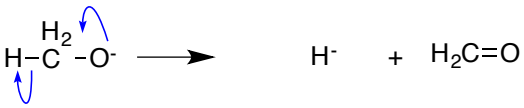
pathway 2



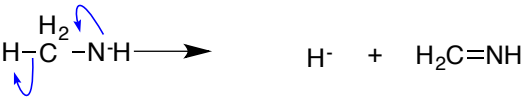
less favorable

less favorable

less favorable



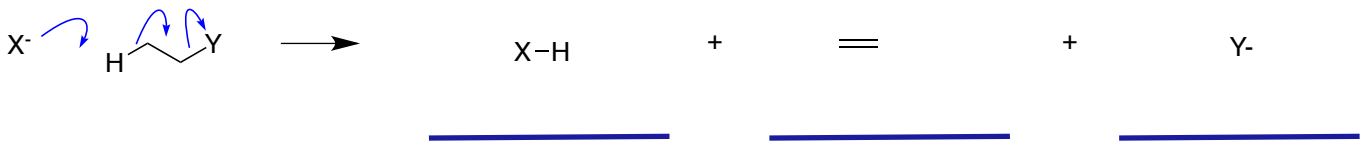
less favorable



less favorable

Effecting Four Bonds

a



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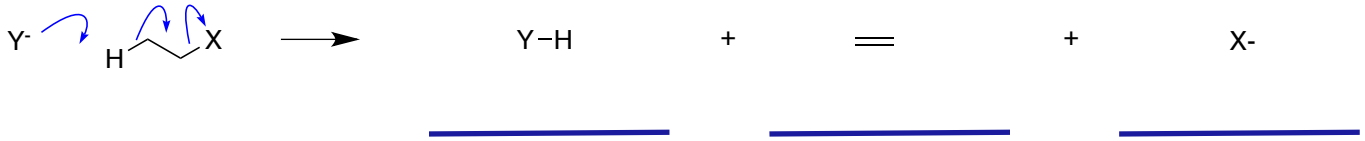
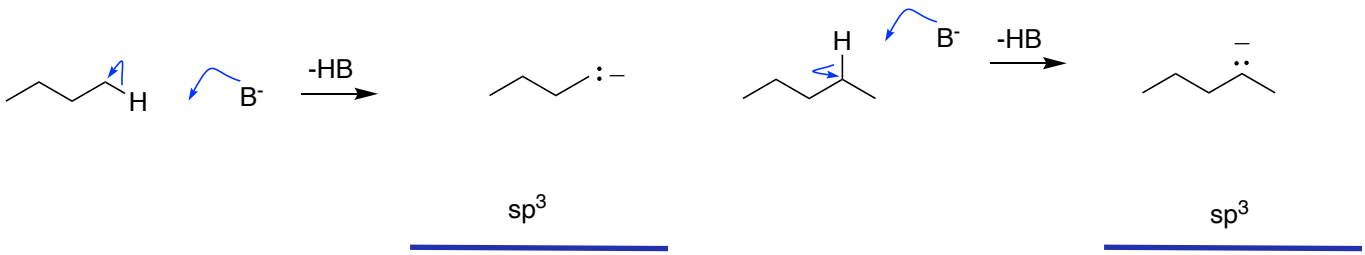
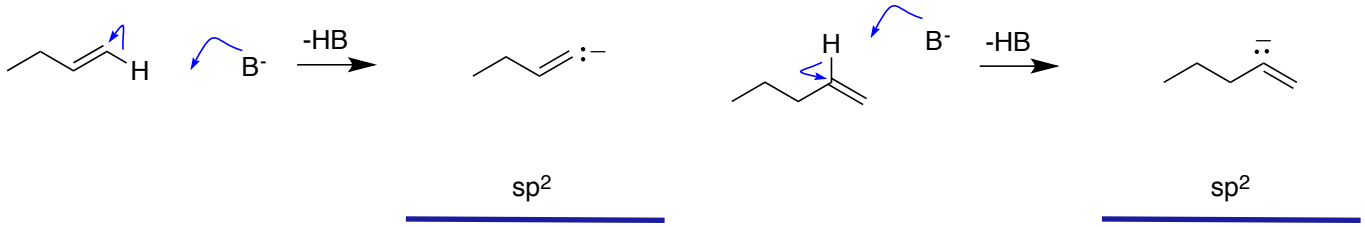


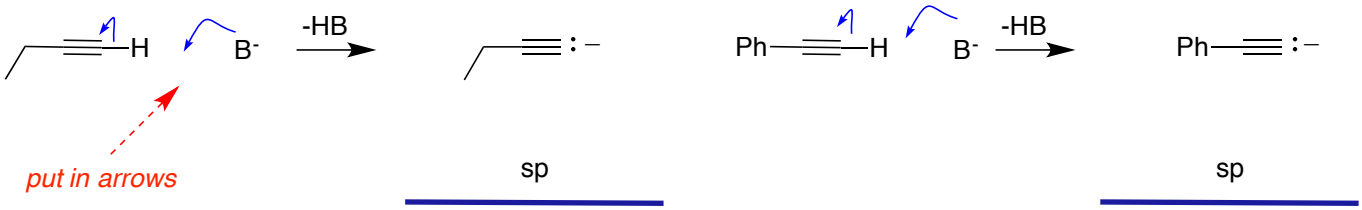
favored if X is more basic than Y

C. Representations Of Charged Hydrocarbon Scaffolds

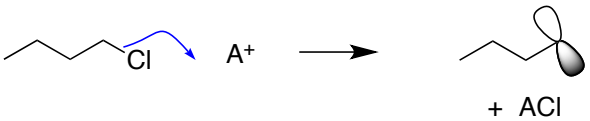
sp^3 hybridized carbon the resulting anion is *sp^3* hybridized.
electrons move *towards C* and the resulting anion is *sp^2* hybridized.
sp -Hybridized carbanions



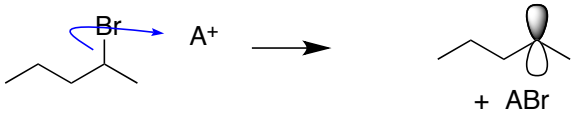




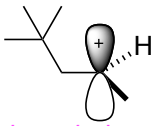
A sp^3-hybridized carbon has __4___
tend to be *sp^2* hybridized.



sp^2

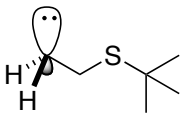


sp^2

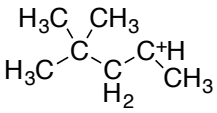


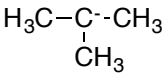
trigonal planar

pyramidal

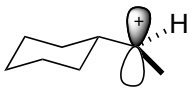


pyramidal

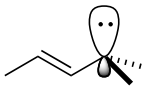




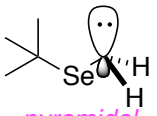
$C^-H_2CH_2SC(Me)_2CH_3$



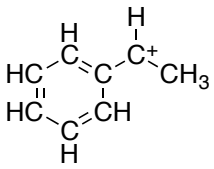
trigonal planar

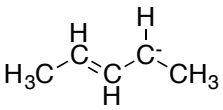


pyramidal



pyramidal



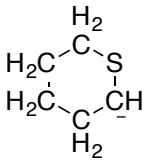


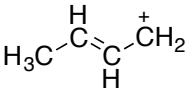
$^tBuSeCH_2^-$

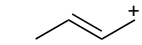
sp^2 hybridized, and carbanions C^-R_3 are *sp^3*-hybridized. Explain why this is so by considering the number of electrons around carbon in C^+H_3 and in C^-H_3.

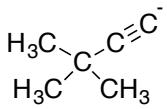
Carbon in C^+R_3 has to accommodate *three atoms* containing *six* shared electrons around it.

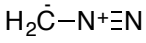
Carbon in C^-H_3 has to accommodate *three atoms and one lone pair* containing *eight* shared electrons around it.

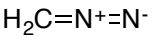


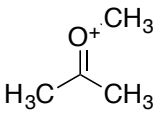




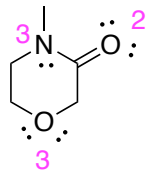


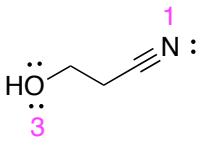


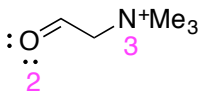


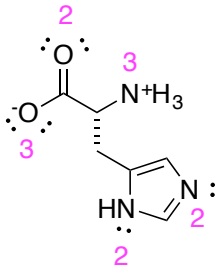


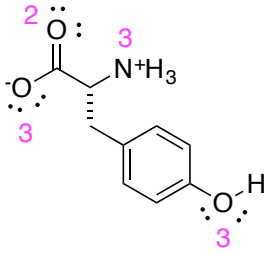
D. Heteroatoms, Lone Pairs, And Moving Electrons







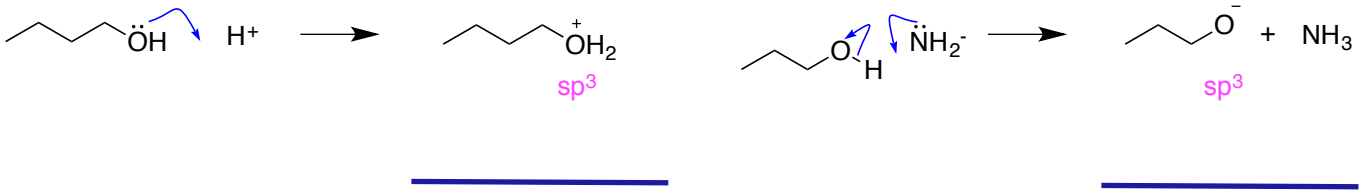


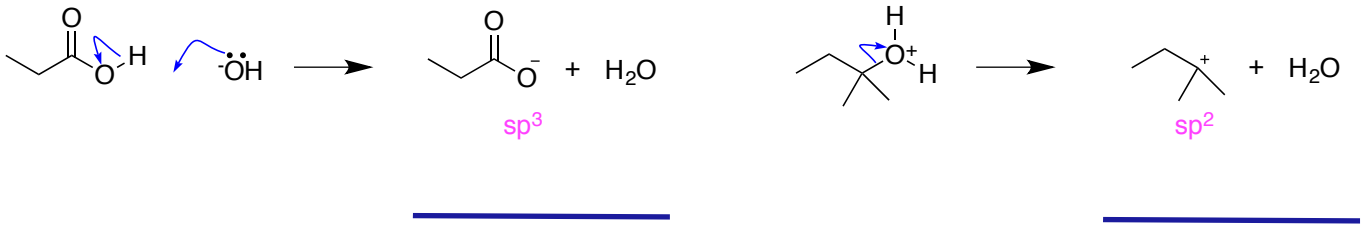


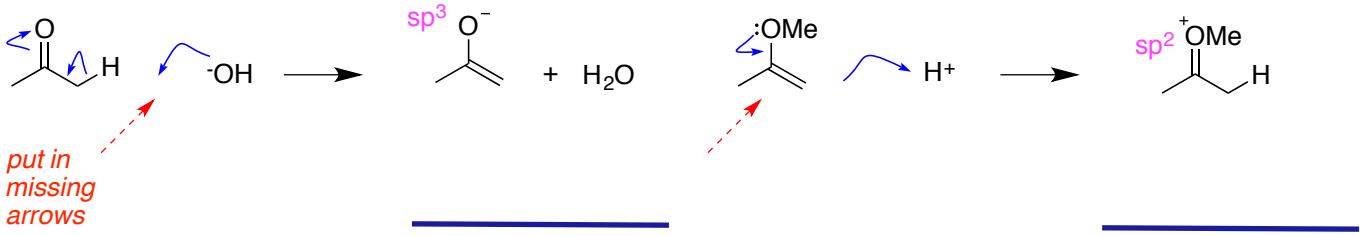
Surprise! In the answer on bottom left, *both* nitrogens are sp^2 for reasons related to aromaticity which is covered later in the book.

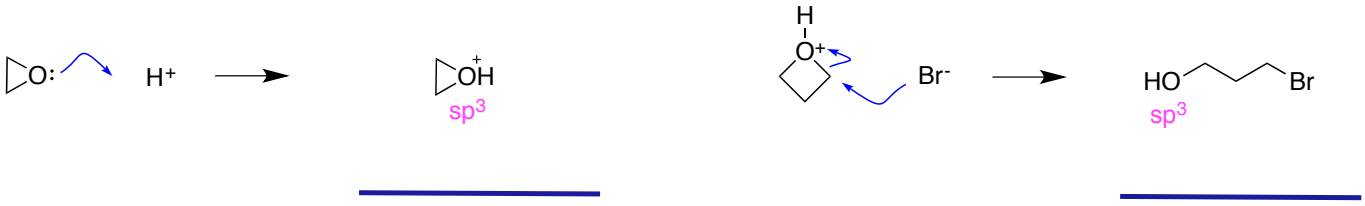
is not a change in the
gives sp^3 hybridized protonated

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

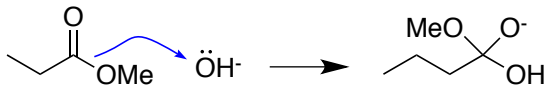


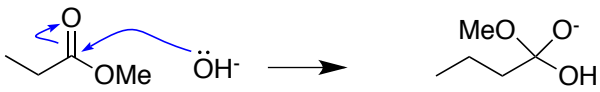


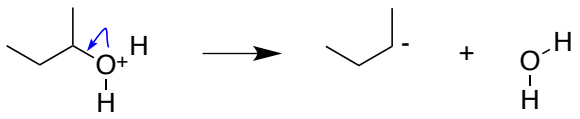


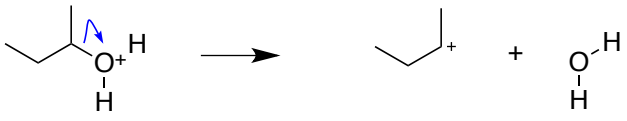


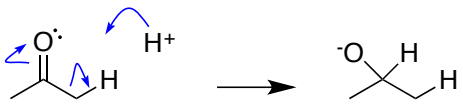
usually

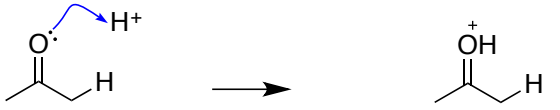

O
OMe
ÖH-
MeO
O-
OH


O
OMe
ÖH-
MeO
O-
OH

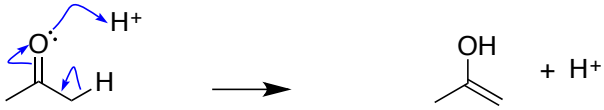

H
O+
H
-
+
O
H

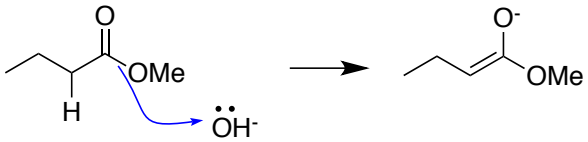

H
O+
H
+
+
O
H

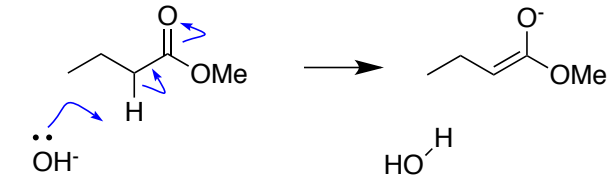

O
H+
H
-O
H
H

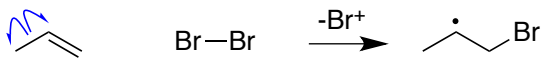

O
H+
H
+
OH
H

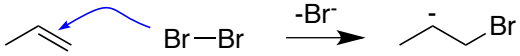
OR

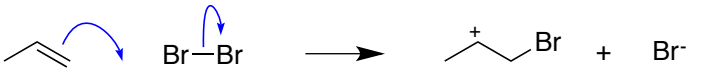

O
H+
H
OH
+ H+


O
OMe
H
ÖH-
O-
OMe

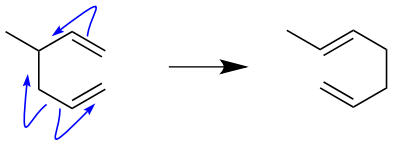

O
OMe
H
ÖH-
O-
OMe
H
HO



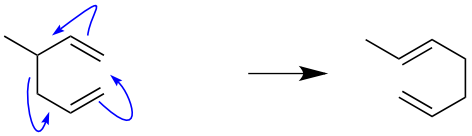




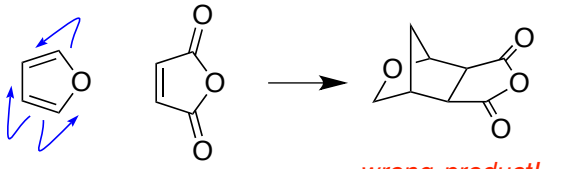
put in missing arrows



should be

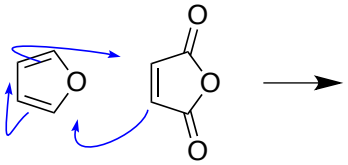


show all arrows



wrong product!

should be



show all arrows