Chapter 6. Reactions of Alkynes

- Alkynes: hydrocarbons that contain a carbon-carbon triple bond with the general formula C_nH_{2n-2}..
- Alkynes are usually very reactive.

6.1 The Nomenclature of Alkynes

- Replace the ending “ane” of alkane with “yne”.
- Choose the longest continuous chain containing the triple bond as a parent chain.
- Number in a direction that gives the alkyne functional groups the lowest possible number.
- If the compound contains more than one substituent, the substituents are listed in alphabetical order.

6.2 How to Name a Compound That Has More than One Functional Group

- Double bond is a functional group.
- If there are two double bonds in a molecule, it ends with “diene”.
- U\Number the chain in the direction that gives the lowest possible numbers to the carbons participating in the double bonds.
- When the functional groups are a double bond and a triple bond, the chain is numbered in the direction that produces the name containing the lowest possible number, regardless of which functional group gets the lowest number.
- If there is a tie between a double bond and a triple bond, the double bond gets the lowest number.
- A chain is numbered to give the lowest possible number to the functional group with the higher priority.

6.3 Physical Properties of Unsaturated Hydrocarbons

- Alkynes have linear structure, and the linear structures of alkynes give stronger van der Waals interaction, so alkynes have higher boiling points.
- Alkynes are soluble in nonpolar solvents.

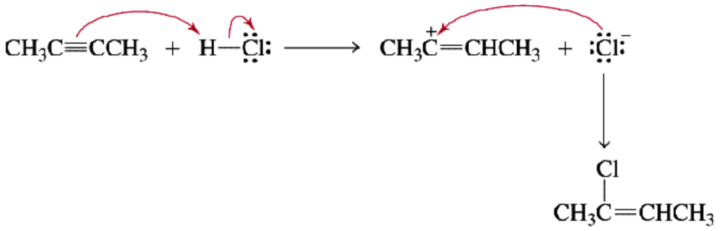
6.4 The Structure of Alkynes

- The structures of alkynes are linear with sp hybridized carbon.

- Two remaining p orbitals on each carbon are perpendicular each other and to sp orbitals, and the remaining p orbitals will overlap each other to form π bonds.
- The bonding electrons in an sp hybrid orbital (50% s character) of a C-H bond in acetylene are closer to the nucleus than the electrons in the hybrid orbital of the C-H bonds of ethylene or ethane.

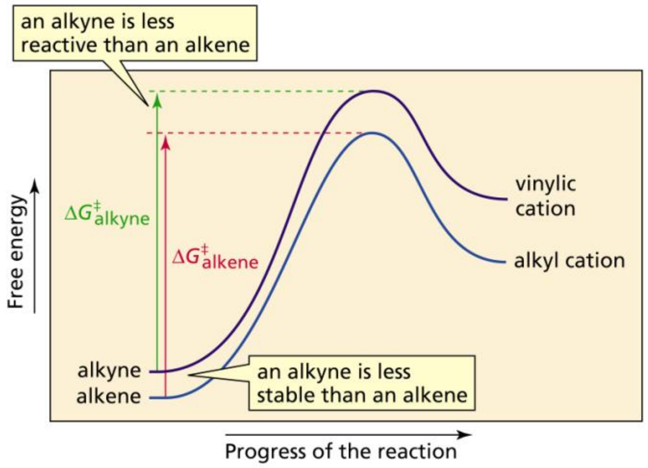
6.5 How Alkynes React

- Alkynes are electron-rich molecule, so they are *nucleophiles*.
- Therefore, they react with electrophiles => undergo electrophilic addition.



$$CH_3C{\equiv}CCH_3 + H{-}\ddot{\underset{..}{Cl}}{:} \longrightarrow CH_3\overset{+}{C}{=}CHCH_3 + {:}\ddot{\underset{..}{Cl}}{:}^- \longrightarrow CH_3\overset{Cl}{\overset{|}{C}}{=}CHCH_3$$

- Electrophilic addition to a terminal alkyne is regioselective.
- Since the product is an alkene, a second electrophilic addition reaction can occur.
- An alkyne is more stable and less reactive than an alkene. => How does the reaction occur?
- Reactivity depends on activation energy. Two conditions must be met for an alkyne to react.
  1. The transition state for the first step of an electrophilic addition reaction for an alkyne must be less stable than the transition state for the first step of an electrophilic addition reaction for an alkene.
  2. The difference in the stabilities of the transition states must be greater than the difference in the stabilities of the reactants.



- Why is the transition state for the first step of an electrophilic addition reaction for an alkyne less stable than that for an alkene? => The intermediate formed when a proton adds to an alkyne is a vinylic cation, whereas the intermediate formed when a proton adds to an alkene is an alkyl cation.
- Vinylic cations are less stable than similarly substituted alkyl cations, because the positive charge is on a more electronegative carbon.

1. The positive charge in a vinylic cation is on an sp carbon (50% s character), while the positive charge on an alkyl cation is on an sp^2 carbon (33% s character).
2. Hyperconjugation is less effective in a vinylic cation.

6.6. Addition of Hydrogen Halides and Addition of Halogens to an Alkyne

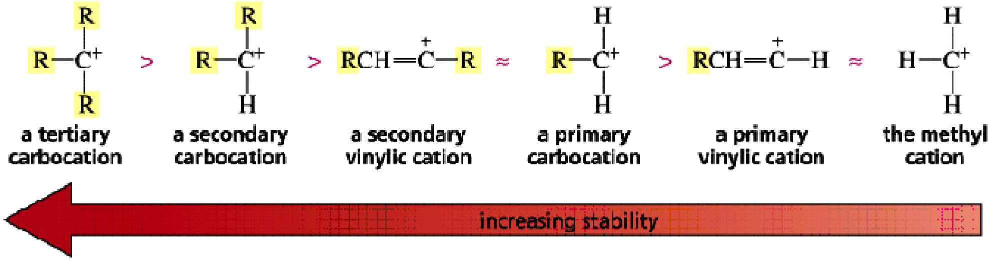
- The addition of a hydrogen halide to a terminal alkyne follows Markovnikov's rule (regioselective), because the secondary vinylic cation is more stable than the primary one.
- When the second equivalent of hydrogen halide adds to the double bond, the electrophilic (H^+) adds to the sp^2 carbon bonded to the greater number of hydrogens.
- The addition of hydrogen halide to an alkyne stops after the addition of one equivalent of hydrogen halide unless excess of hydrogen is present.

1. The rate of addition of the hydrogen halide to the alkyne is greater than the rate of addition of the hydrogen halide to the alkene.
2. The electron-withdrawing halide atom diminishes the reactivity of the alkene toward electrophiles.
3. An alkene is less reactive than an alkyne.

- If there are excess amount of hydrogen halides, the second equivalent of hydrogen halide will be added to the alkene to form a *geminal dihalide* and follows Markovnikov's rule.
- The rate of a reaction depends on the free energy of activation; depends on the stability of the reactant and the stability of the transition state.

1. An alkyne is less stable than an alkene because π bond of an alkyne is weaker than π bond of an alkene.
2. But the intermediate from an alkyne, pi-complex, is far less stable than the intermediate from an alkene, alkyl cation (Hammond postulate).
3. Therefore, the alkene has the greater reactivity.

- In the presence of peroxide, HBr adds to a terminal alkyne in an anti-Markovnikov's rule, because Br radical is the electrophile (Please check the mechanism in the textbook) relative stabilities of carbocations

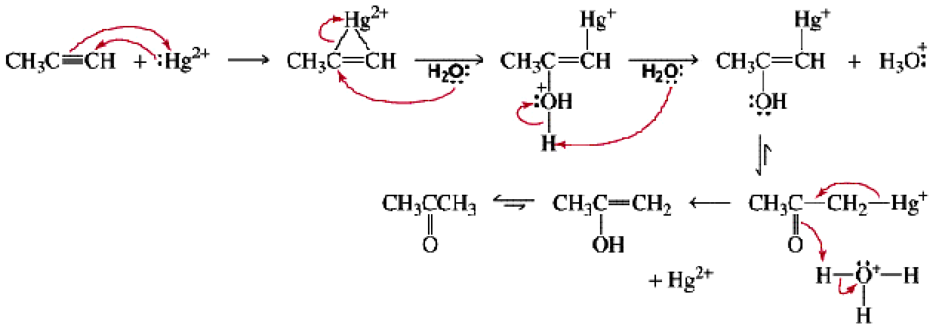


6.7 Addition of Water to an Alkyne

- An alkyne undergoes acid-catalyzed addition of water to form an enol, which immediately rearrange to a ketone.
- The isomeric relation between an *enol* and a *ketone* is called **tautomers**.
- Terminal alkynes are less stable than internal alkynes toward addition of water.
- The addition of water to the terminal alkynes undergoes if mercuric ion is added to the acidic mixture.

1. First step: formation of a cyclic mercurium ion.
2. Second step: water attacks the most substituted carbon of the intermediate.

mechanism for the mercuric-ion-catalyzed hydration of an alkyne



6.8 Addition of Borane to an Alkyne: Hydroboration-Oxidation

- Borane adds to the alkynes in the same way of alkene, but the enol product will undergo tautomerization to form a carbonyl product.
- Mechanism

1. Addition of borane
2. Oxidation : boron is replaced by an OH group.

- The overall reaction follows anti-Markovnikov’s rule.
- Key difference between Mercuric ion catalyzed addition of water and hydroboration-

oxidation

1. Mercuric-ion catalyzed addition of water to a terminal alkyne produces a ketone.
2. Hydroboration-oxidation of the alkyne produces an aldehyde.

6.9 Addition of Hydrogen to an Alkyne

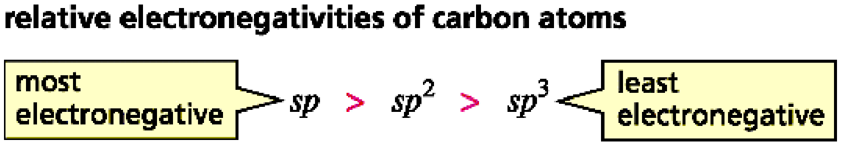
- Hydrogens add to an alkyne in the presence of a metal catalyst such as palladium, platinum, or nickel, with *syn* addition (cis product).
- However, it is not easy to stop the hydrogenation at the stage of alkenes because the alkenes are also reactive to the hydrogenation.
- Therefore, mild catalysts are required to stop the hydrogenation at the stage of alkenes: Lindlar's catalysts
- Alkynes can be converted into alkenes using an equivalent of sodium or lithium in liquid ammonia, and produce trans alkenes.

1. First step: transfer the s orbital electron from sodium to the pi-framework of the triple bond to form a radical anion.
2. Second step: radical anion abstracts a proton from ammonia to form a vinylic radical.
3. Third step: transfer the s orbital electron from sodium to the vinylic radical to form a vinylic anion.
4. Fourth step: vinylic radical abstracts a proton from another molecule of ammonia.

- The vinylic anion intermediate can be in either a cis or a trans form, but the trans form is more stable to form a trans product.

6.9 A Hydrogen Bonded to an sp Hybridized Carbon Is "Acidic"

- In general, the closer the electrons are to the nucleus, the more electronegative is the atom.
- The sp electrons are closer to the nucleus than the sp^2, sp^3 electrons, and they are more electronegative than the sp^2, sp^3 electrons.



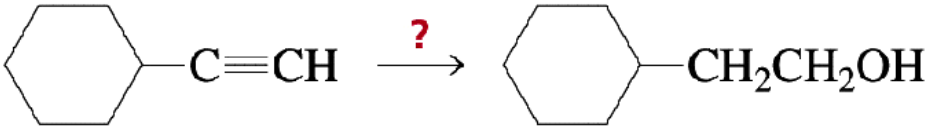
- Therefore, alkynes are more acidic than alkenes and alkanes.
- However, strong base such as sodium amide is required to lose proton from alkynes.

6.10 Synthesis Using Acetylide Ions

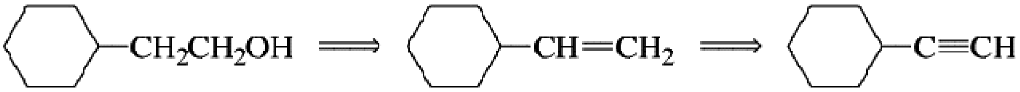
- Alkylation reaction: acetylide anion can be a good nucleophile which is useful in organic synthesis.

6.12 Designing a Synthesis I: An Introduction to Multistep Synthesis

- Synthesis must consider time, cost, and yield.
- Well designed synthesis should have the least steps.
- Retrosynthesis: Think about the synthesis backward.
- Example:



retrosynthetic analysis



Chapter 7. Electron Delocalization and Resonance. More About Molecular Orbital Theory

- Localized electrons: electrons that are restricted to a particular region such as lone pair electrons, bonding electrons.
- **Delocalized electrons**: electrons that are shared by more than two atoms.

7.1 Benzene Has Delocalized electrons

- Experimental results with benzene

1. Molecular formula is C_6H_6 with triene.
2. Benzene does not undergo an addition reaction with hydrogen halides
3. When benzene reacts with bromine in the presence of a catalyst ($FeBr_3$), a bromine atom replaces a hydrogen atom from benzene and produces only one compound.
4. When the substituted product undergoes a second substitution, three isomeric disubstituted products are obtained.

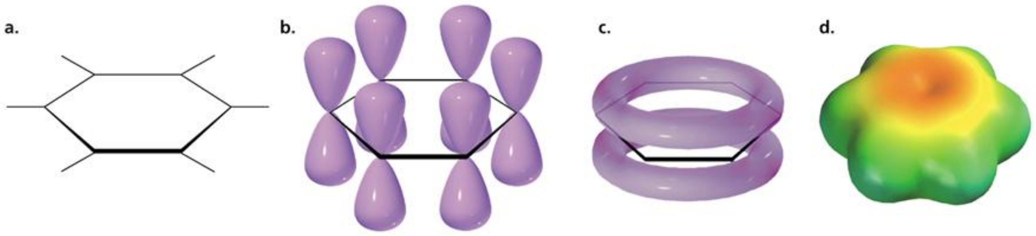
- Conclusion we can get from the experimental results

1. Benzene is an acyclic compound with 4 π bonds, a cyclic compound with 3 π bonds or a bicyclic compound with 2π bonds etc.
2. The double bonds in benzene are not normal double bonds.
3. All the hydrogens in benzene are all identical (single product).
4. Benzene is not an acyclic compound.

- Single bonds rapidly become double, as the adjacent double bonds become single bonds.
- Benzene is a very stable compound compared to cyclic triene, and the difference in energy is called resonance energy.
- Structure of benzene by X-ray crystallography : a planar molecule in which all six carbon-carbon bonds have the same length (1.39 Å, which is shorter than a carbon-carbon sing bond but longer than double bond) and all hydrogen atoms are equal. And all the carbon-carbon bonds have the same electron density, which means the electrons are delocalized.

7.2 The Bonding in Benzene

- Benzene is a planar molecular with six sp^2 hybridized carbons.
- Since benzene is planar, the six p orbitals are parallel and these p orbitals can overlap each other => π electrons are shared by all six carbons, and the six π electrons are delocalized.
- Benzene does not have any double bonds, which explains why benzene does not undergo electrophilic addition reaction.



7.3 Resonance Contributors and the Resonance Hybrid

- The structure using localized electrons is called a *resonance contributor*, a *resonance structure*, or a *contributing resonance structure*, but these are not actual structures.
- The actual structure with delocalized electrons is called a resonance hybrid.
- Resonance contributors are imaginary. Only the resonance hybrid is real.
- The actual structure lies somewhere between the structures of the resonance contributors.

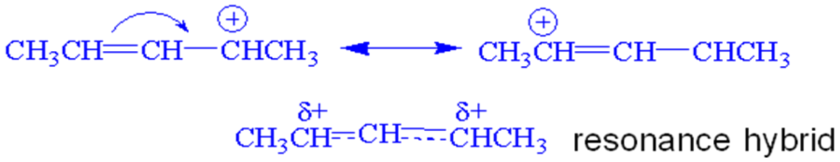
7.4 How to Draw Resonance Contributors

- Rules for drawing resonance contributors

1. Only electrons move.
2. Only π electrons and nonbonding electrons can move, not the atoms.
3. The total number of electrons in the molecule does not change, and neither do the numbers of paired and unpaired electrons.

- The ways electrons can move (the electrons move toward an sp^2 hybridized atom).

1. Move π electrons toward a positive charge or toward a π bond.

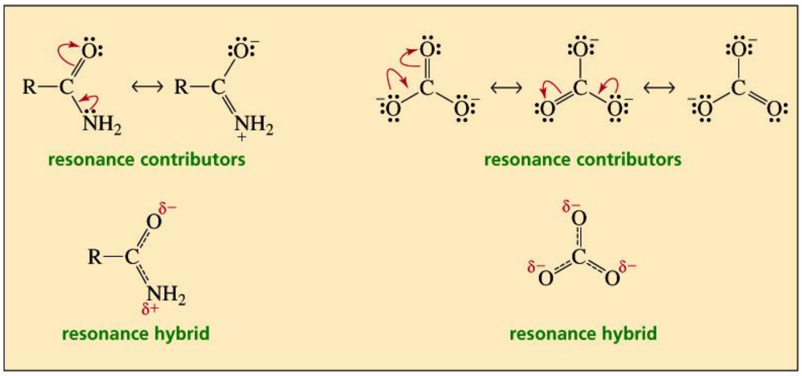


$$CH_3CH{=}CH{-}\overset{+}{C}HCH_3 \longleftrightarrow CH_3\overset{+}{C}HCH{=}CH{-}CHCH_3$$

$$CH_3\overset{\delta+}{C}H{=}CH{-}\overset{\delta+}{C}HCH_3$$

resonance hybrid

2. Move a nonbonding pair (lone-pair) of electrons toward a π bond .

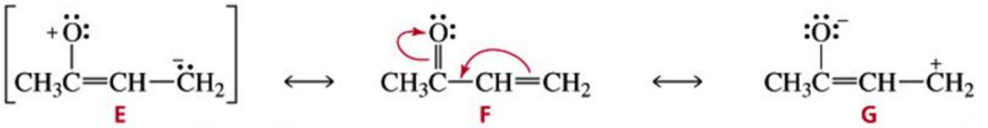


3. Move a single nonbonding electron toward a π bond : radicals can have resonance if the unpaired electron is on a carbon that is adjacent to an sp^2 hybridized atom..

- Each of the resonance contributors for a particular compound must have the same net charge.
- Electron delocalization occurs only if all the atoms sharing the delocalized electrons lie in the same plane so that the p orbitals can overlap.

7.5 The Predicted Stabilities of Resonance Contributors.

- All resonance contributors do not contribute equally to the resonance hybrid.
- The degree of contribution of a resonance structure to the resonance hybrid depends on its predicted stability: The greater the predicted stability of the resonance contributor, the more it contributes to the resonance hybrid.
- The features that decrease the predicted stability of a contributing resonance structure
  1. An atom with an incomplete octet
  2. A negative charge that is not on the most electronegative atom or a positive charge that is not on the least electronegative atom



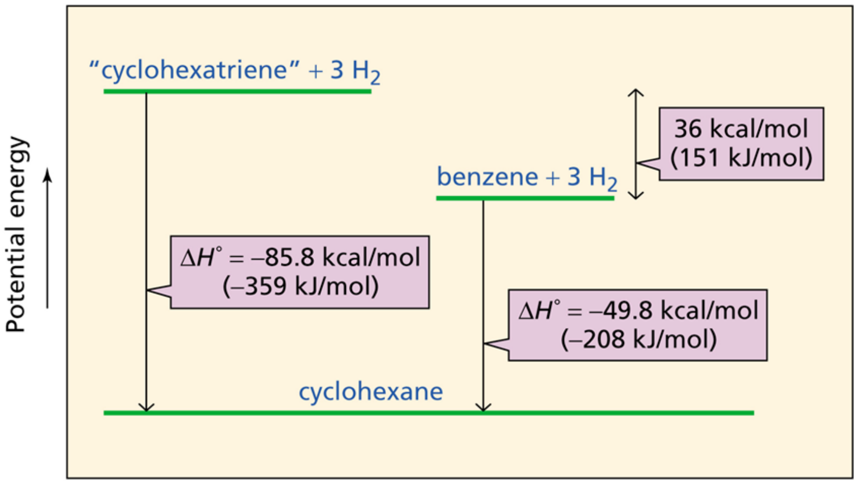
resonance contributor obtained by moving π electrons away from the more electronegative atom

resonance contributor obtained by moving π electrons toward the more electronegative atom

  3. Charge separation: needs energy to keep the charges separated.

7.6 Delocalized Energy Is the Additional Stability Delocalized Electrons Give to a Compound

- **Resonance energy** (delocalization energy): the *extra stability* a compound gains by having delocalized electrons. Therefore, the resonance energy tells us how much more stable a compound with delocalized electrons is than it would be if its electrons were localized
- The resonance energy of benzene (the energy difference between benzene and imaginary cyclohexatriene): 36kcal/mol



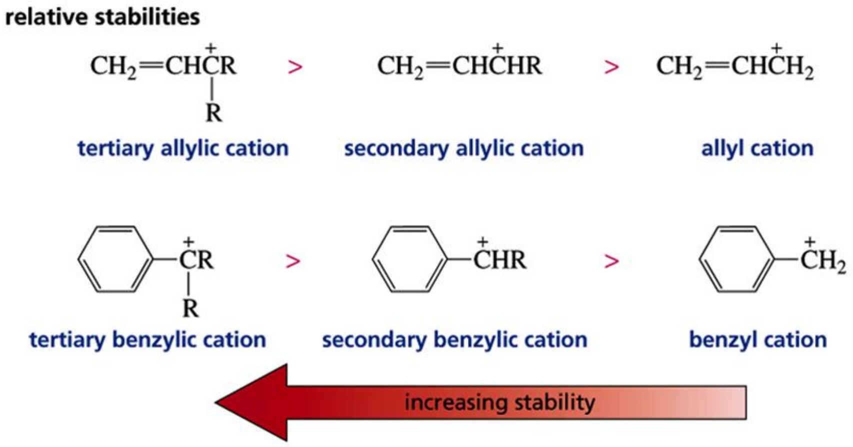
- A resonance hybrid is more stable than the predicted stability of any of its resonance contributors.
- The resonance energy depends on the number and predicted stability of the resonance contributors: the greater the number of relatively stable resonance contributors, the greater is the resonance energy.

- The more nearly equivalent the resonance contributors, the greater the resonance energy.

7.7 Examples Illustrating the Effect of Delocalized Electrons on Stability

- Stability of Diens
  1. Conjugated diene which has conjugated double bonds is more stable than isolated dienes due to a) the delocalization and b) hybridization of the orbitals forming the carbon-carbon single bond.
  2. The closer the electrons are to the nucleus, the shorter and stronger is the bond.
  3. Allens are cumulated double bonds that are adjacent to one another.
- Since allylic and benzylic cations (positive charge on a benzylic carbon) have delocalized

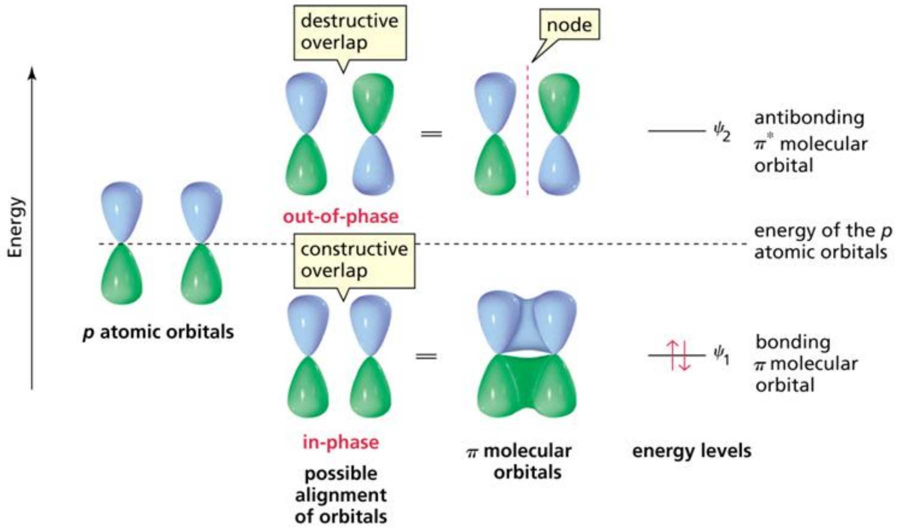
electrons, so they have resonance contributors which makes them more stable than primary carbocations.



- A tertiary allylic cation is more stable than a secondary allylic cation.

7.8 A Molecular Orbital Description of Stability.

- Side-to-side overlapping of in-phase p orbitals produces a *bonding* π molecular orbital, ψ_1, which has a lower energy than the p orbitals.
- Side-to-side overlapping of out-of-phase p orbitals produces an *antibonding* π molecular orbital, ψ_2, which has a higher energy than the p orbitals. And the antibonding MO has a node between the lobes of opposite phases.
- *Nonbonding* MO: no overlap between the p orbitals, and it has a same energy as the p orbitals.



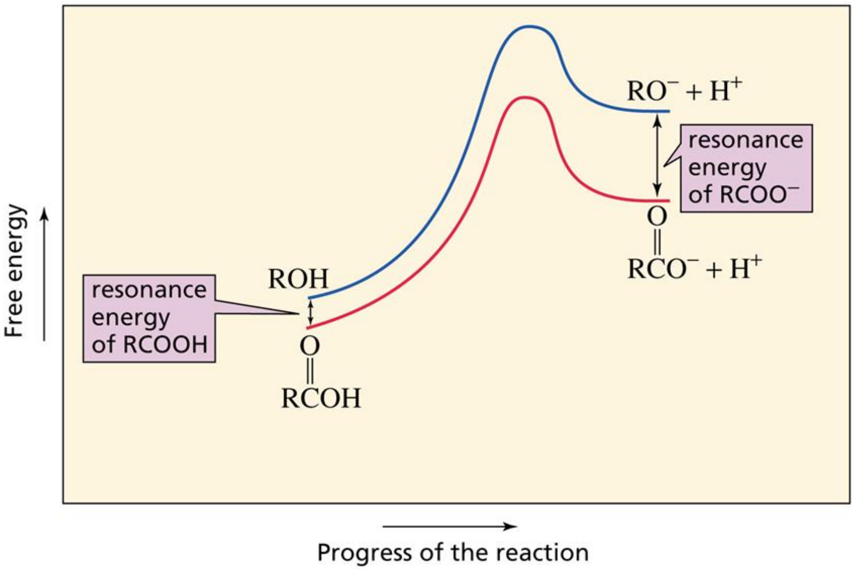
- The π electrons are placed in MO following the following rules; the aufbau principle, the

Pauli principle, the Hund’s rule.

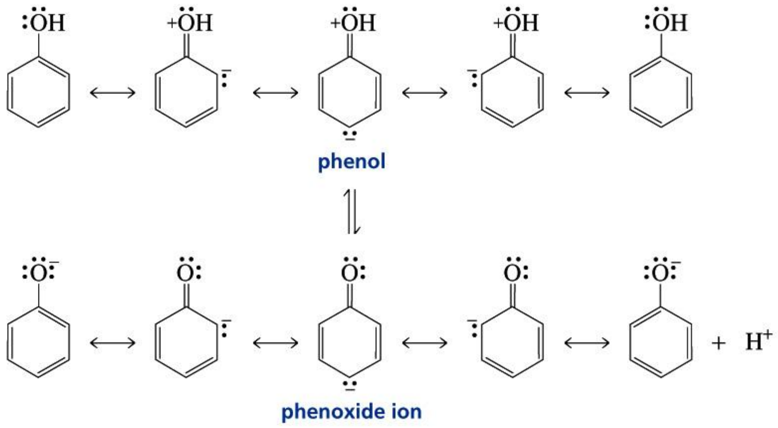
- Molecular orbitals can be obtained by the linear combination of atomic orbitals.
- The molecular orbitals have different energy level depending on the structure of them.
- Highest occupied molecular orbital (**HOMO**): the highest-energy molecular containing electrons.
- Lowest unoccupied molecular orbital (**LUMO**): the lowest-energy molecular orbital containing no electrons.
- HOMO of one reagent will interact with LUMO of the other reagent through electron transfer.
- If the molecule absorbs light of an appropriate wavelength, the electron in HOMO will be promoted to LUMO, it is the theoretical basis of UV spectroscopy.
- Some of the molecular orbitals have the same energy level with the atomic orbitals, because there is no overlap between atomic orbitals, and they are called nonbonding molecular orbitals.
- As the MOs increases in energy, the number of nodes increases, the number of bonding interactions decreases, and the MOs alternate from being symmetric to being asymmetric.
- Benzene is the most stable. It is because of the large delocalization energies. And we call them aromatic compounds (**same plane, 4n+2 pi electrons, all pi electrons are conjugated**)

7.9 How Delocalized Electrons Affects pKa

- Even though both a carboxylic acid and an alcohol have hydroxy group, a carboxy acid is more acidic than an alcohol, because a carboxylate has the resonance energy by delocalization of electrons.



- Phenol is a stronger acid than an alcohol in which an OH group is bonded to an sp^3 carbon, because of the stabilization of phenol's conjugate base by increased resonance energy and electron withdrawal.

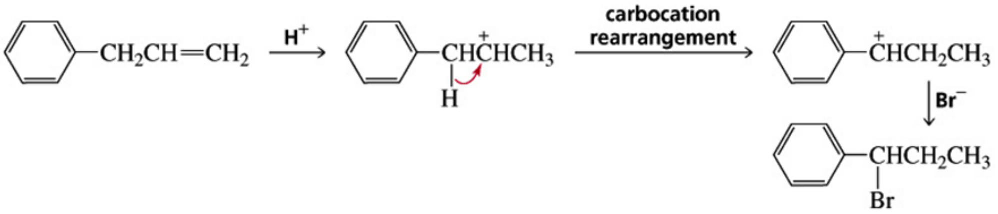


1. The OH group of phenol is attached to an sp^2 carbon that is more electronegative than sp^3 carbon to which the OH group of cyclohexanol is attached. Greater inductive electron withdrawal by the sp^2 carbon stabilizes the conjugate base by decreasing the electron density of its negatively charged oxygen
2. Both phenol and phenolate have delocalized electrons, but the resonance energy of the phenolate ion is greater than that of phenol because three of phenol's resonance contributors have separated charges.

- A protonated amine is a stronger acid than a protonated alkylamine, because sp^2 carbon (aniline) has the greater electronegativity compared to an sp^3 carbon (alkylamine) and aniline has the resonance energy due to the delocalized electrons.

7.10 Delocalized Electrons Can Affect the Product of a Reaction

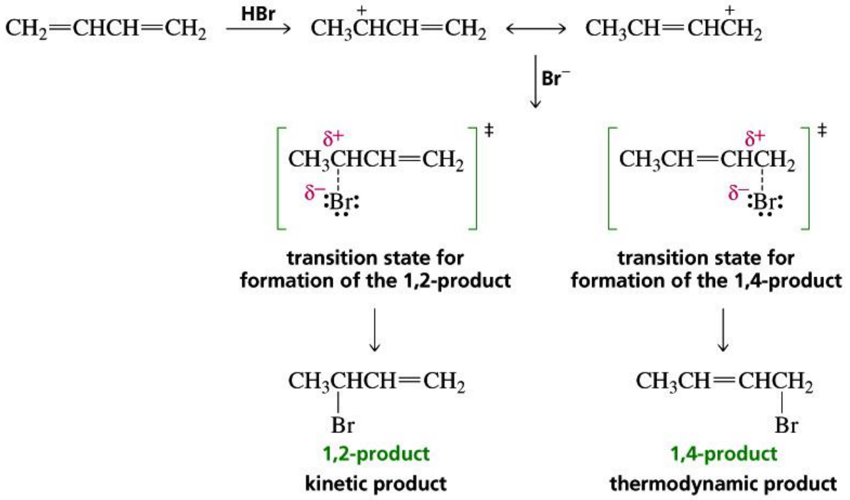
- Control the regioselectivity: When there is a benzylic carbocation as an intermediate, which is stabilized by resonance, the regioselectivity does not need to follow Markpvnikov's rule. Even carbocation rearrangement can occur to get the stable benzylic intermediate.



- When a conjugated diene reacts with a limited amount of electrophilic reagent, two addition products are obtained due to the delocalization(look at the mechanism).

1. 1,2-addition product(direct addition)
2. 1,4-addition product(conjugate addition)

- Why are there two different products form the reaction of a conjugated diene? => need to look at the mechanism.



- Mechanism of addition reaction in conjugated dienes.

1. The electrophilic proton adds to C-1 to form an allylic cation, which can form resonance structures.
2. The proton addition does not occur at C-2 or C-3 because it forms a primary carbocation, and the resulting carbocation would not be stabilized by resonance.
3. In the second step, the bromide ion can attack either C-2 (direct addition) or C-4 (conjugate addition) to form the 1,2-addition product or the 1,4-addition product.
4. If the diene is asymmetrical, the major products of the reaction are those obtained by adding the electrophile to whichever terminal sp^2 carbon results in formation of the more stable carbocation.

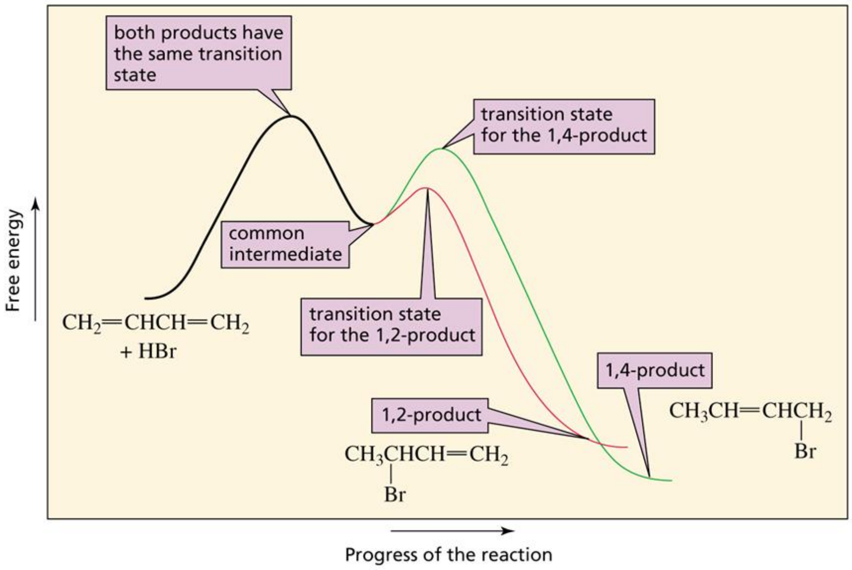
- Control the reactivity: If there is an electron donating substituents next to the positive charge, the positive charged intermediate is delocalized being more stable, so the reaction rate is faster than others.

7.11 Thermodynamic vs. Kinetic Control of Reactions

- Thermodynamic product is the most stable compound energetically.
- Kinetic product is the product which formed faster
- **Thermodynamic control**: the relative amounts of the products depend on their stability.
- **Kinetic control**: the relative amounts of the products depend on the rate.
- In the addition of HBr to 1,3-butadiene, which is conjugate diene.

1. 1,4-addition product is the thermodynamic product, because it has more alkyl groups bonded to sp^2 carbons.
2. 1,2-addition product is the kinetic product, because the transition state for formation of the 1,2-product resembles a secondary allylic carbon, but the transition state for formation of the 1,4-product resembles a primary allylic carbon, which is less stable compared to a secondary allylic carbon.

- In general, the thermodynamic product and kinetic product are same.



- For a reaction in which the kinetic products and the thermodynamic products are not the same, the major product depends on the reaction condition.

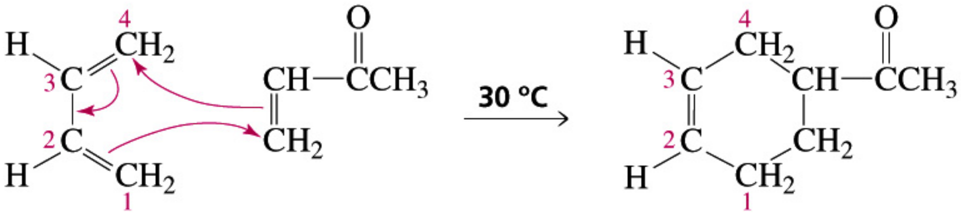
1. In the mild condition, the kinetic product is the major product => Since the energy given is not enough to overcome the activation energy for the reverse reaction, the reaction is irreversible. And the activation energy for the 1,2-product is lower than the activation energy for 1,4-product, so the major product is the kinetic product.

2. In the more vigorous condition, the thermodynamic product is the major product => Since the reaction has enough energy to overcome the activation energy for both forward and reverse reaction, the reaction is reversible. Since the reaction is reversible, the major product is the thermodynamic product, which is more stable.

- Do not assume that the 1,2-product is the kinetic product and the 1,4-product is the thermodynamic product for all conjugated dienes.
- Why is the 1,2 addition product formed faster in 1,3 diene? -> because of the more stable secondary allylic cation and proximity effect.

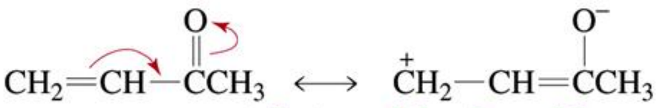
7.12 The Diels-Alder Reaction: A 1,4-Addition Reaction.

- Diels-Alder reaction: a cyclization reaction by forming two carbon-carbon bonds from a diene and a dienophile, and it occurs in one step. It is sometimes called [4+2] cycloaddition reaction, pericyclic reaction. It is *a concerted* reaction.

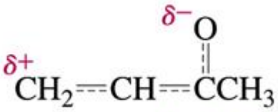


a 1,4-addition reaction to 1,3-butadiene

- Dienophiles with an electron-withdrawing group bonded to one of the sp^2 carbons are more reactive in Diels-Alder reaction, because the electron-withdrawing group polarizes the double bond, which makes the reaction easier to initiate.
- The electrons from C-1 of the conjugated diene attack the partially positively charged sp2 carbon, and the other sp^2 carbon of the dienophile is the nucleophile that adds to C-4 of the diene.

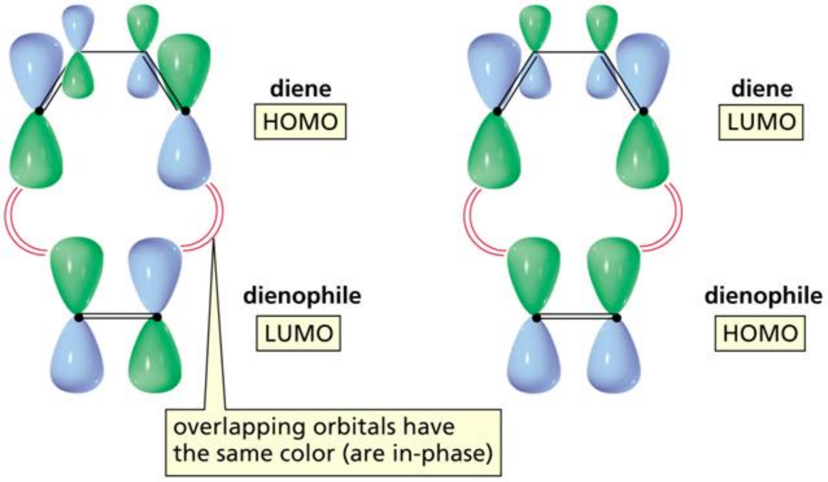


resonance contributors of the dienophile

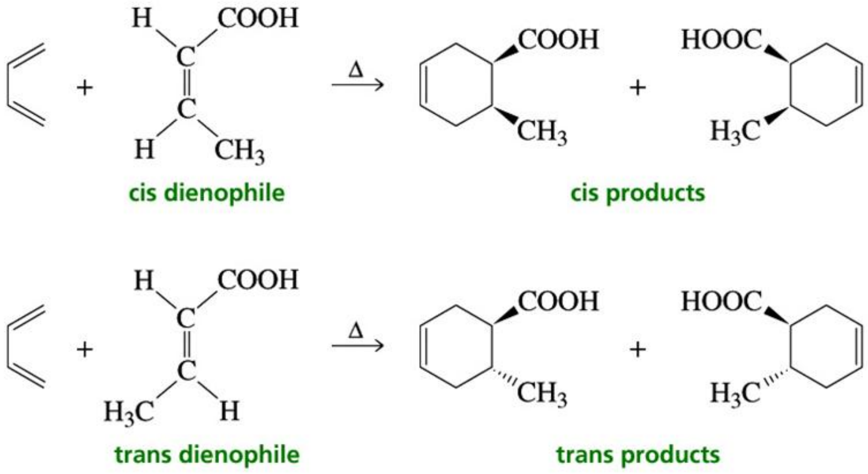


resonance hybrid

- The two new σ bonds that are formed in a Diels-Alder reaction result from a transfer of electron density between the reactants. Electron transfer from HOMO to LUMO.

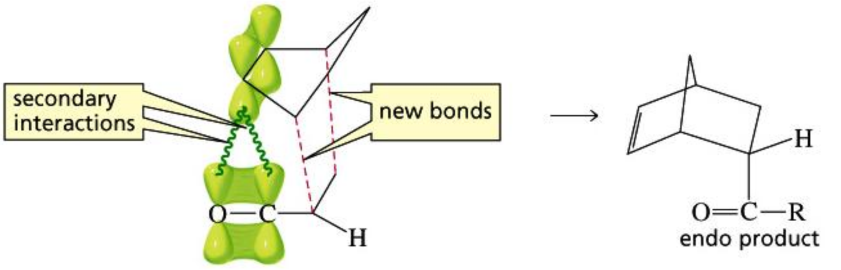


- Conservation of orbital symmetry: pericyclic reactions occur as a result of the overlap of in-phase orbitals.
- The Diels-Alder reaction is stereospecific; the configuration of the reactants is maintained: **syn** addition.

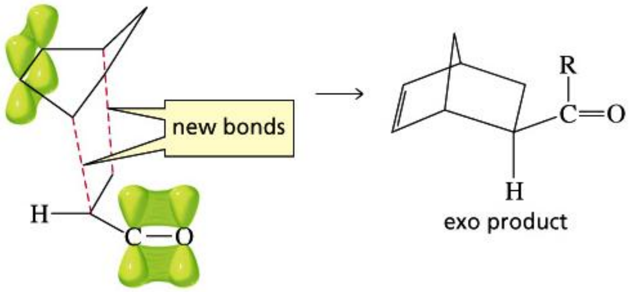


- If both the diene and the dienophile are asymmetrical, two products can be formed, and the relative yield depends on the charge distribution of the reactants.
- The partially positively charged carbon atom of the dienophile will attack the most negatively charged carbon of the diene.
- For the Diels-Alder reaction, the conjugated diene must have s-cis conformation.
- Two possible configurations for the Diels-Alder reaction products.

1. Endo: the substituent is closer to the longer of the two unsubstituted bridges.
2. Exo: the substituent is closer to the shorter of the two unsubstituted bridges.



secondary orbital overlap
in the endo transition state



no secondary orbital
overlap in the exo transition state