Curly Arrows And Electron Flow

A. Introduction

B. Electron Flow

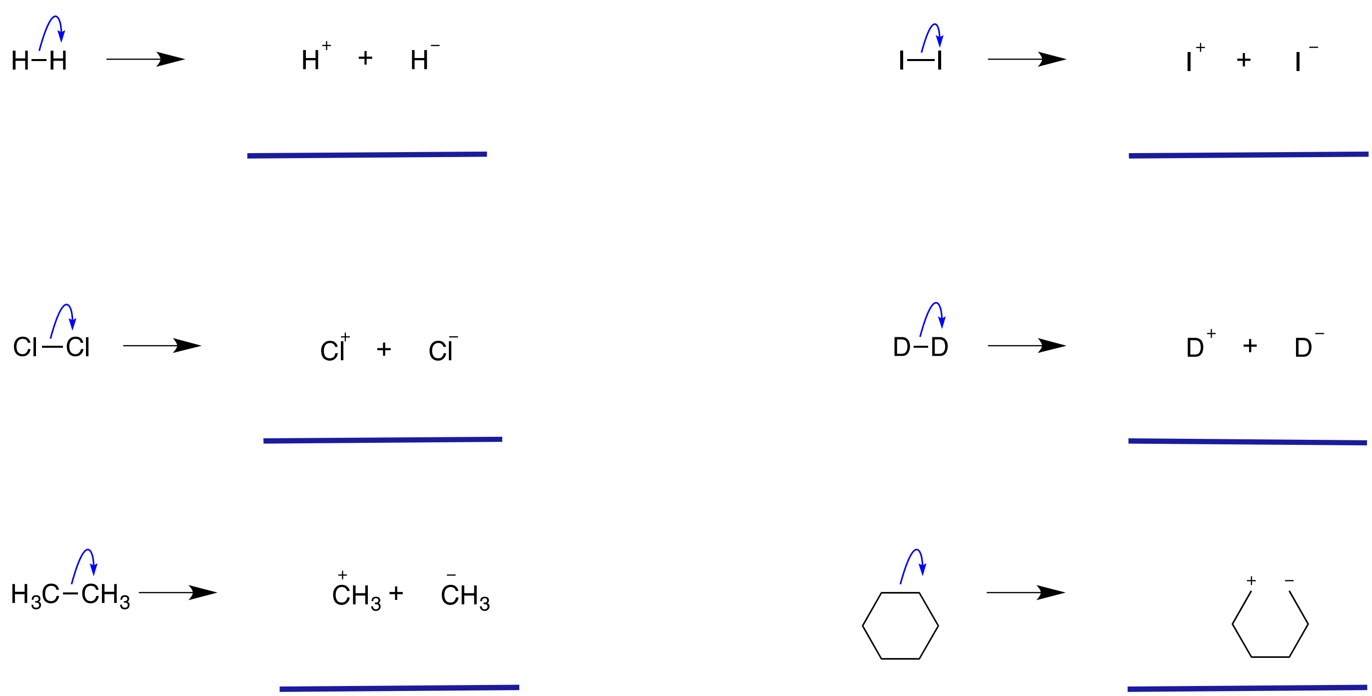
of electrons is illustrated using a *full* arrow.

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

energetically *uphill*

Affecting Only One Bond

the following *heterolytic* bond fission reactions

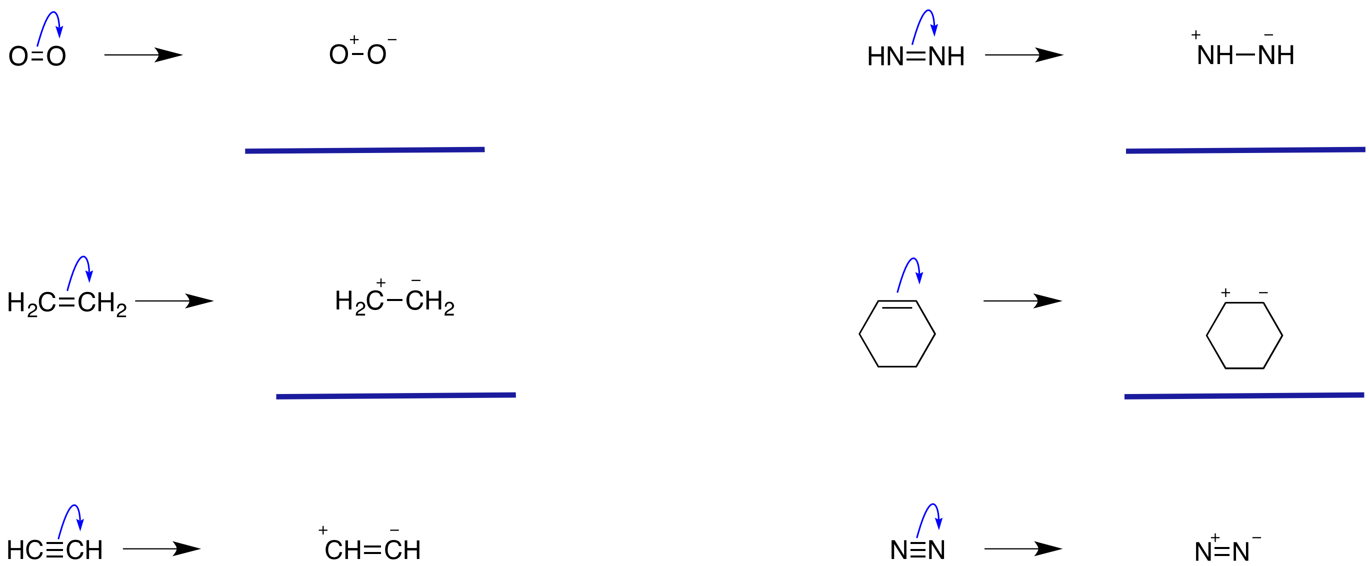


precise English *need not be* absolutely true; it is *possible* to tell lies

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.

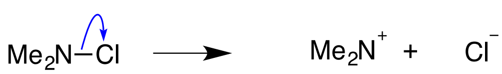
pathway 1 | *pathway 2*

more favorable

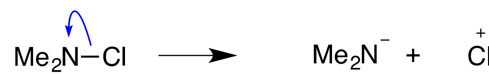
less favorable

more favorable

less favorable

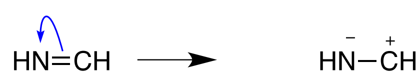


more favorable

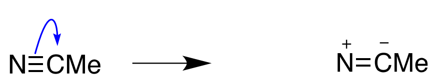


less favorable

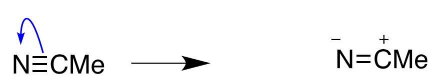
less favorable



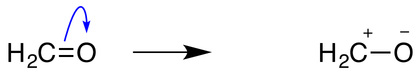
more favorable



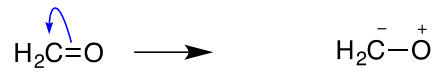
less favorable



more favorable



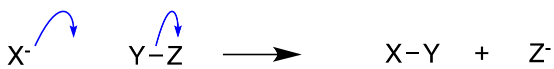
more favorable



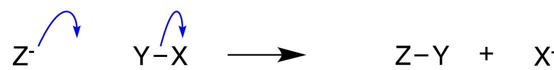
less favorable

Affecting Two Bonds

a



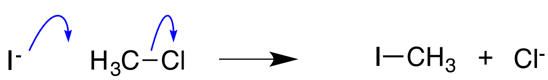
b



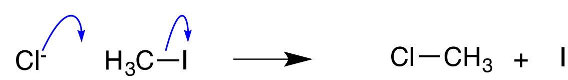
Pathway **a** tends to be *disfavored* if X is more electronegative than Z.

pathway 1

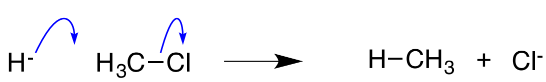
pathway 2



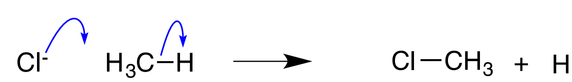
more favorable



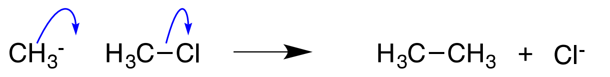
less favorable



more favorable



less favorable



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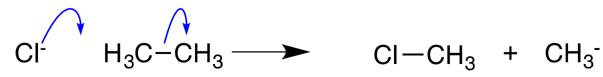
more favorable



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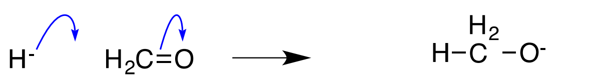
less favorable



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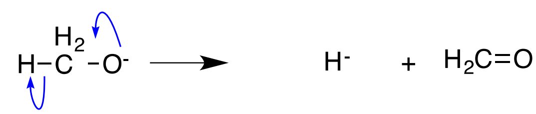
more favorable



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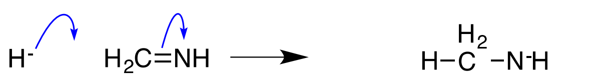
less favorable



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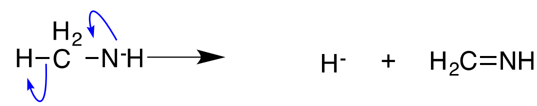
more favorable



______

less favorable

Affecting Four Bonds

a

______ ______ ______

b

______ ______ ______

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

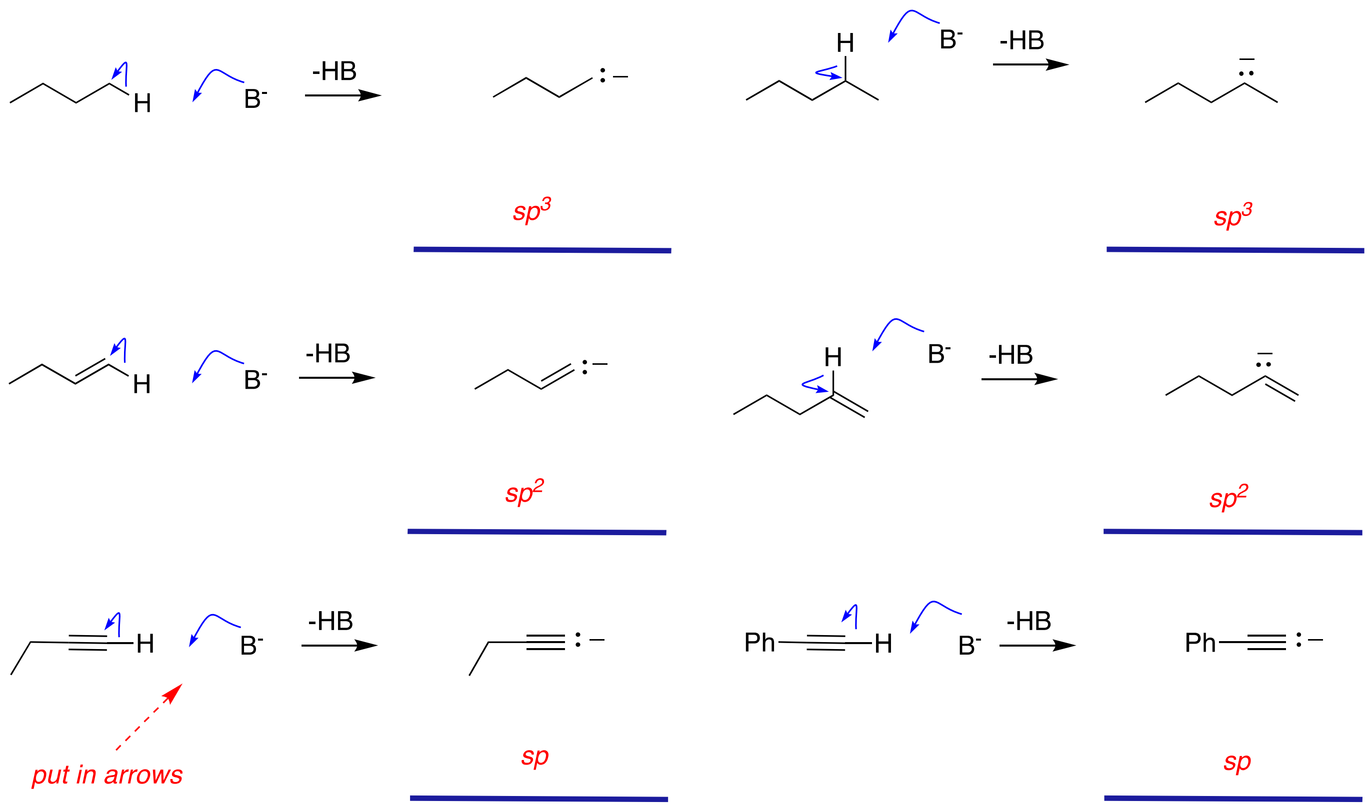
Representations Of Charged Hydrocarbon Scaffolds

the way they pronounce "*unionized*".

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

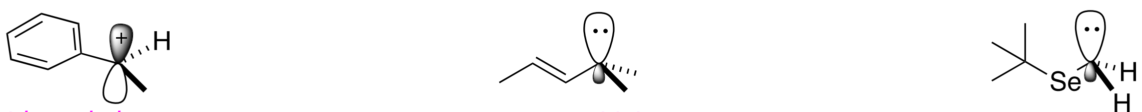
electrons move *towards C* and the resulting anion is *sp*^{2}-hybridized.

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

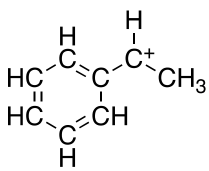


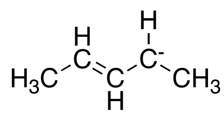
A *sp³*-hybridized carbon has __4__ groups around it.
carbocations formed from *sp³*-hybridized atoms tend to be *sp²*-hybridized.

sp²   *sp²*



trigonal planar   *pyramidal*   *pyramidal*



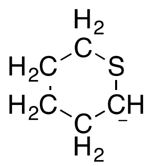


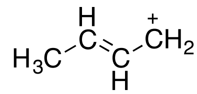
$^tBuSeCH_2^-$

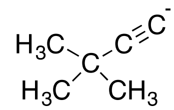
Carbocations of the type C^+R_3 tend to be *sp²*-hybridized, and carbanions C^-R_3 are *sp³*-hybridized.

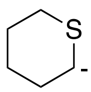
Explain why this is so by considering the number of electrons around carbon in C^+H_3 and in C^-H_3.

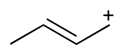
Carbon in C^+R_3 has to accommodate *three atoms* containing *six* shared electrons around it. Carbon in C^-H_3 has to accommodate *three atoms and one lone pair* containing *eight* shared electrons around it.

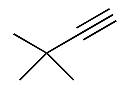






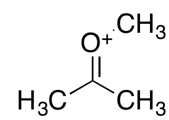


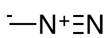


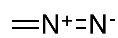


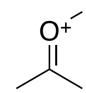
$H_2\bar{C}-N^+\equiv N$

$H_2C=N^+=N^-$

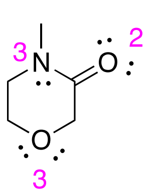


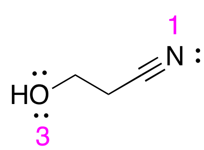


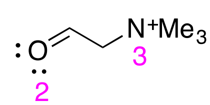


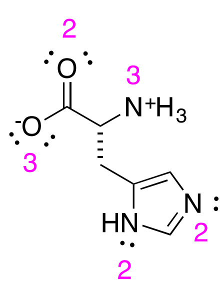


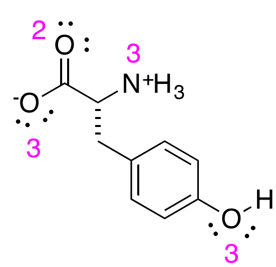
C. Heteroatoms, Lone Pairs, And Moving Electrons









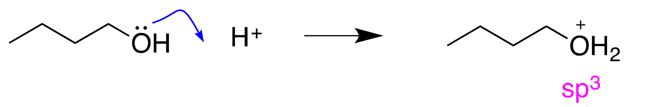


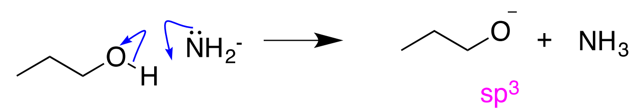
These answers are for the form shown in the diagram (of course resonance makes the O atoms equivalent)

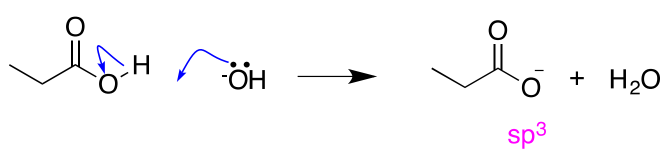
There *is not* a change in the number of groups
sp^3-hybridized heteroatoms gives *sp*^{3}-hybridized protonated

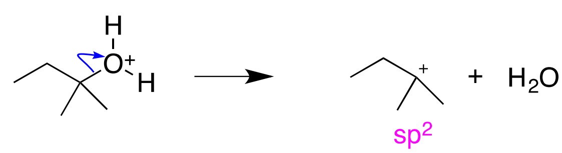
sp^2-hybridized heteroatoms become *sp*^{2}-hybridized protonated heteroatoms, and *sp*-hybridized heteroatoms become *sp*-hybridized protonated heteroatoms.

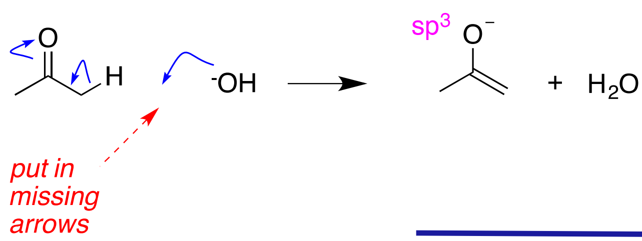
Conversely, there can be a change in hybridization state when electrons shift to atoms without protonation (*eg* between the oxygens of carbonyl groups).

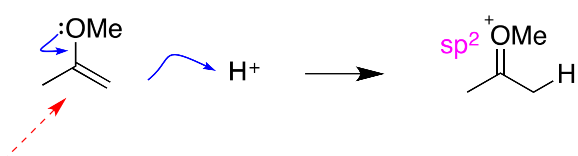


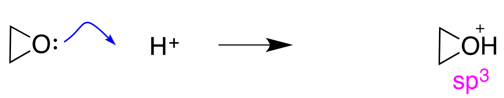


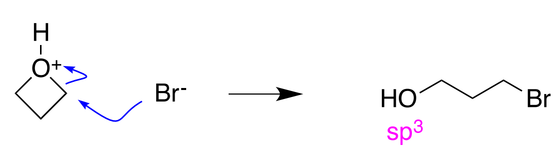




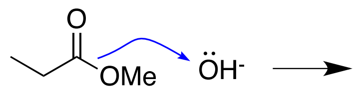


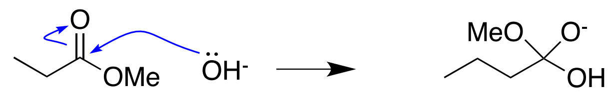


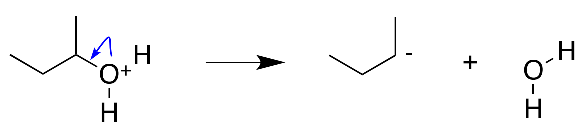


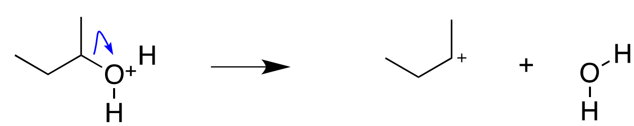


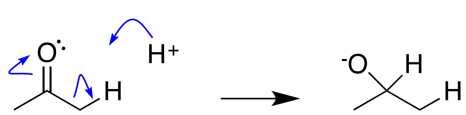
it is *usually* advisable to put the pen on the electron density and push

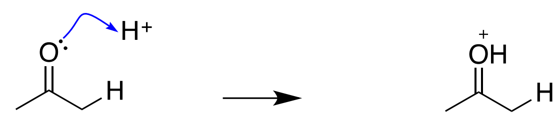












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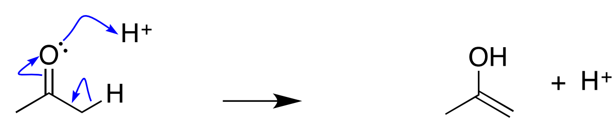
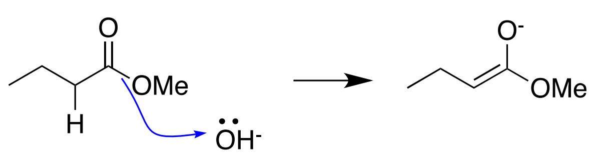
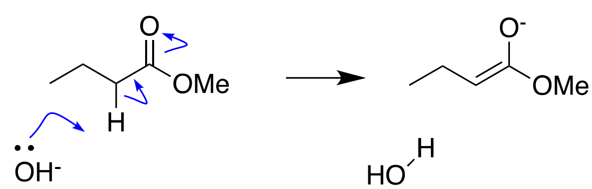
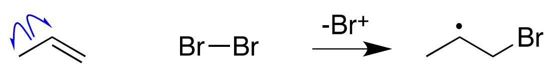
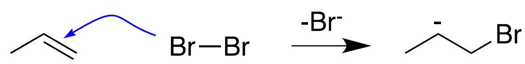
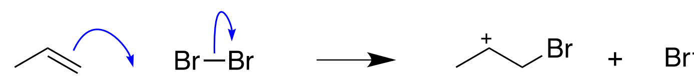




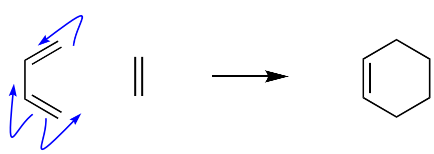




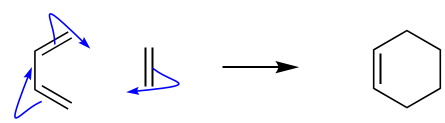


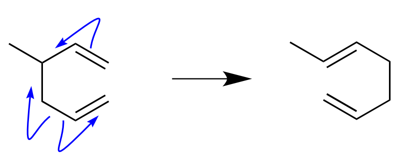


put in missing arrows



should be





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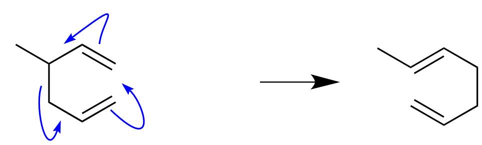
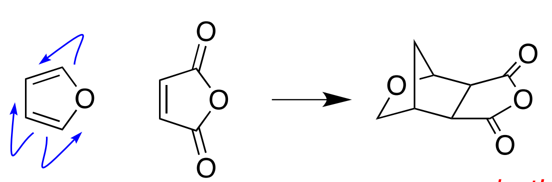
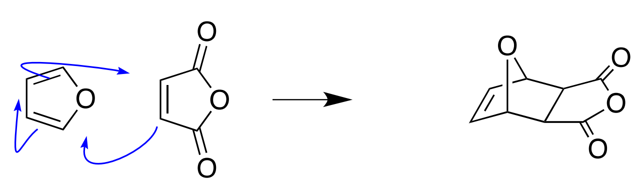


show all arrows



wrong product!

should be



show all arrows