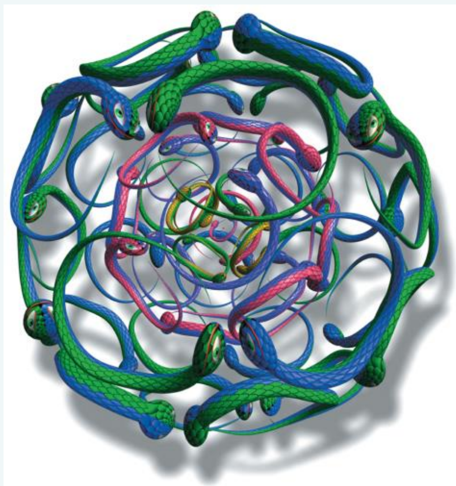
Chapter 7



Delocalized Electrons and Their Effect on Stability, p*K*a, and the Products of a Reaction • Aromaticity and the Reactions of Benzene

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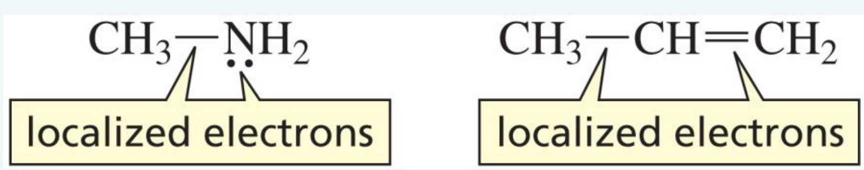
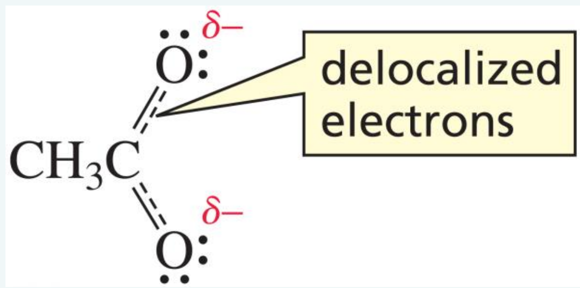
University of California, Santa Barbara

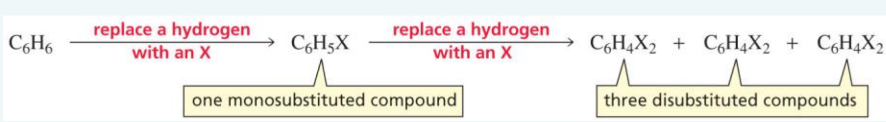
Localized Electrons



Delocalized Electrons

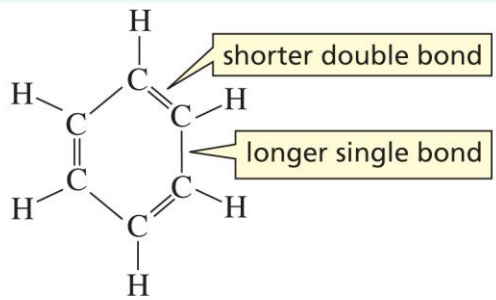


What is the structure of Benzene?

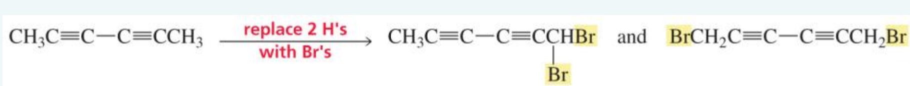


Degree of Unsaturation = 4

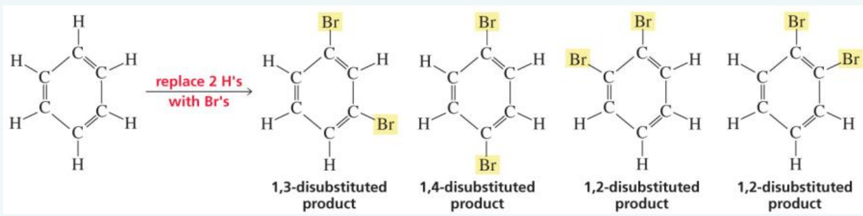
$CH_3C{\equiv}C{-}C{\equiv}CCH_3$



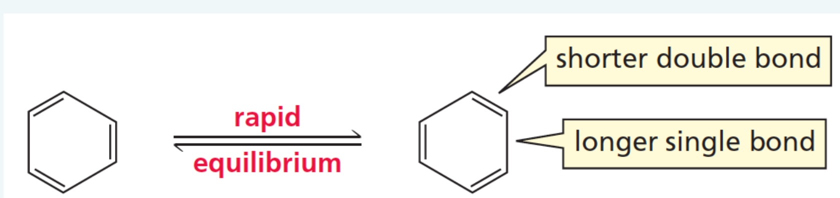
Two Disubstituted Products

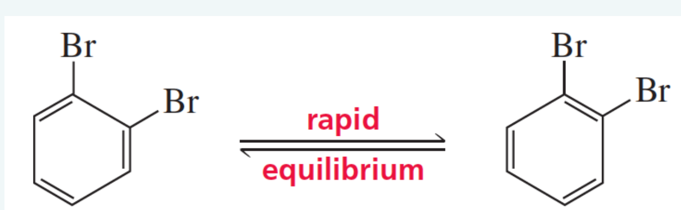


Four Disubstituted Products

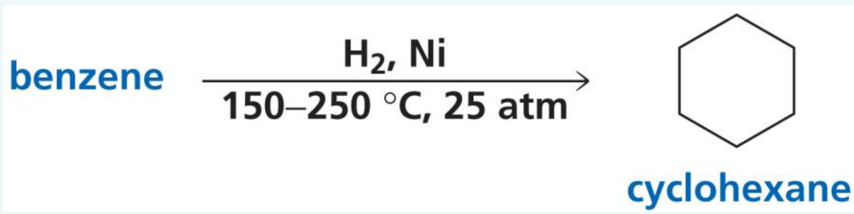


Two are in Rapid Equilibrium

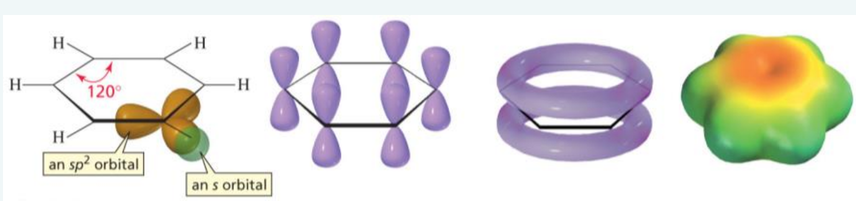




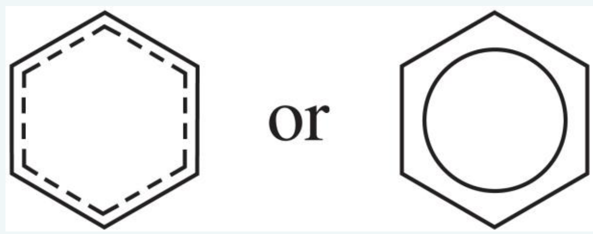
It was confirmed that Benzene is cyclic in 1901



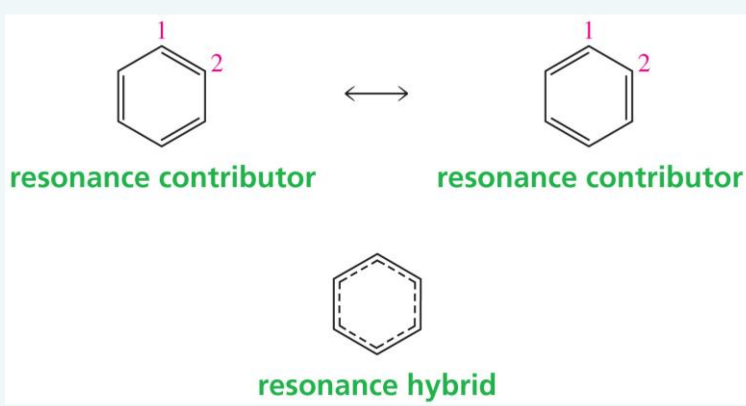
The Structure of Benzene



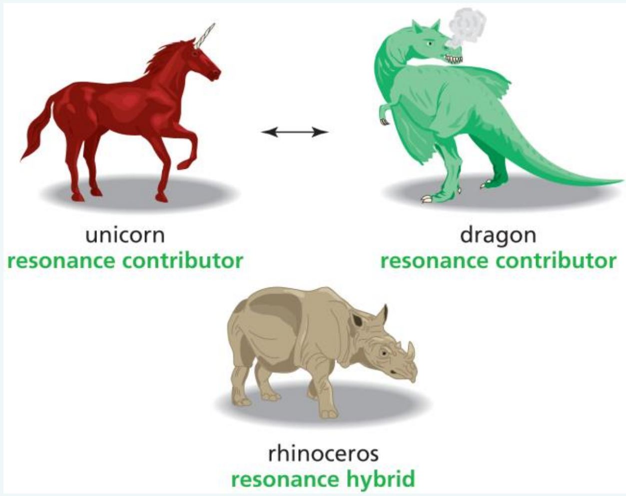
Showing Delocalized Electrons



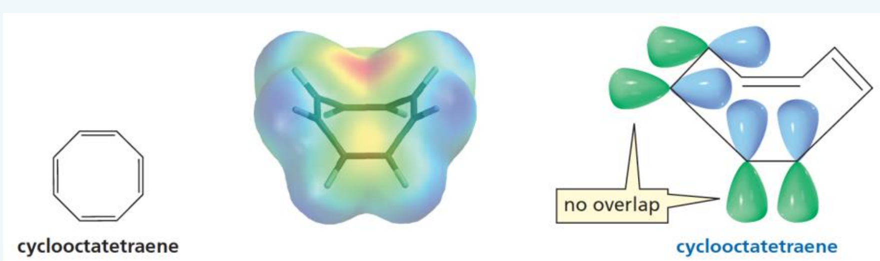
Resonance Contributors
Resonance Hybrid



Resonance Contributors Resonance Hybrid

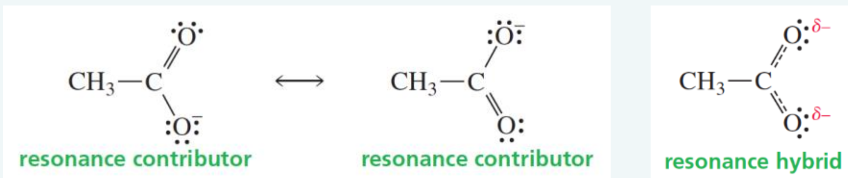


Cyclooctatriene does not have Delocalized Electrons



Cyclooctatetraene is not planar.

Delocalized Electrons



Delocalized electrons result from the *p* orbital of one atom overlapping the *p* orbitals of two adjacent atoms.

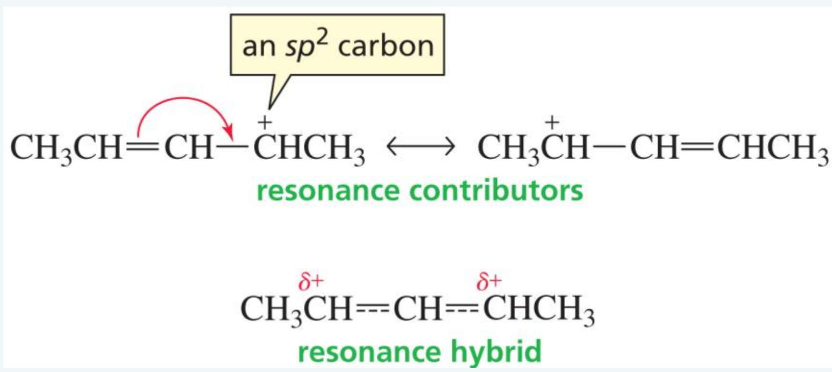
Rules for Drawing Resonance Contributors

1. Only electrons move.

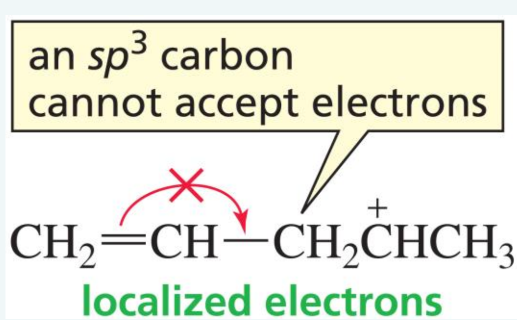
2. Only π electrons and lone-pair electrons move.

1. The total number of electrons in the molecule does not change.

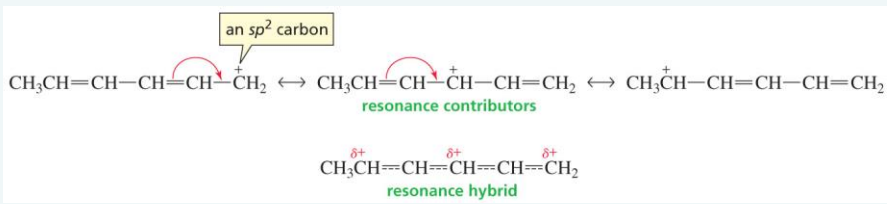
Move π Electrons to an sp^2 Carbon



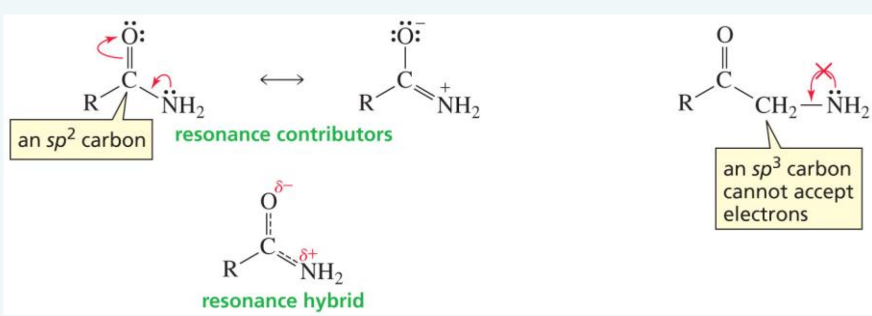
Cannot Move Electrons to an sp^3 Carbon



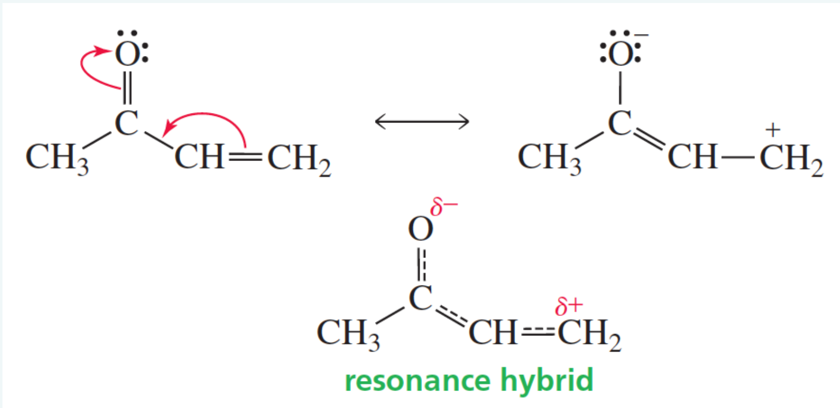
Move π Electrons to an sp^2 Carbon



Move Lone-Pair Electrons to an sp^2 Carbon

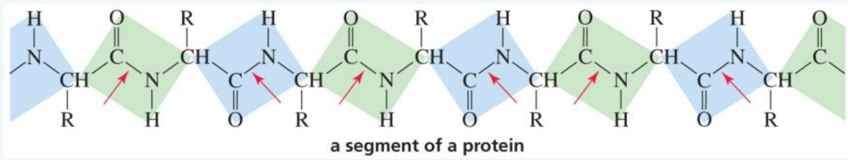


Move Lone-Pair Electrons to an sp^2 Carbon

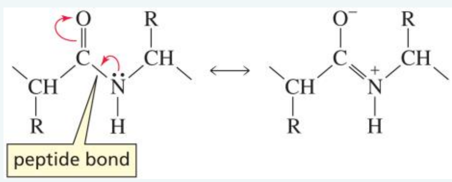


Moving Electrons away from the most Electronegative Atom

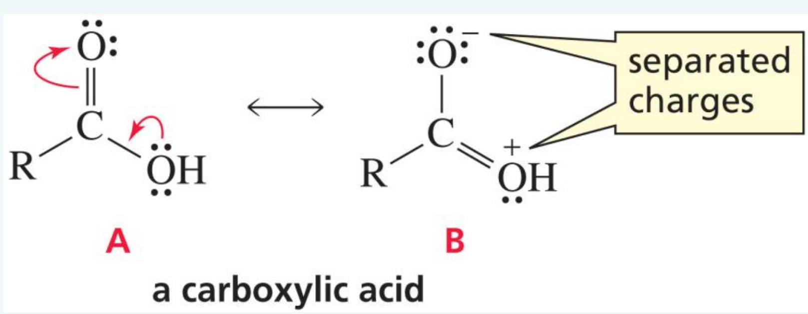
How delocalized Electrons affect Protein Structure



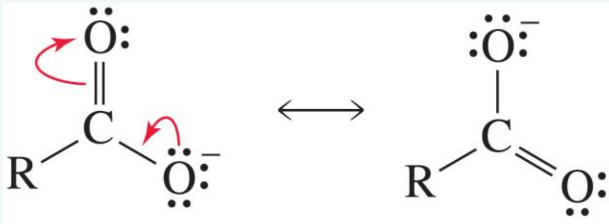
red arrows point at peptide bonds



A is more Stable than B

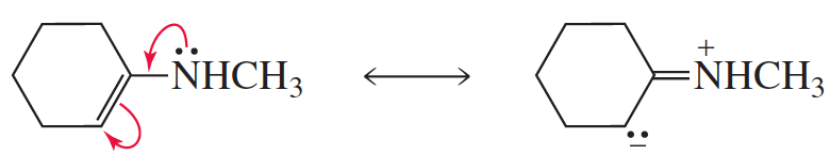


C and D are equally Stable



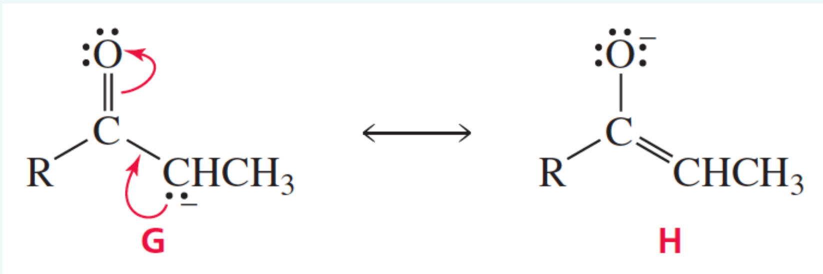
a carboxylate ion

E is more Stable than F



F has separated charges, with N holding a positive charge.

H is more Stable than G

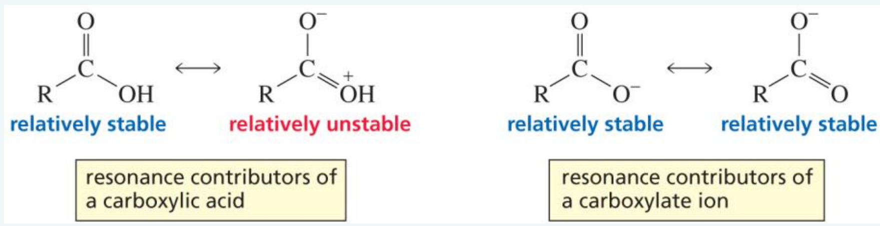


Oxygen better accommodates the negative charge

Delocalization Energy

- The delocalization energy is the extra stability a compound has as a result of having delocalized electrons.
- Electron delocalization is also called resonance.
- Delocalization energy is also called resonance energy.
- The resonance hybrid is more stable than any of its resonance contributors is predicted to be.

The greater the number of Relatively Stable Resonance Contributors, the greater the Delocalization Energy

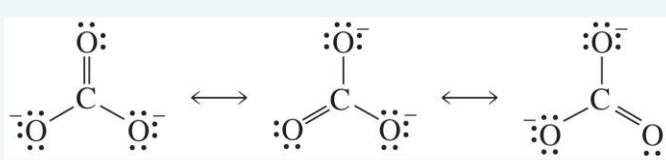


The delocalization energy is greater for the carboxylate ion than for the carboxylic acid.

The number of Relatively Stable Resonance Contributors is what is important

Little delocalization energy

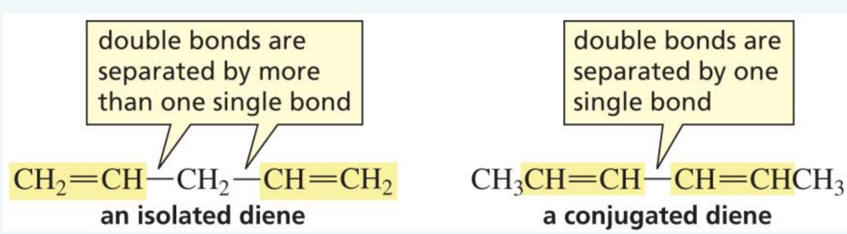
Significant delocalization energy



Summary

- The greater the predicted stability of a resonance contributor, the more it contributes to the resonance hybrid.
- The greater the number of relatively stable resonance contributors, the greater the delocalization energy.
- The more nearly equivalent the resonance contributors, the greater the delocalization energy.

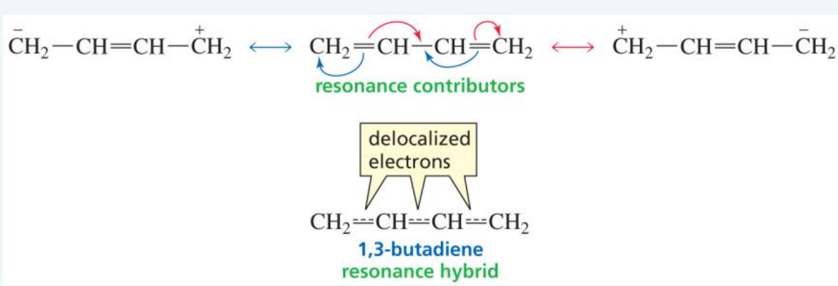
Conjugated and Isolated Dienes



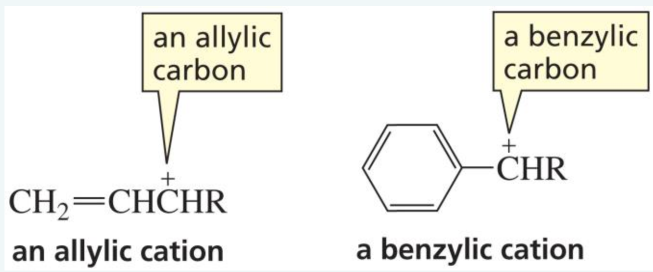
The smaller the Heat of Hydrogenation, the more stable the Compound

	Heat of hydrogenation	$\Delta H°$ (kcal/mol)	$\Delta H°$ (kJ/mol)
$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 + 2\,H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_2CH_3$ 1,4-pentadiene an isolated diene	60.2 kcal/mol	−60.2	−252
$CH_2{=}CH{-}CH{=}CHCH_3 + 2\,H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_2CH_3$ 1,3-pentadiene a conjugated diene	54.1 kcal/mol	−54.1	−226

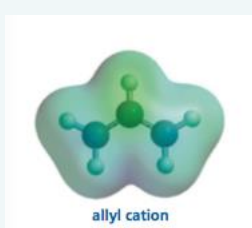
Conjugated Dienes have Delocalized Electrons

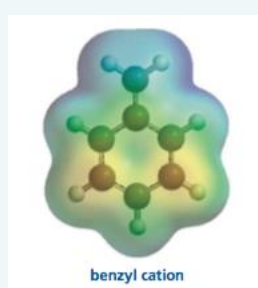


Allylic and Benzylic Cations



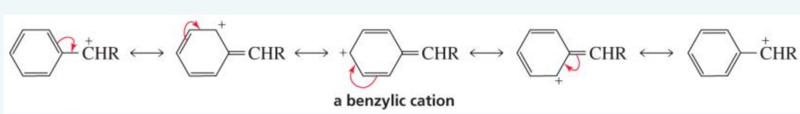
Allylic and Benzylic Cations



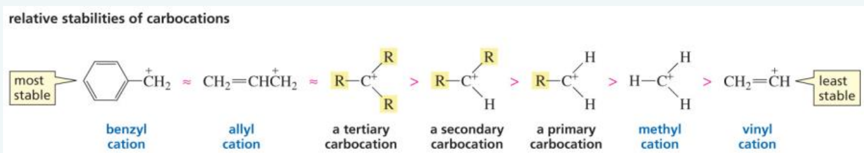


Resonance Contributors for an Allylic Cation

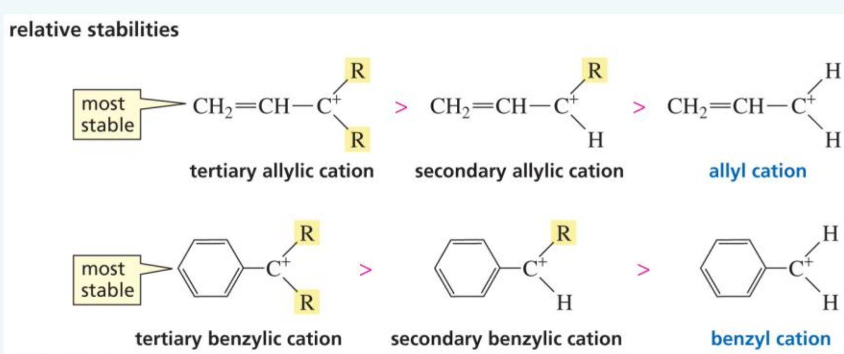
Resonance Contributors for a Benzylic Cation



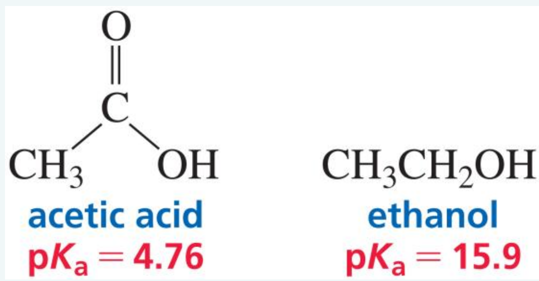
Relative Stabilities of Carbocations



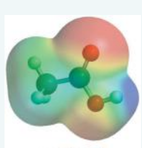
Relative Stabilities of Carbocations



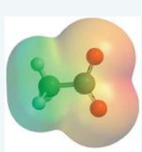
Delocalized Electrons affect pK_a Values



Proton loss is accompanied by greater Delocalization Energy



The negative charge is localized on one oxygen.



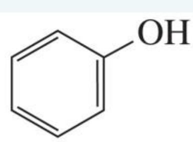
The negative charge is shared by two oxygens.

No Electron Delocalization

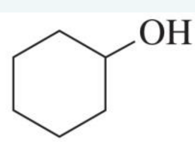
$$CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$$

ethanol — ethoxide ion

Phenols *versus* Alcohols



phenol
pK_a = 10

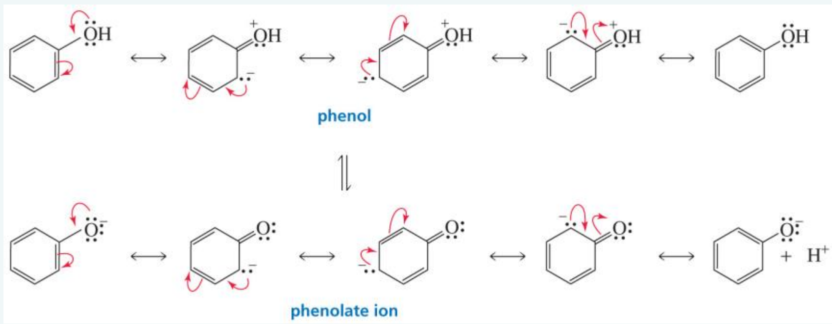


cyclohexanol
pK_a = 16

CH_3CH_2OH

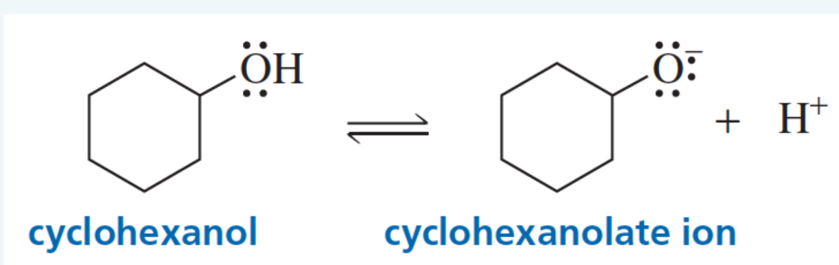
ethanol
pK_a = 16

Why Phenols are more Acidic



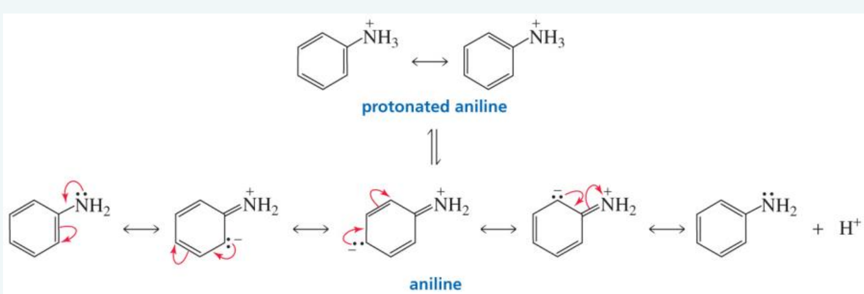
The base has greater delocalization energy than the conjugate acid.

No Electron Delocalization



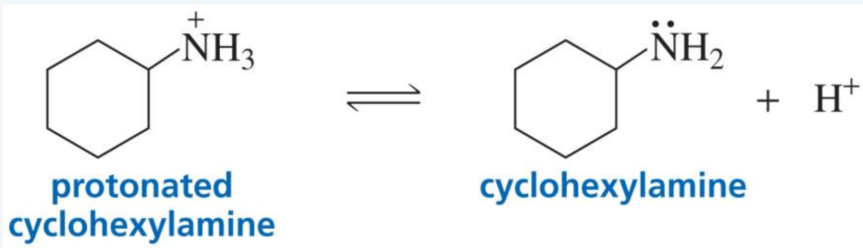
Protonated Anilines *versus* Protonated Amines

Why Protonated Anilines are more Acidic



The base has greater delocalization energy than the conjugate acid.

No Delocalized Electrons

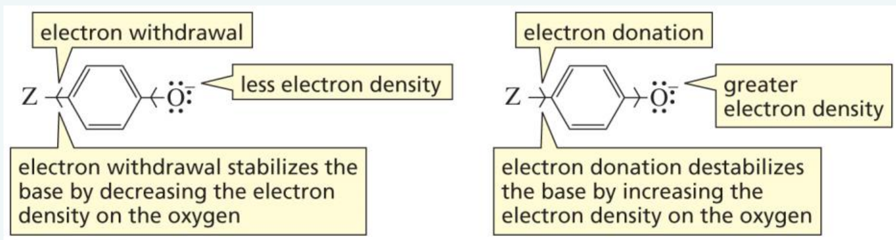


Important!

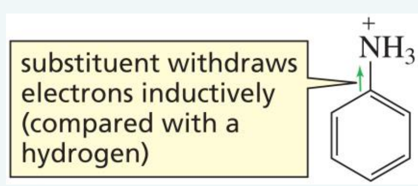
Table 7.1 Approximate pK_a Values

pK_a < 0	pK_a ≈ 5	pK_a ≈ 10	pK_a ≈ 15
$R\overset{+}{O}H$ / H	$RC(=O)OH$	$R\overset{+}{N}H_3$	ROH
$RC(=\overset{+}{O}H)OH$	$C_6H_5\overset{+}{N}H_3$	C_6H_5OH	H_2O
H_3O^+			

Electronic Effects: Substituents on the Benzene Ring affect pK_a Values

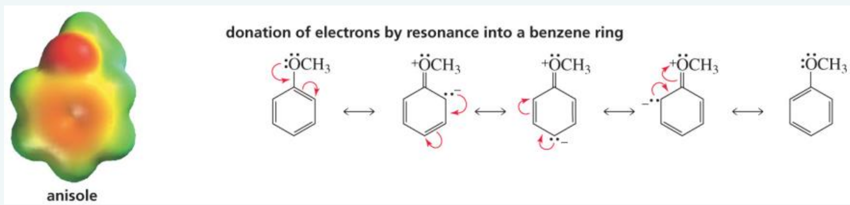


Inductive Electron Withdrawal and Donation



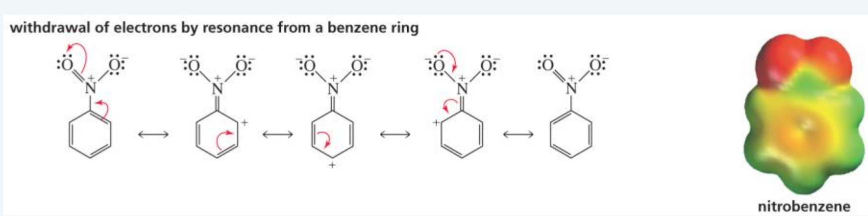
- A substituent more electronegative than a hydrogen withdraws σ electrons inductively from the benzene ring more than a hydrogen will.
- An alkyl group donates electrons into the ring by hyperconjugation.

Resonance Electron Donation



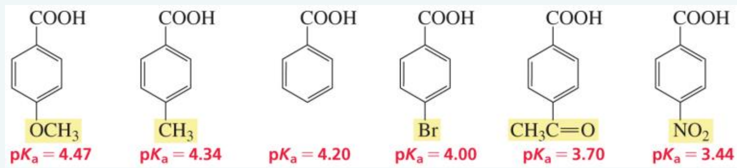
A lone pair on an atom directly attached to the ring donates electrons by resonance.

Resonance Electron Withdrawal



An atom directly attached to the ring that is doubly or triply bonded to an electronegative atom withdraws electrons by resonance.

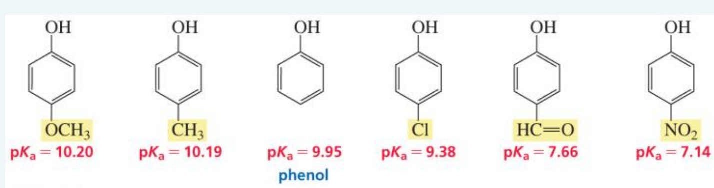
Substituents on the Benzene Ring Affect the pK_a of Benzoic Acid



electron donating groups decrease the acidity
(destabilize the conjugate base)

electron withdrawing groups increase the acidity
(stabilize the conjugate base)

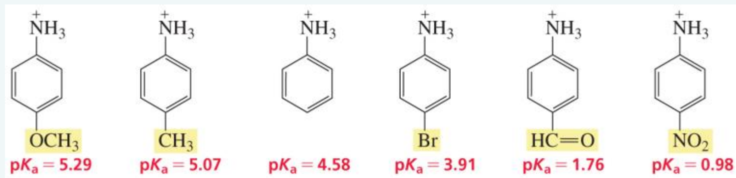
Substituents on the Benzene Ring Affect the pK_a of Phenol



electron donating groups decrease the acidity
(destabilize the conjugate base)

electron withdrawing groups increase the acidity
(stabilize the conjugate base)

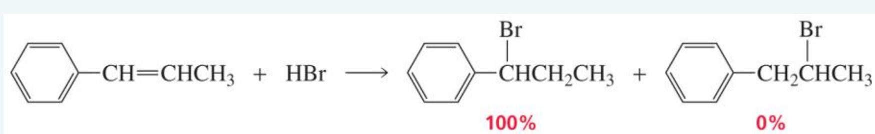
Substituents on the Benzene Ring Affect the pK_a of Protonated Aniline



electron donating groups decrease the acidity
(destabilize the conjugate base)

electron withdrawing groups increase the acidity (stabilize the conjugate base)

Delocalized Electrons can affect the product of a Reaction



a secondary benzylic cation a secondary alkyl carbocation

Isolated and Conjugated Dienes

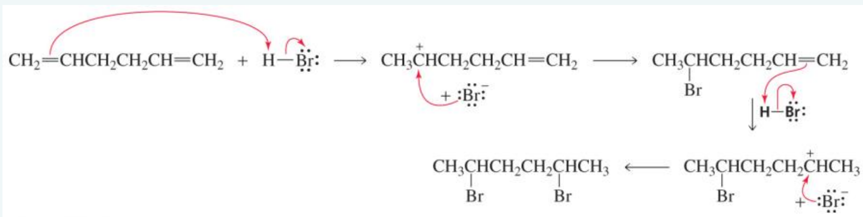
$CH_2{=}CHCH_2CH_2CH{=}CH_2$ — an isolated diene

$CH_3CH{=}CH{-}CH{=}CHCH_3$ — a conjugated diene

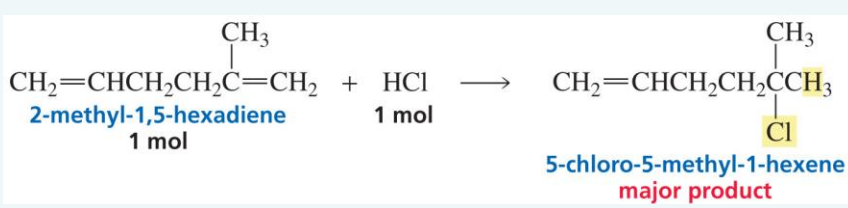
Reactions of Isolated Dienes

$$\underset{\text{1,5-hexadiene}}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + \underset{\text{excess}}{HBr} \longrightarrow CH_3\underset{\substack{|\\ Br}}{C}HCH_2CH_2\underset{\substack{|\\ Br}}{C}HCH_3$$

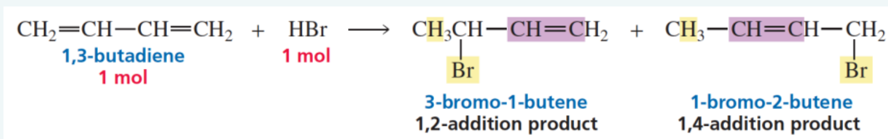
The Mechanism



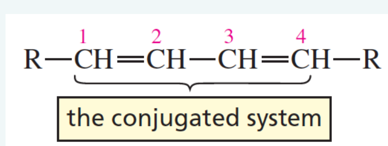
Double Bonds can have Different Reactivities

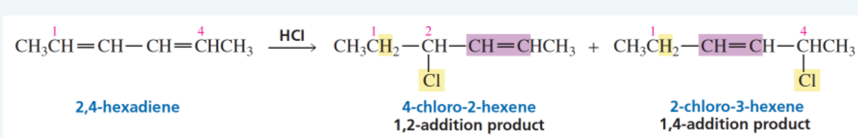


Reactions of Conjugated Dienes

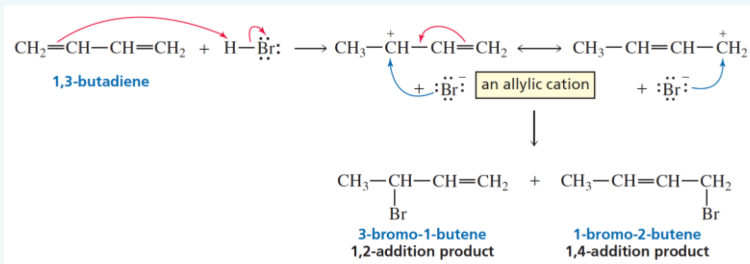


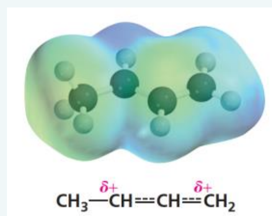
1,2-Addition and 1,4-Addition



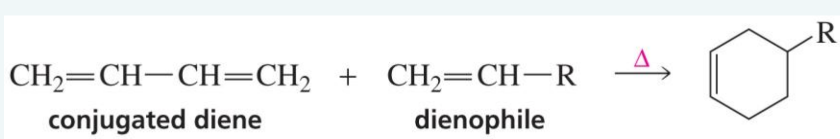


Mechanism for the Reaction of a Conjugated Diene

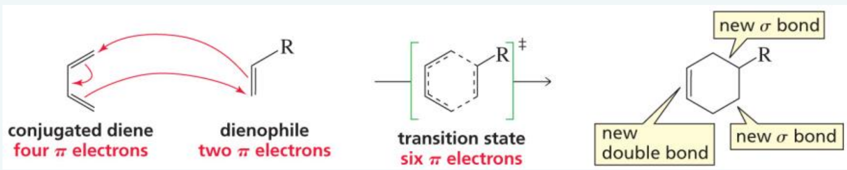




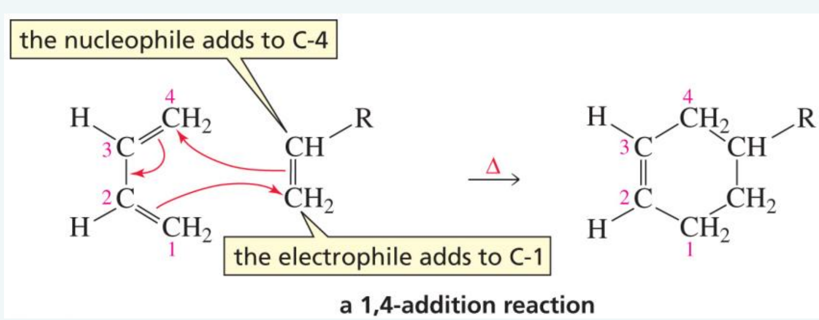
The Diels–Alder Reaction forms a Six-Membered Ring



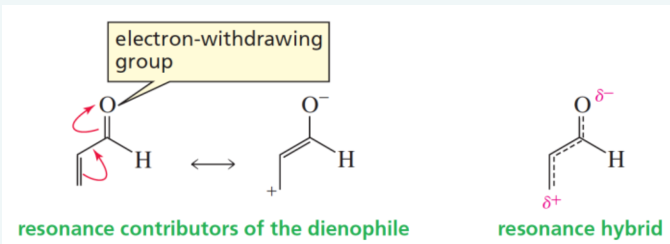
The Mechanism

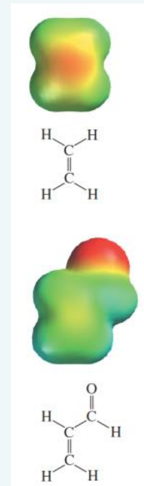


Faster if there is an Electron Withdrawing Group on the Dienophile

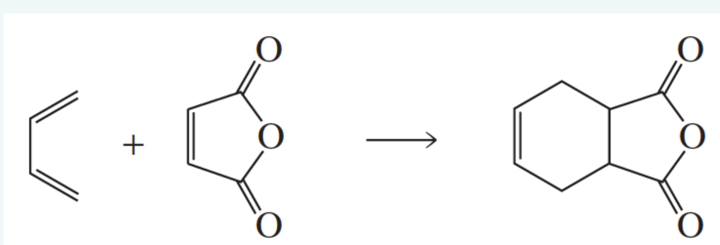


The Electron Withdrawing Group makes the Electrophile a better Electrophile

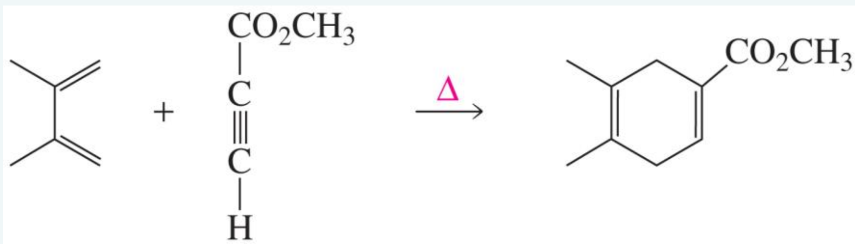




Another Diels–Alder Reaction

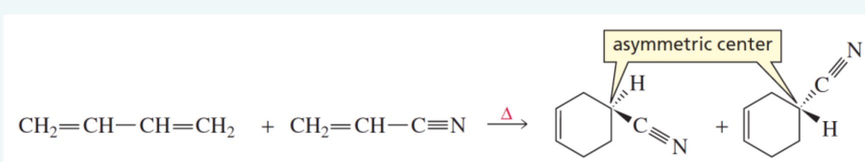


Alkynes can also be Dienophiles



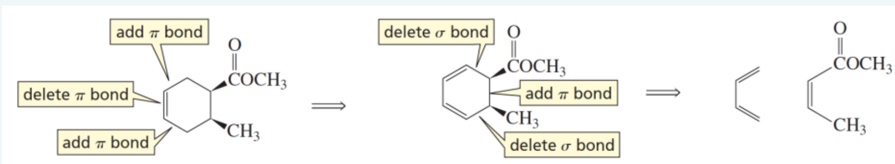
The cyclic product has two double bonds.

The Stereochemistry of the Diels–Alder Reaction

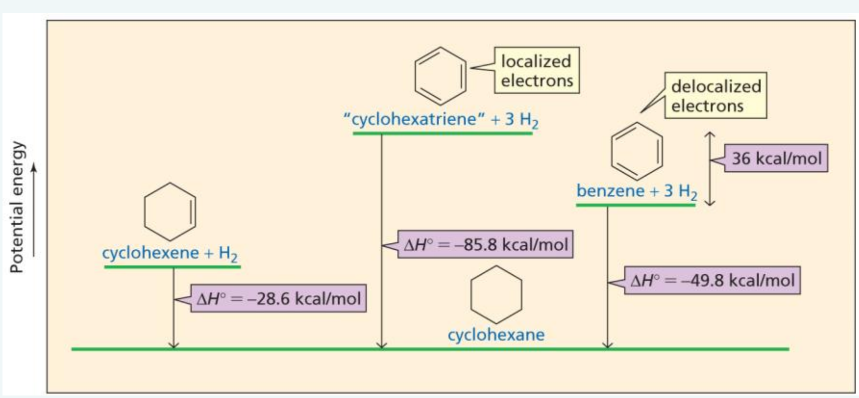


The product will be a racemic mixture.

How to Determine the Reactants of a Diels–Alder Reaction



Benzene is an Aromatic Compound

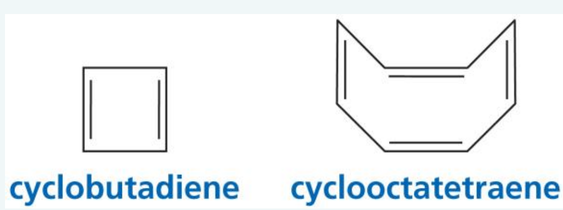


The delocalization energy of benzene is 36 kcal/mol.

Criteria for a Compound to be Aromatic

- It must have an uninterrupted cloud of π electrons.(cyclic, planar, every ring atom must have a *p* orbital).
- The π cloud must have an odd number of pairs of π electrons.

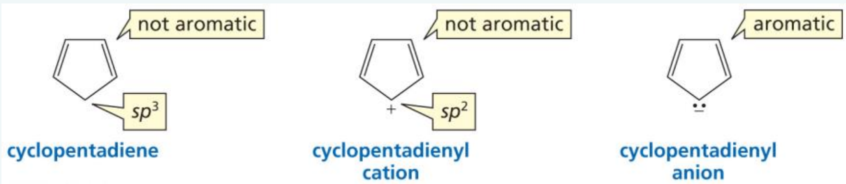
Examples of Compounds that are not Aromatic



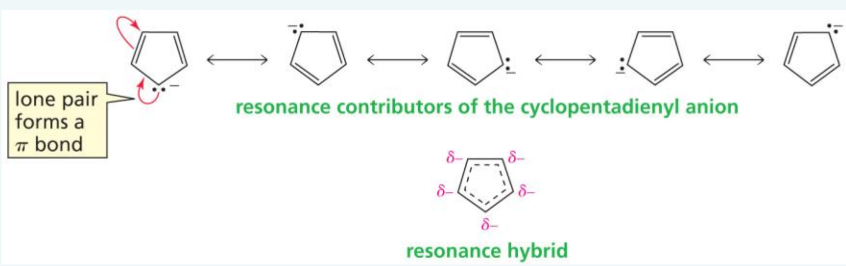
Cyclobutadiene has an even number of pairs of π electrons.

Cyclooctatetraene has an even number of pairs of π electrons and it is not planar.

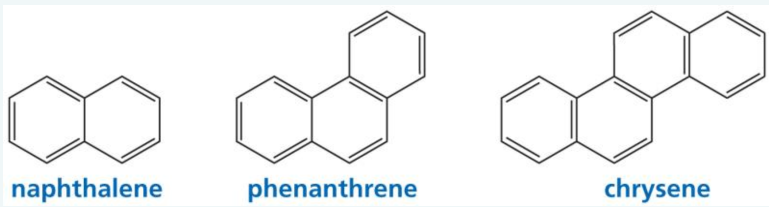
Nonaromatic and Aromatic Compounds



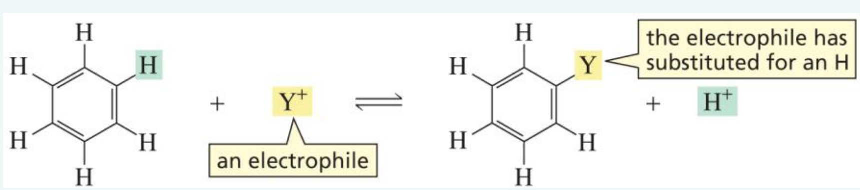
Resonance Contributors and the Resonance Hybrid



Aromatic Compounds

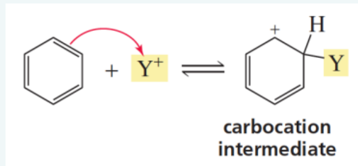


How Benzene Reacts

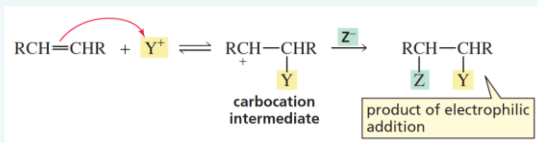


Aromatic compounds such as benzene undergo electrophilic aromatic substitution reactions.

Benzene Reacts with Electrophiles

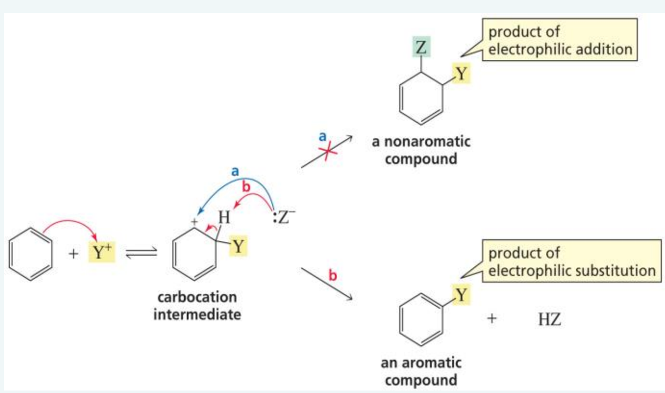


The π electrons above and below the ring make benzene a nucleophile.



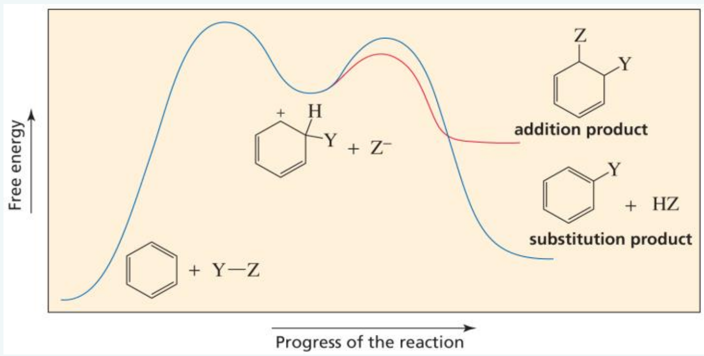
Benzene attacking an electrophile is like an alkene attacking an electrophile.

Benzene undergoes Substitution, not Addition



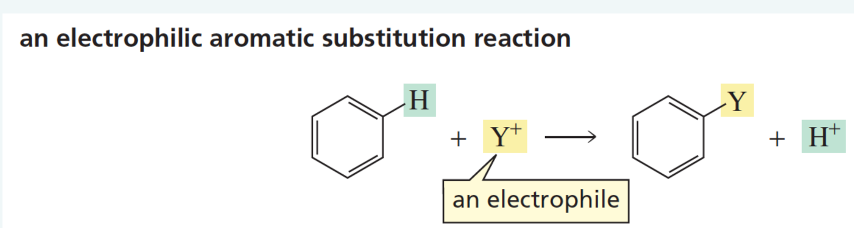
Aromaticity is restored in the product from electrophilic substitution.

Benzene undergoes Substitution, not Addition



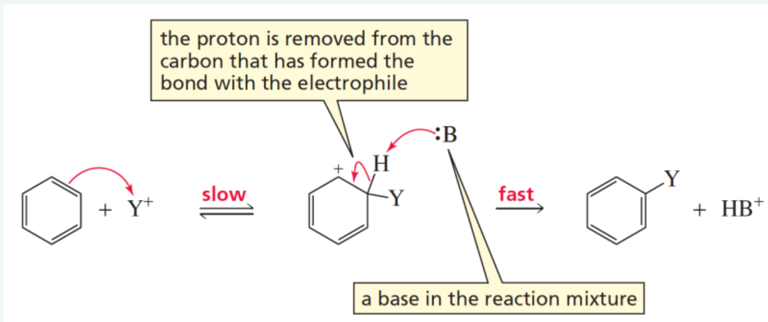
The reaction of benzene with an electrophile forms the aromatic substitution product, not the nonaromatic addition product.

An Electrophilic Aromatic Substitution Reaction

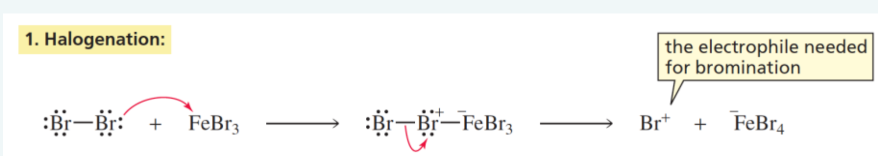


An electrophile (Y^+) substitutes for H^+.

The Mechanism for Electrophilic Aromatic Substitution

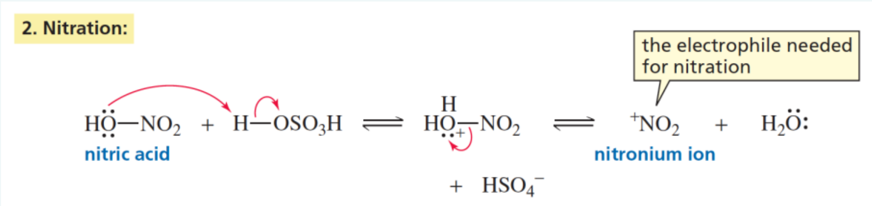


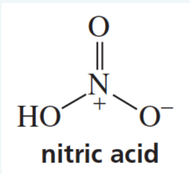
Generating the Electrophile: Halogenation

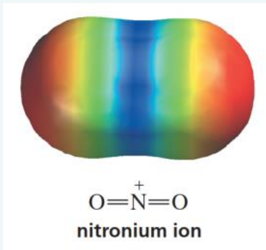


Donating a lone pair to a Lewis acid weakens the Br—Br or Cl—Cl bond.

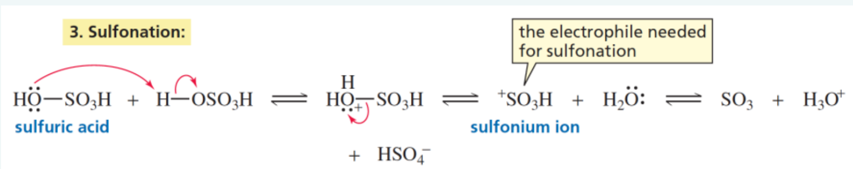
Generating the Electrophile: Nitration



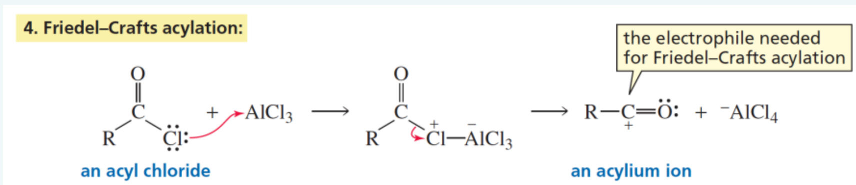


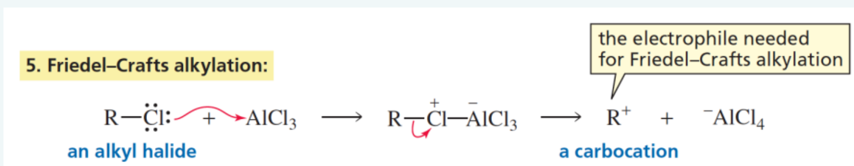


Generating the Electrophile: Sulfonation



Generating the Electrophile: Friedel–Crafts Acylation and Alkylation





Organizing what we know about the Reactions of Organic Compounds