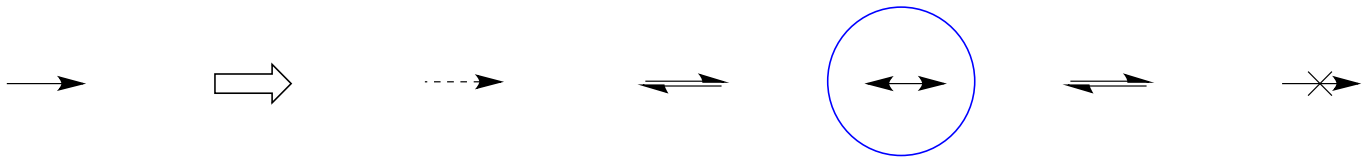
Resonance: Practicing Curly Arrows

A. Introduction

B. Resonance

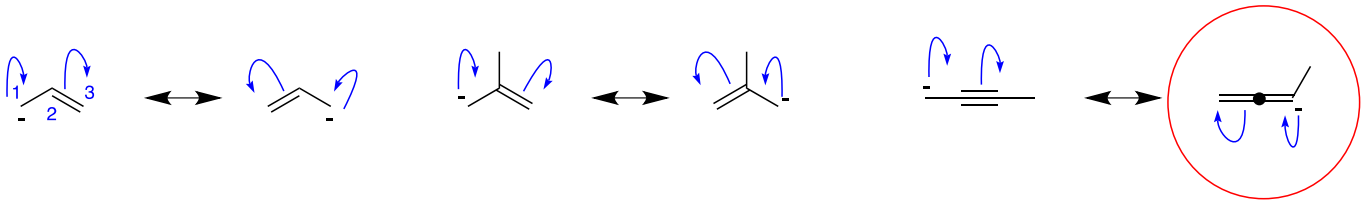
Electrons move *much faster than* atoms in a molecule



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

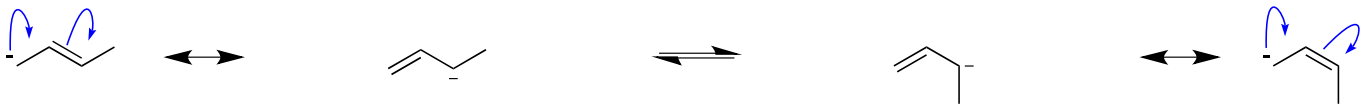
to depict movement of *electrons*.

C. Resonance Stabilized Anions



allene

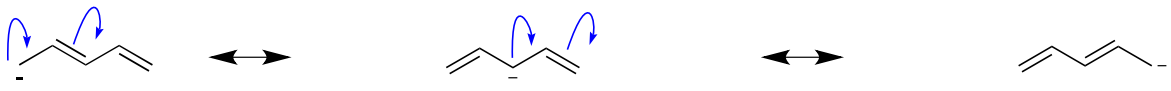
Electron flow *does not* allow the negative charge
The same *is* true for the methyl allyl

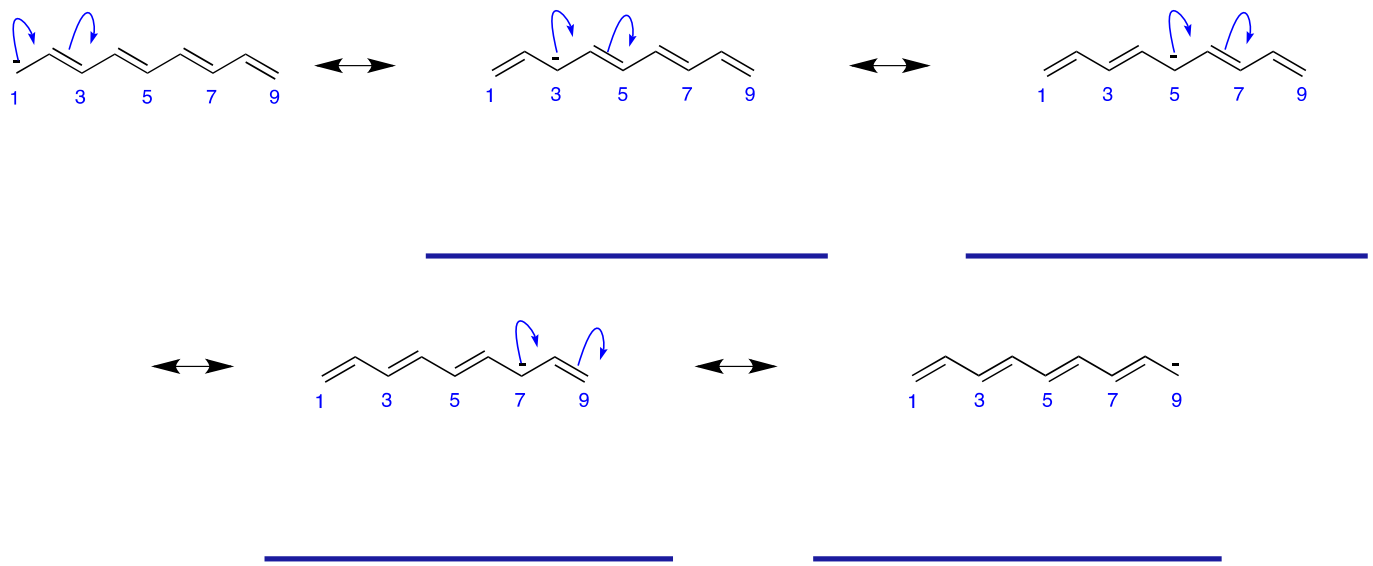


E- *Z-*

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

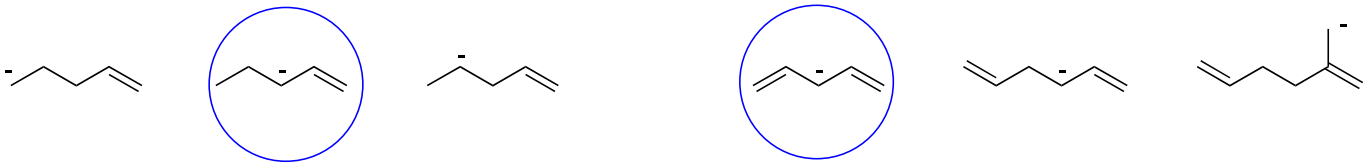
It is *possible* for a molecule to have more than one resonance structure.





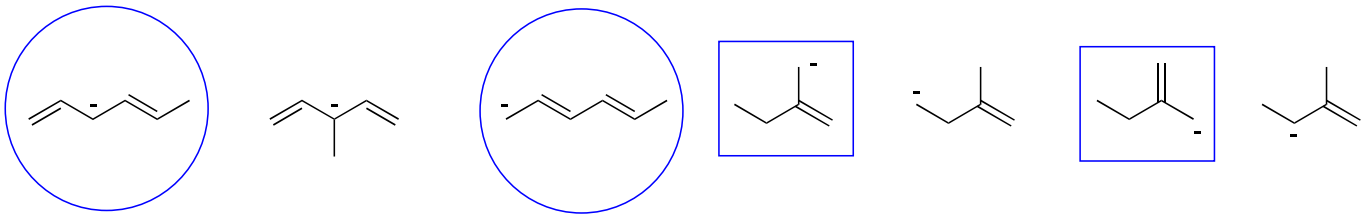
It *is* possible for the negative charge on the nonatetraenyl anion to reside on the 1,3,5,7,9-carbon atoms.
The negative charge in that anion *never* can be found on C^2, C^4, C^6
it *does* appear that the negative charge hops

drawn is likely to be *more* stable



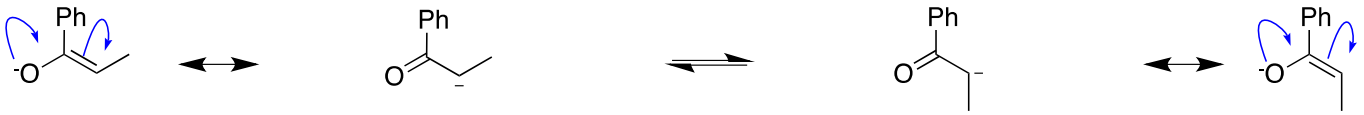
Anions that have several resonance structures are said to be *delocalized / resonance stabilized* relative to ones that do not

The allyl anion *less* stable than the pentadienyl anion



It *is* possible for the negative charge to hop

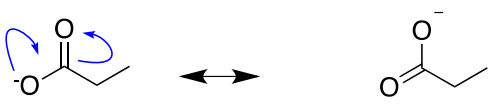
E-enolate *Z-enolate*

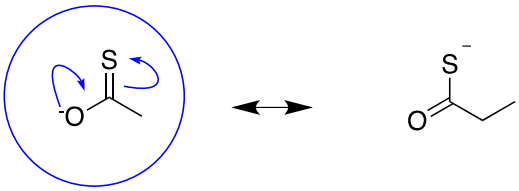


E-enolate *Z-enolate*

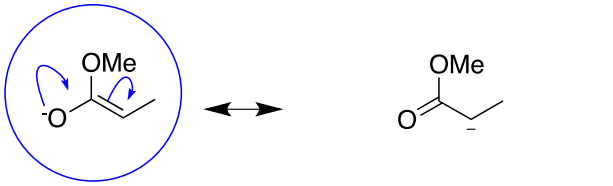
Z-enolate *E-enolate*

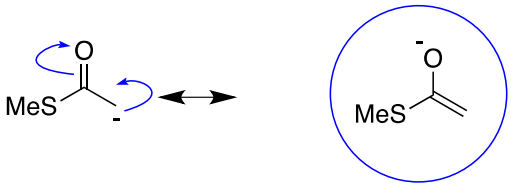
has the charge on the most *electronegative* atom.

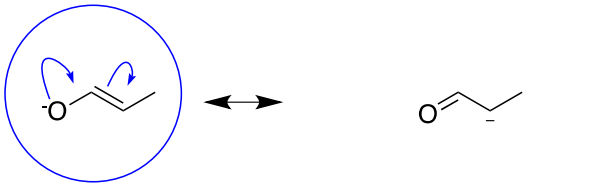


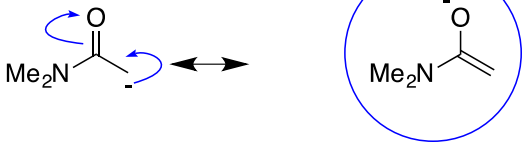


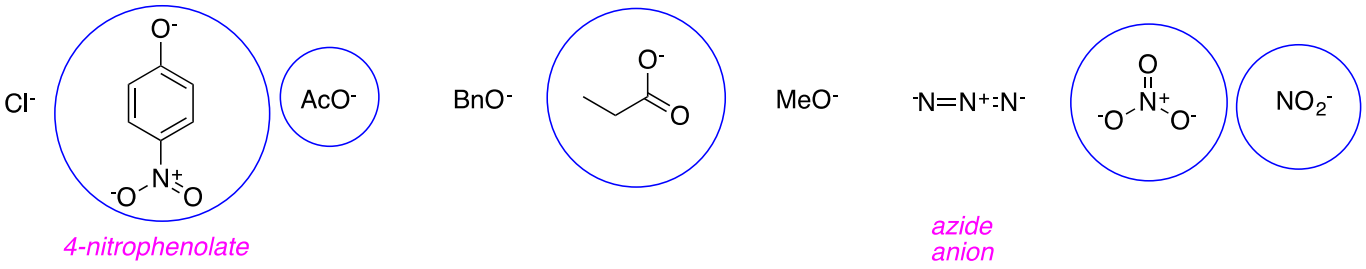
(^Equal Stability^)

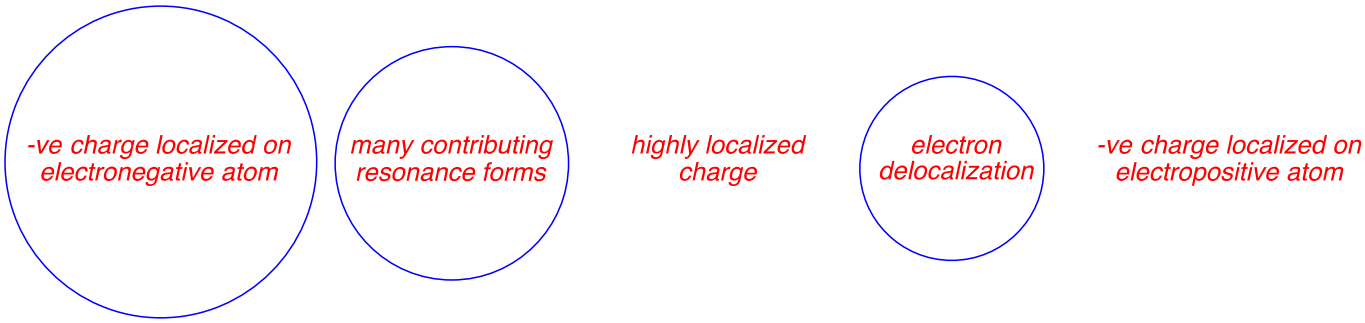










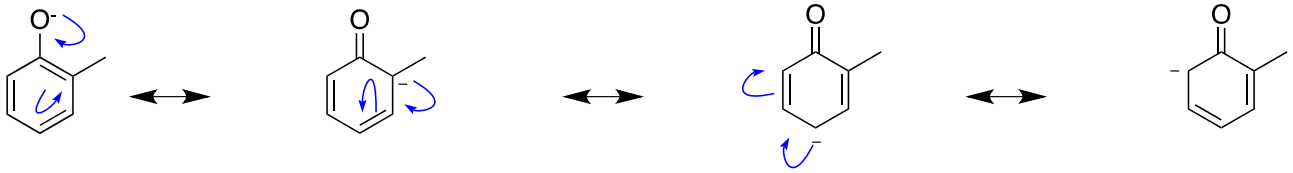


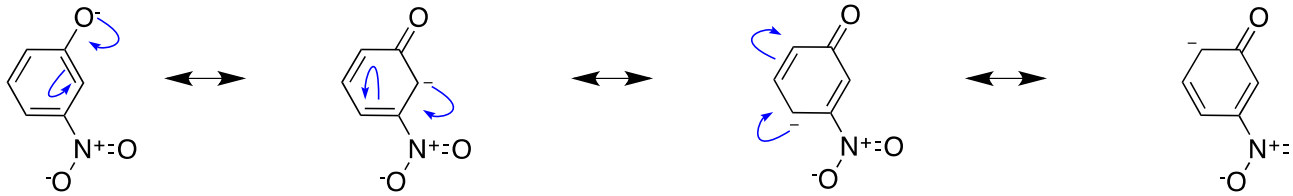
How Resonance Stabilization Of Anions Influences Acidity

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

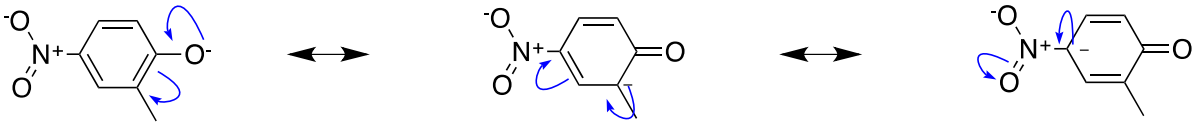
Higher concentrations of protons correspond to *low* pK_a and *low* pH values for the acid HA.

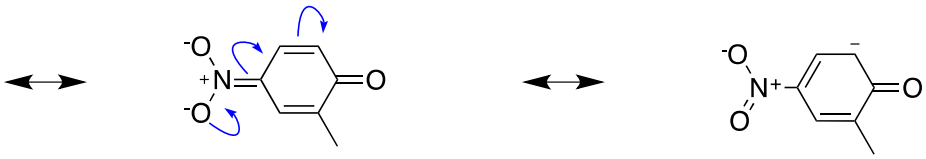
3 1 3 1





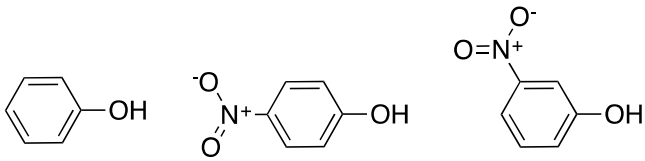
it *is not* possible for both the *O*-atoms



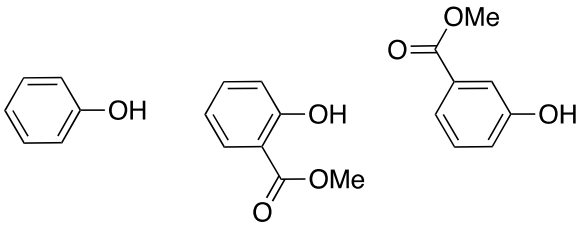


it *is* possible for both the *O*-atoms

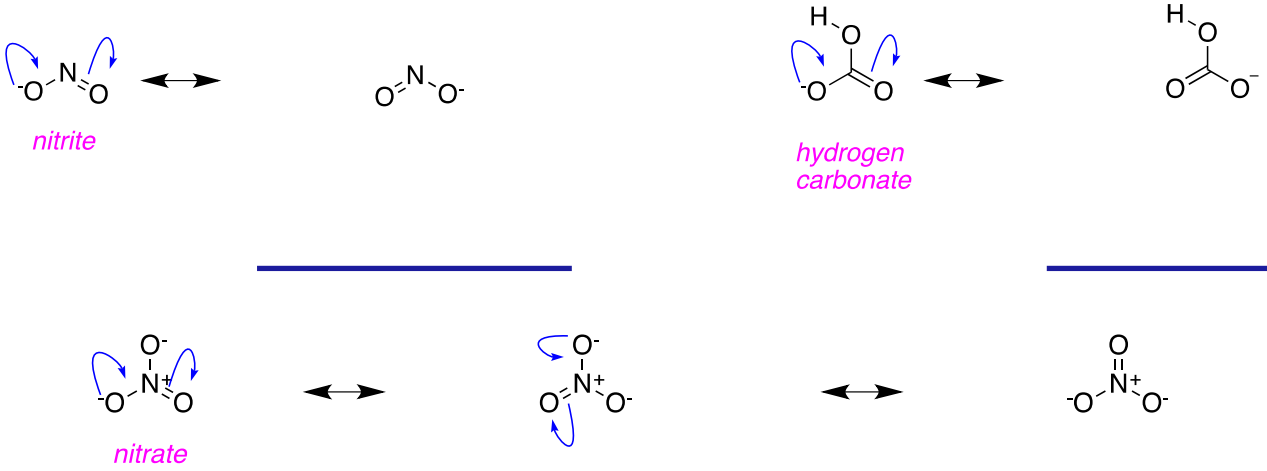
it *is* possible for both the *O*-atoms of the nitro group tend to be *more* stable than their 3-isomers.



3 1



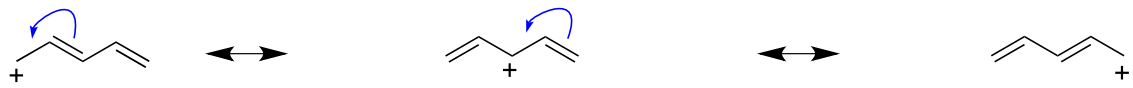
3 1

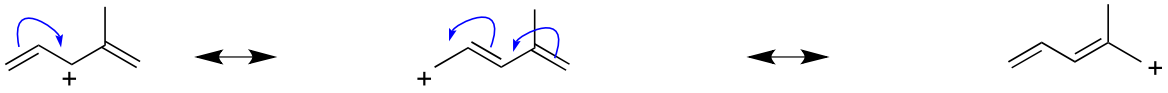


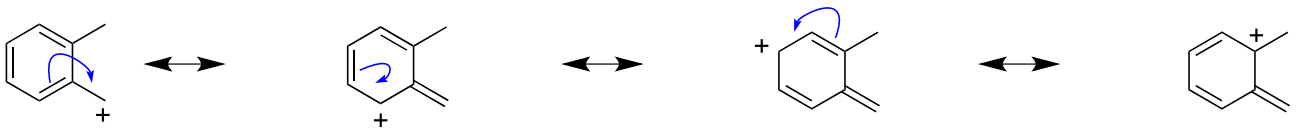
nitric acid should be a *stronger* acid than nitrous and carbonic acid.
strongest acid in the series is HNO_3.

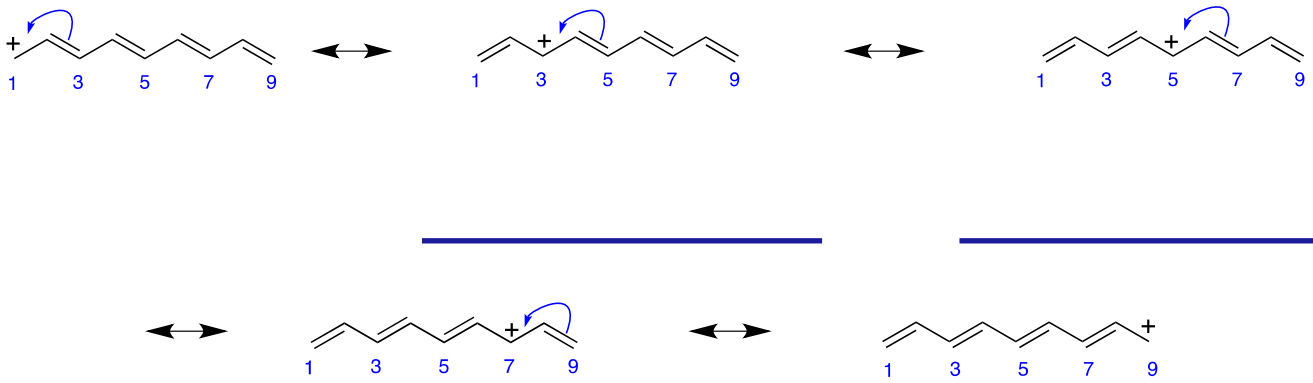
D. Resonance Stabilized Cations

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



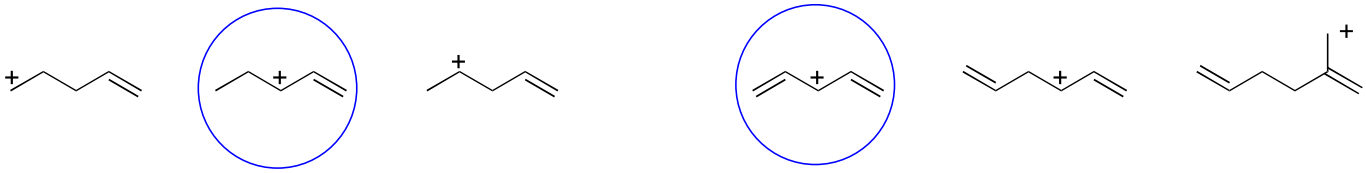






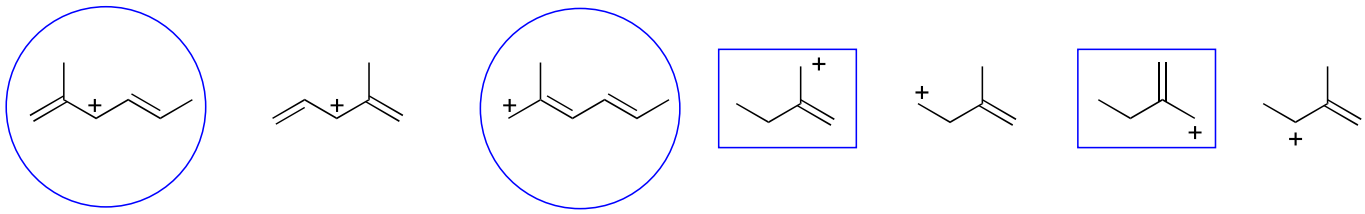
nonatetraenyl cation *can* reside on the 1,3,5,7,9-carbon atoms and it is *never* found on C^2, C^4, C^6, and C^8; consequently, it *does* appear to hop

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



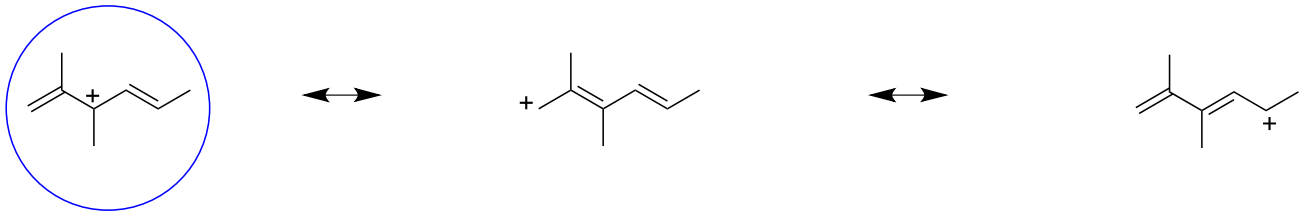
It *is* possible for the positive charge to hop between atoms

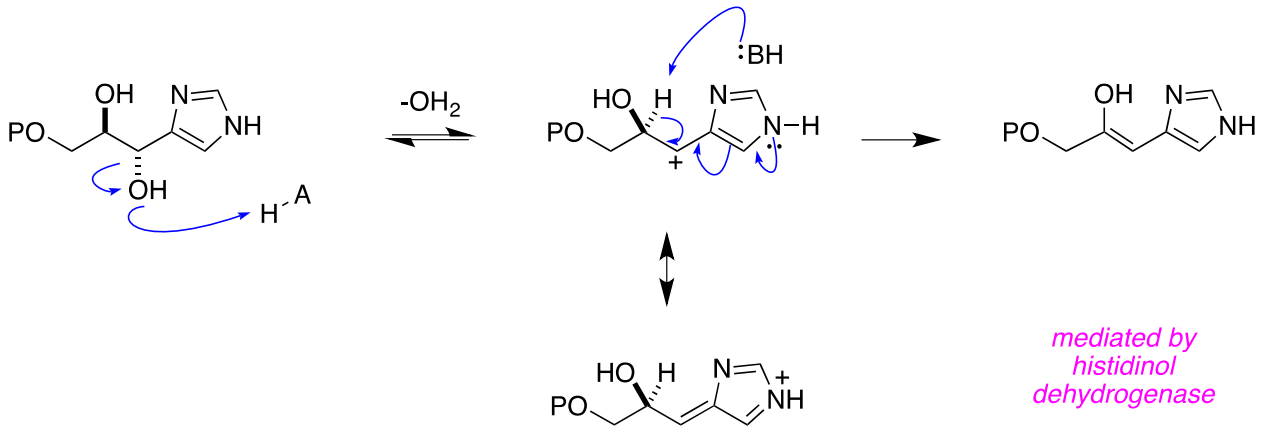
the charge on the most *electropositive* atom.

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.

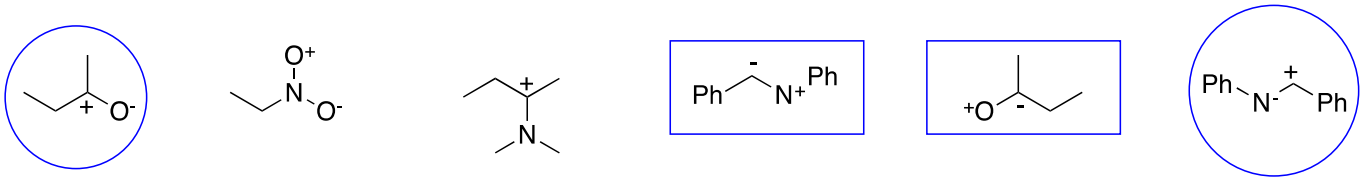




mediated by histidinol dehydrogenase

E. Resonance In Neutral Molecules

tend to be significantly *less* stable



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

diazomethane

ozone

methyl azide

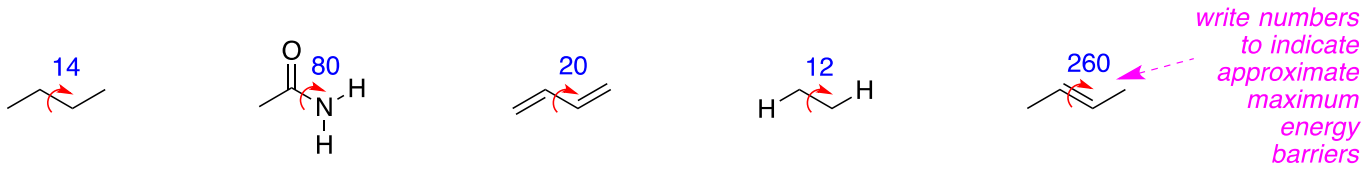
nitrous oxide

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}