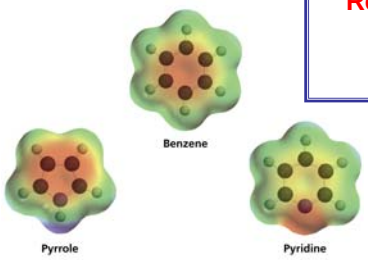
Organic Chemistry
5th Edition
Paula Yurkanis Bruice

Chapter 14

Aromaticity Reactions of Benzene

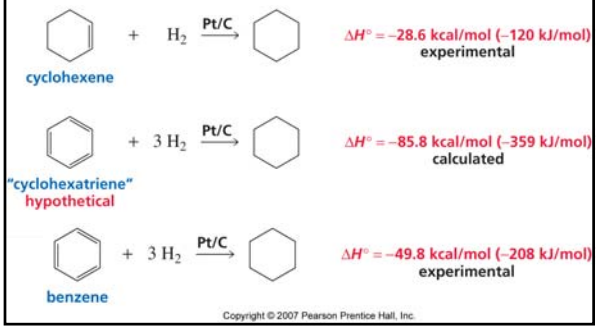


14.1 Aromatic

- In 1825, Michael Faraday, extracted a compound named benzene after heating whale oil under pressure to produce a gas used to illuminate building
- "Pheno" ("to shine)
- Aromatic (pleasing fragrances) vs. aliphatic compounds

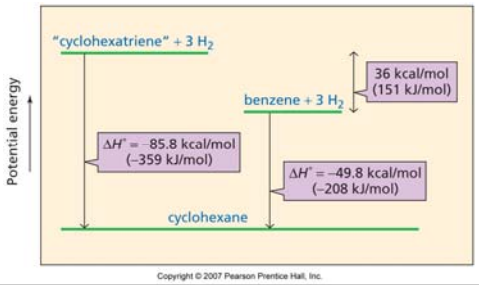
Aromatic Compounds Are Unusually Stable

Benzene is an aromatic compound



Benzene is unusually stable because of electron delocalization

Compounds with unusually large resonance energies, like benzene, are called aromatic compounds



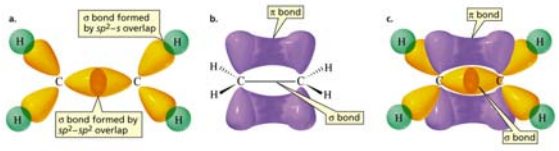
14.2 Criteria for Aromaticity

1. A compound must have uninterrupted cyclic cloud of π electrons above and below the plane of the molecule (cyclic, p orbital, planar)

2. The π cloud must contain an odd number of pairs of π electrons

Bonding in Ethene: A Double Bond

Ethene: $CH_2=CH_2$, sp^2 hybridization



A double bond has one sigma bond and one pi bond.

Hückel's Rule

- For a planar, cyclic compound to be aromatic, its uninterrupted π cloud must contain $(4n + 2)$ π electrons, where *n* is any whole number
- That means (2n+1) pairs of p electrons

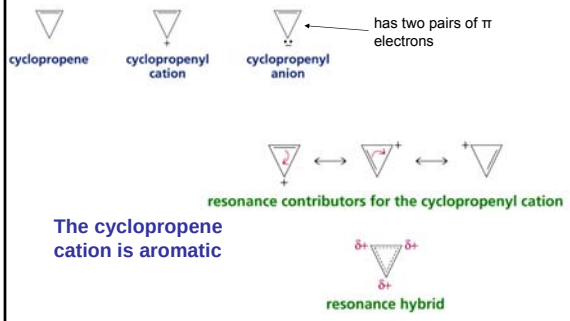
14.3 Aromatic Hydrocarbons

Monocyclic hydrocarbons with alternating single and double bonds are called annulenes

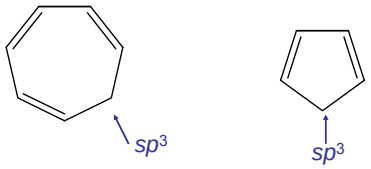
Cyclobutadiene is not aromatic because it has an even number of electron pairs

Cyclooctatetraene is not aromatic because it is nonplanar

Neither cyclopropene nor the cyclopropenyl anion is aromatic



The cyclopropene cation is aromatic



cycloheptatriene

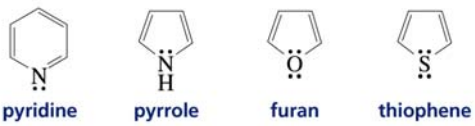
interrupted π cloud not aromatic

cyclopentadiene

2 pairs of π electrons not aromatic

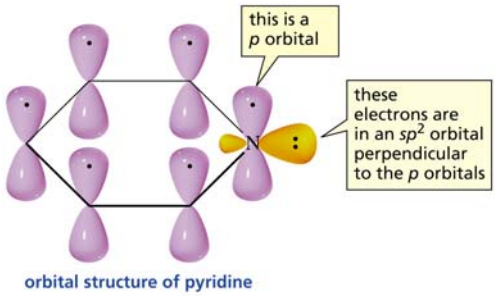
These compounds are aromatic

14.4 Aromatic Heterocyclic Compounds



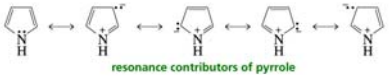
A heterocyclic compound is a cyclic compound in which one or more of the ring atoms is an atom other than carbon

Pyridine Is Aromatic

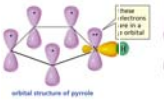


orbital structure of pyridine

Pyrrole Is Aromatic

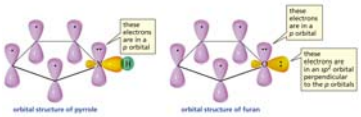


resonance contributors of pyrrole



orbital structure of pyrrole

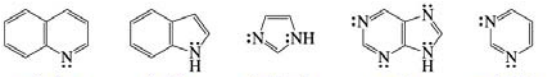
Furan Is Aromatic



orbital structure of pyrrole orbital structure of furan

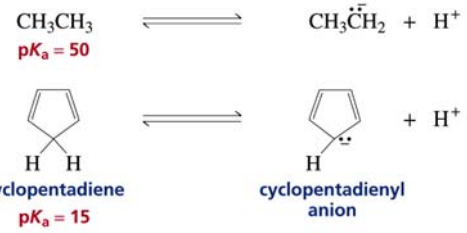
resonance contributors of furan

Examples of Heterocyclic Aromatic Compounds



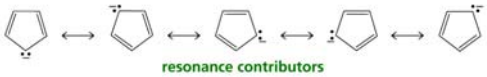
quinoline indole imidazole purine pyrimidine

15.4 The Effect of Aromaticity on the pK_a Values of Some Compounds



The more stable its conjugate base, the stronger is the acid.

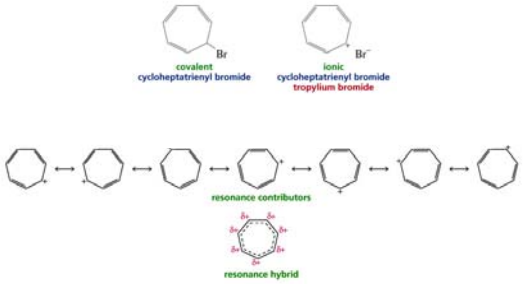
Aromaticity



resonance contributors

resonance hybrid

Aromaticity influences chemical reactivity



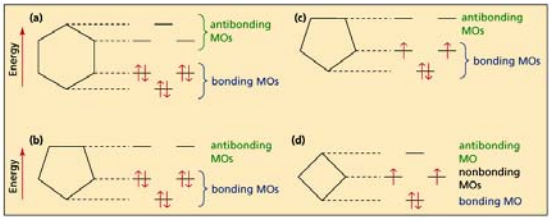
14.6 Antiaromaticity

A compound is antiaromatic if it is a planar, cyclic compound with an uninterrupted ring of π cloud, but it contains even number of pairs of π electrons

relative stabilities

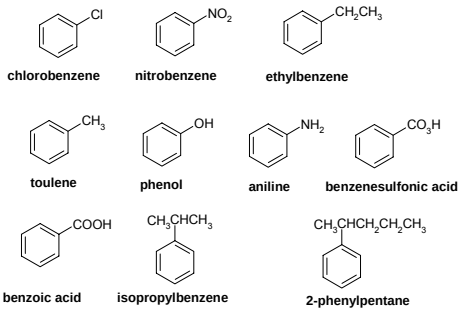
aromatic compound > cyclic compound with localized electrons > antiaromatic compound

15.7 A Molecular Orbital Description of Aromaticity and Antiaromaticity

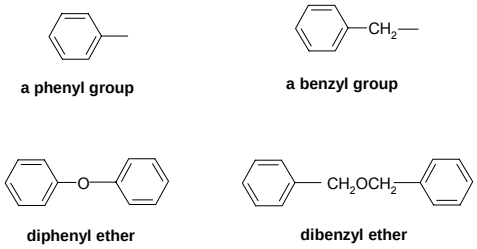


Frost device (or a Frost circle)

14.8 Nomenclature

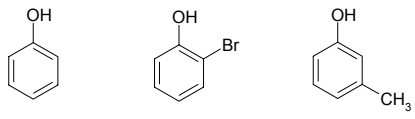


Phenyl and Benzyl Groups

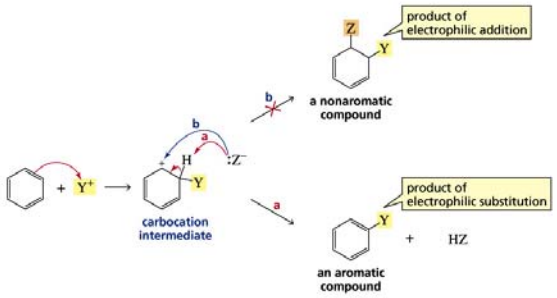


Aryl (Ar) Group

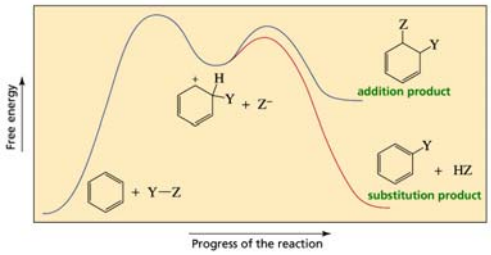
- **An aryl group (Ar) is the general term for either a phenyl group or a substituted phenyl group.**
- **ArOH could be any of the following:**



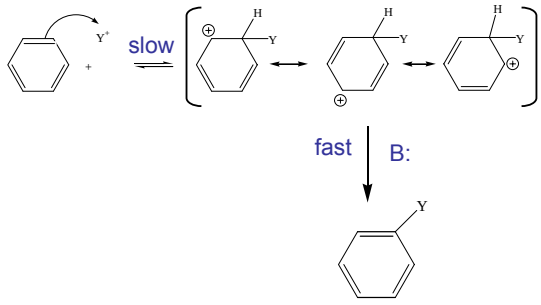
14.9 Benzene is a nucleophile that reacts with an electrophile



Reaction Coordinate Diagrams for the Two Benzene Reactions



14.10 General Mechanism for Electrophilic Aromatic Substitution of Benzene

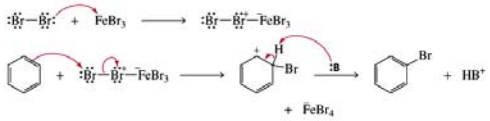


14.11 Halogenation of Benzene

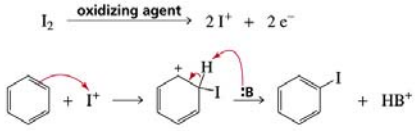
bromination

bromobenzene

mechanism for bromination

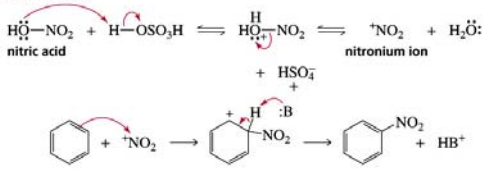


mechanism for iodination



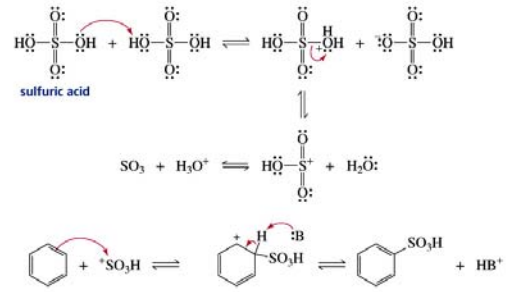
14.12 Nitration of Benzene

mechanism for nitration



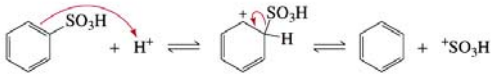
14.13 Sulfonation of Benzene

mechanism for sulfonation

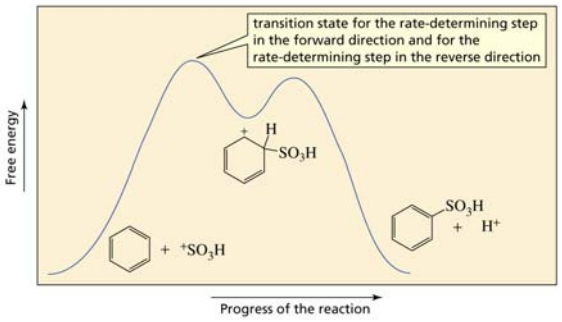


Sulfonation of benzene is a reversible reaction.

mechanism for desulfonation

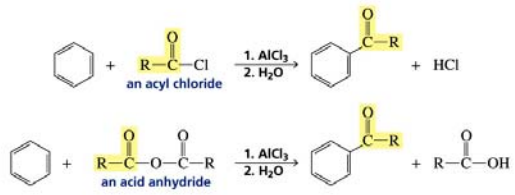


Principle of microscopic reversibility.



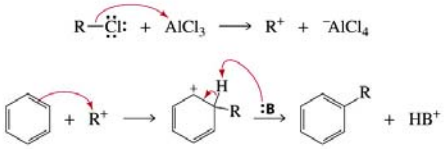
14.14 Friedel–Crafts acylation must be carried out with more than one equivalent of $AlCl_3$

Friedel–Crafts acylation

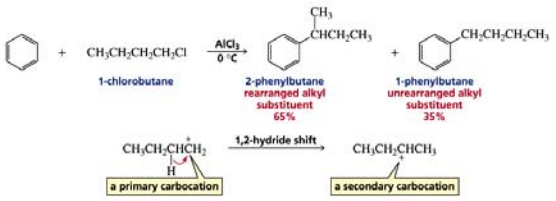


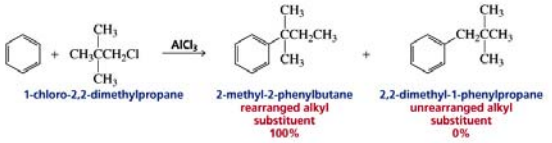
14.15 Friedel-Crafts Alkylation of Benzene

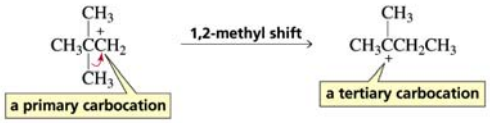
mechanism for the Friedel–Crafts alkylation



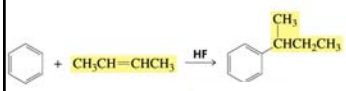
The carbocation will rearrange to a more stable species



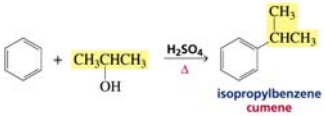




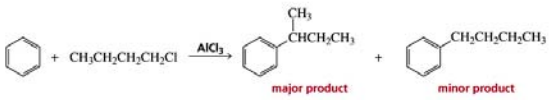
Alkylation of benzene by an alkene



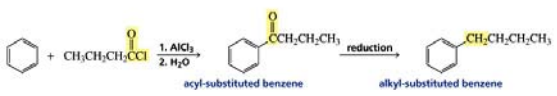
alkylation of benzene by an alcohol



14.16 It is not possible to obtain a good yield of an alkylbenzene containing a straight-chain group via Friedel–Crafts alkylation

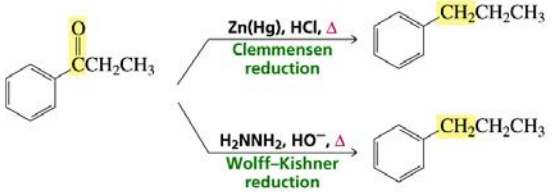


However, a Friedel–Crafts acylation–reduction works well

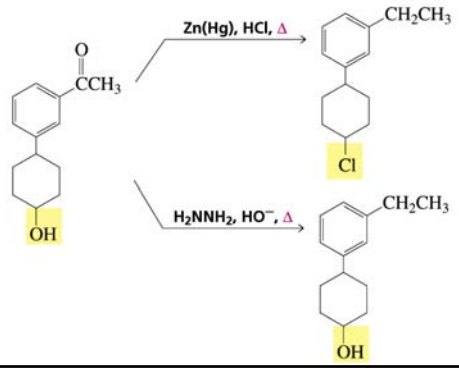


This method avoids using a large excess of benzene in the reaction

Methodologies Used for the Reduction Step

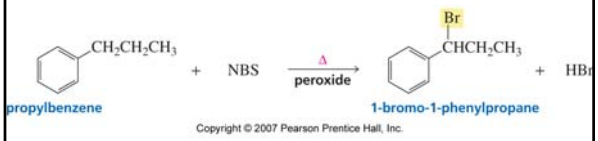


One needs to consider an alternative if there is another functional group present in the compound

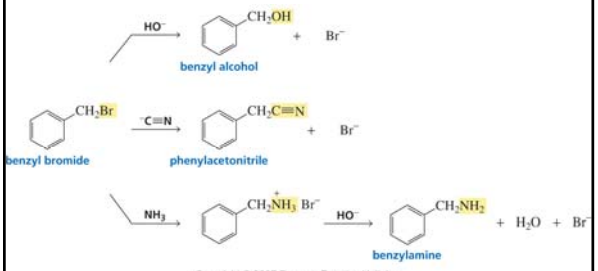


14.19 Chemical Modification of Substituents of Benzene

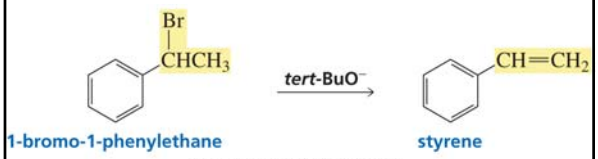
Reactions of alkyl substituents



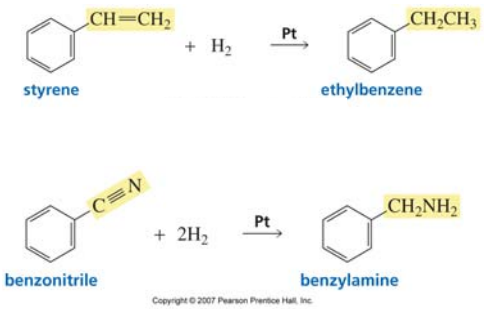
The resulting halide product can undergo a nucleophilic substitution reaction

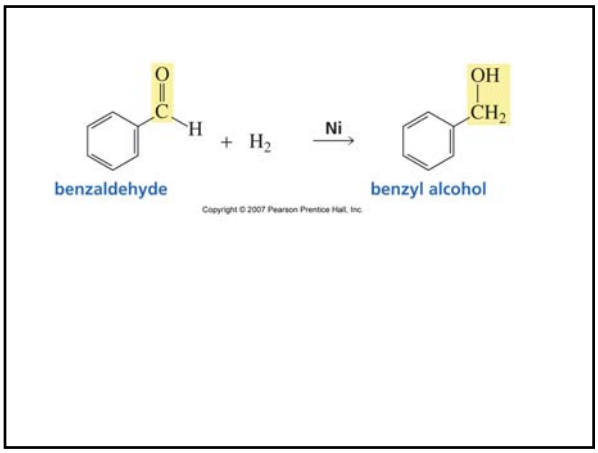


Remember that halo-substituted alkyl groups can also undergo E2 and E1 reactions (Section 9.8)

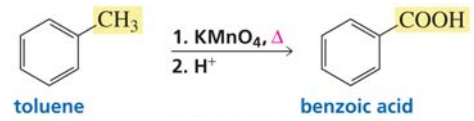


Substitutions with double and triple bonds can undergo catalytic hydrogenation (Section 4.11 and 6.9)

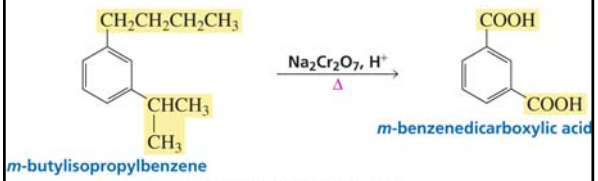




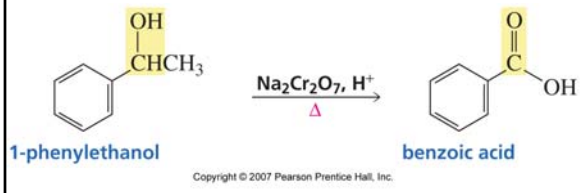
Oxidation of an alkyl group bonded to a benzene ring…



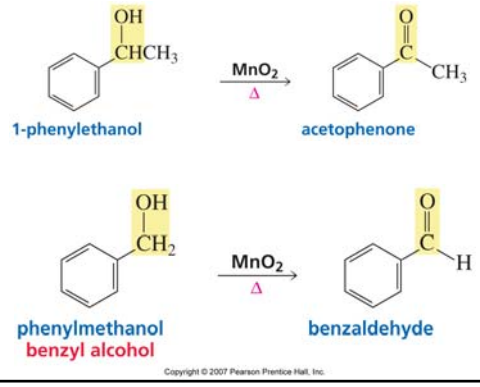
Provided that a hydrogen is bonded to the benzylic carbon,



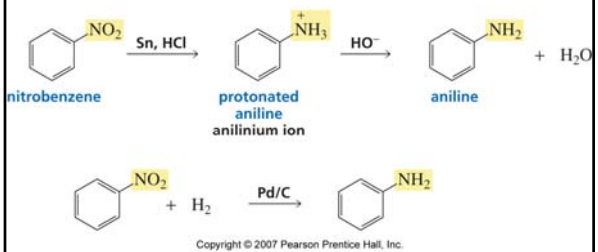
The same reagent that oxidizes alkyl substituents will oxidize benzylic alcohols



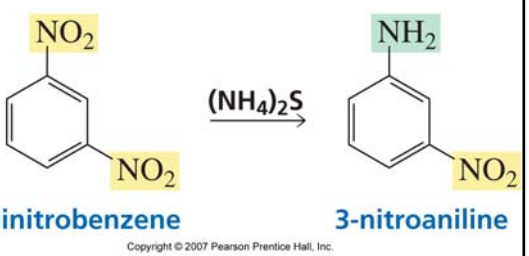
However, aldehydes or ketones can be generated if a milder oxidizing agent is used



Reducing a Nitro Substituent



It is possible to selectively reduce just one of the two nitro groups



Homework

31, 37, 39, 43