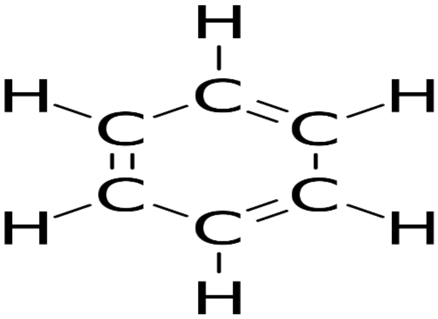
The Islamic University

Department of Pharmaceutical Chemistry

Title of the course: *Organic Chemistry* I

Level: 1st Class, 2nd Semester

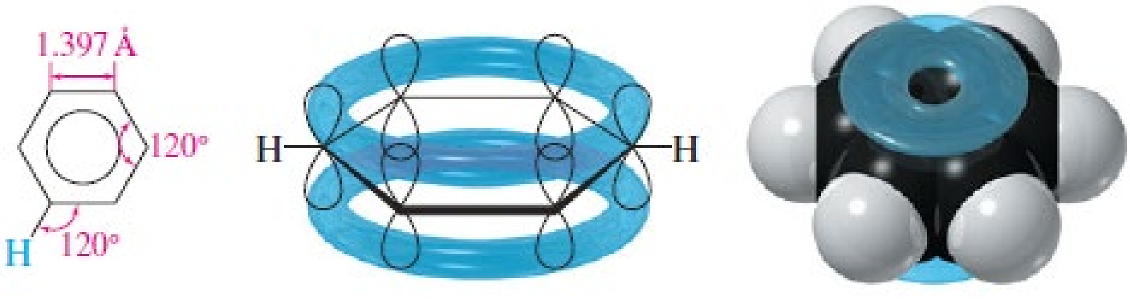
Aromatic



Dr.Tabarek Alnaqib

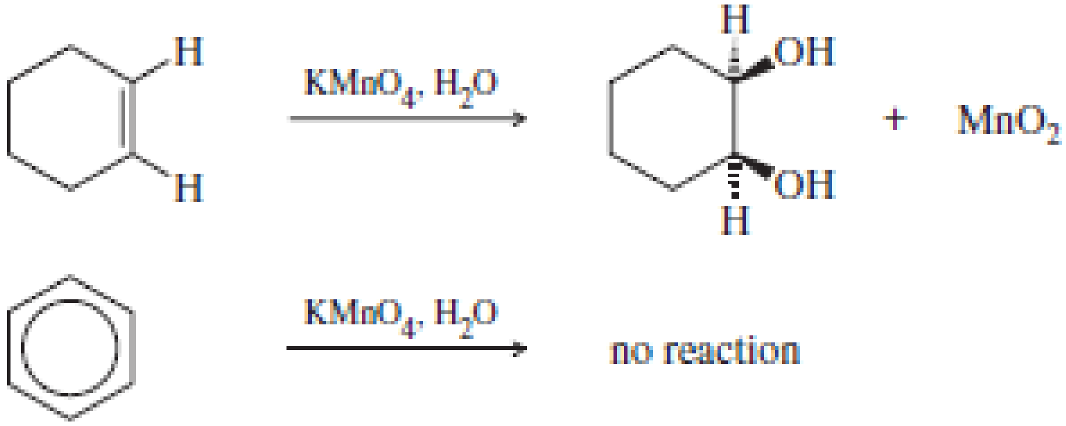
Aromatic compounds : also known as "mono- and polycyclic aromatic hydrocarbons", are organic compounds containing one or more aromatic rings.

Using this resonance picture, we can draw a more realistic representation of benzene . Benzene is **a ring of six sp2** carbon atoms, each bonded to one hydrogen atom. **All the carbon–carbon bonds are the same length**, and all the bond angles are exactly **120°.** **aromatic compound** to be a cyclic compound containing some number of conjugated double bonds and having an unusually large resonance energy.

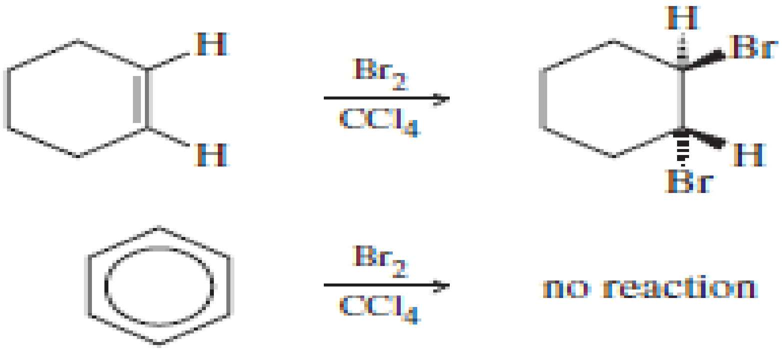


The Unusual Reactions of Benzene

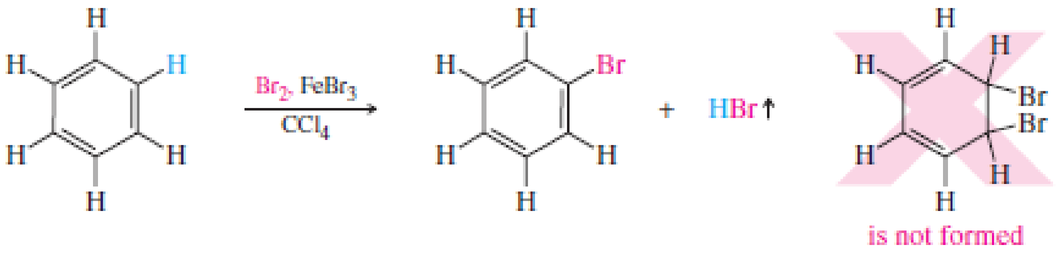
We might expect benzene to undergo the typical reactions of polyenes. In fact, its reactions are quite unusual. For example, an alkene decolorizes potassium permanganate by reacting to form a glycol (Section 8-14). The purple permanganate color disappears,and a precipitate of manganese dioxide forms. When permanganate is added to benzene, however, no reaction occurs.



Most alkenes decolorize solutions of bromine in carbon tetrachloride (Section 8-10).The red bromine color disappears as bromine adds across the double bond. When bromine is added to benzene, no reaction occurs, and the red bromine color remains.

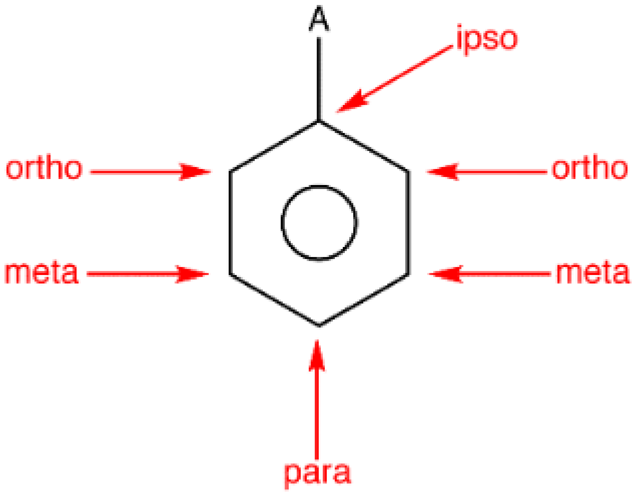


Addition of a catalyst such as ferric bromide to the mixture of bromine and benzene causes the bromine color to disappear slowly. HBr gas is evolved as a by-product, but the expected *addition* of Br_2 does not take place. Instead, the organic product results from *substitution* of a bromine atom for a hydrogen, and all thredouble bonds are retained.



Efficacy and direction in benzene derivatives

Substitution groups can be divided in terms of orientation and activation of electrophilic substitution reactions into three sections:



(1) Activating groups and serve to direct electrophiles to the ortho-para loci. It includes each of the following groups, arranged according to the strength of their influence in directing and activating interaction: where (R) is an alkyl group

$$-\ddot{N}H_2\,(-\ddot{N}HR,\ -\ddot{N}R_2),\ -\ddot{\underset{..}{O}}H\ >\ -\ddot{\underset{..}{O}}R,\ -\ddot{N}HCOCH_3\ >\ -C_6H_5,\ -R$$

(2) Inhibitory groups that direct electrophiles to the ortho-para sites. Halogens include:

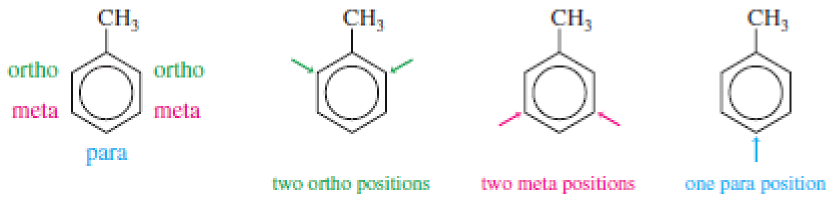
$-\ddot{\underset{\cdot\cdot}{F}}:,\ -\ddot{\underset{\cdot\cdot}{Cl}}:,\ -\ddot{\underset{\cdot\cdot}{Br}}:,\ -\ddot{\underset{\cdot\cdot}{I}}:$

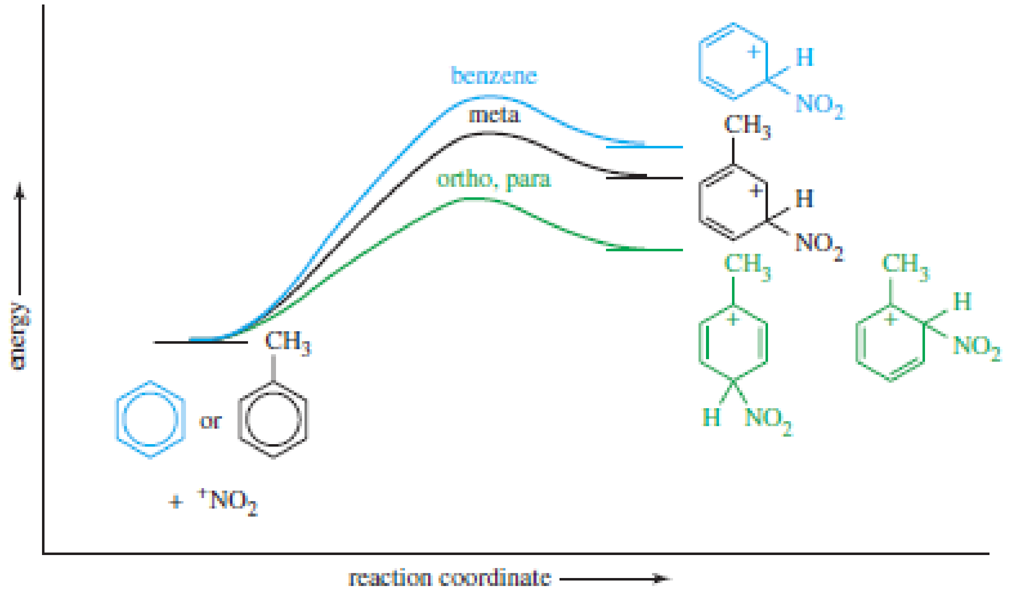
(3) Inhibitory aggregates and serve to direct electrophiles to the meta site. It includes each of the following groups:

$-NO_2,\ -\overset{+}{N}(R)_3,\ -;\ -\ C\equiv N,\ -COOH\,(-COOR),\ -SO_3H,\ -CHO,\ -COR$

Note 1: As the group that gives electrons stabilizes the carbonium ion resulting from the electrophilic attack because it partially contributes to the equation of its positive charge. Thus, the ring is active towards electrophilic substitution. While the group that attracts electrons acts on the instability of the carbonium ion because it contributes to increasing its positive charge, and thus inhibits the ring towards electrophilic substitution.

Example : Nitration of toluene gives a mixture of products, primarily those resulting frommsubstitution at the ortho and para positions. Because of this preference, we say that the methyl group of toluene is an **ortho, para-director.**





The methyl group in toluene is electron-donating; it stabilizes the intermediate sigma complex and the rate-limiting transition state leading to its formation. This stabilizing effect is large when it is situated ortho or para to the site of substitution and the positive charge is delocalized onto the tertiary carbon atom. When substitution occurs at the meta position, the positive charge is not delocalized onto the tertiary carbon, and the methyl group has a smaller effect on the stability of the sigma complex. compares the reaction-energy diagrams for nitration of benzene and toluene at the ortho, meta, and para positions.

Energies Benzene

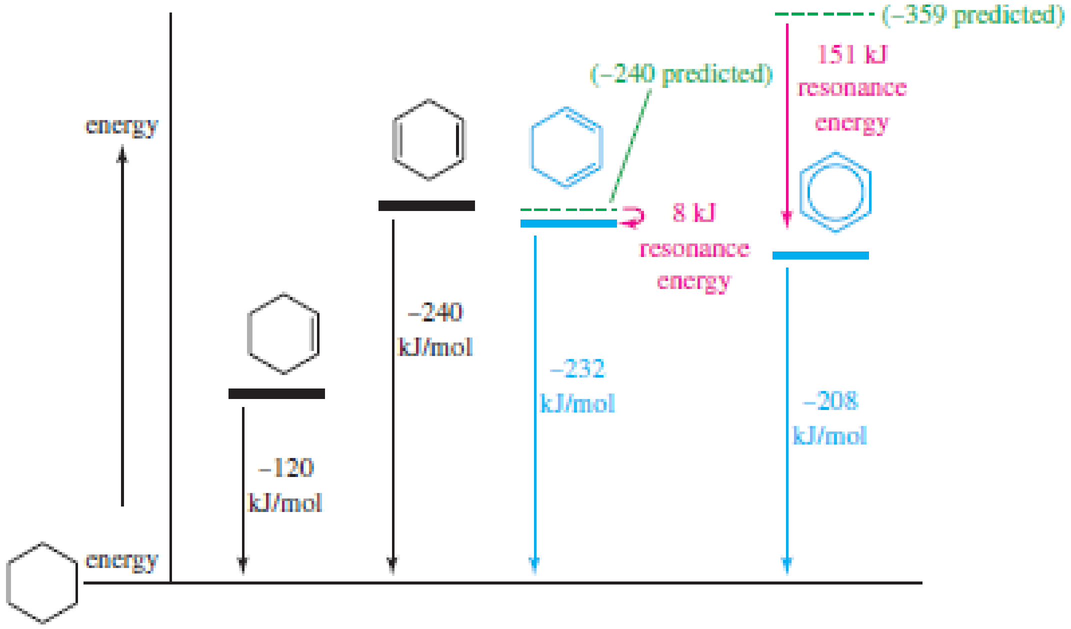
Figure shows how the experimentally determined heats of hydrogenation are used to compute the **resonance energies** of cyclohexa-1,3-diene and benzene, based on the following reasoning:

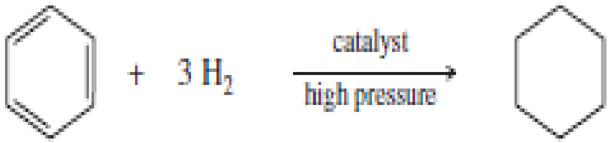
1. Hydrogenation of cyclohexene is exothermic by 120 kJ mol

2. Hydrogenation of cyclohexa-1,4-diene is exothermic by 240 kJ mol

3. Hydrogenation of cyclohexa-1,3-diene is exothermic by 232 kJ mol

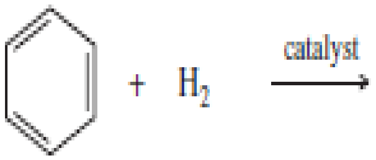
4. Hydrogenation of benzene requires higher pressures of hydrogen and a more active catalyst. This hydrogenation is exothermic by 208 kJ mol, about 151 kJ less than 3 times the value for cyclohexene.





ΔH° = 208 kJ/mol
3 × cyclohexene = 359 kJ/mol
resonance energy = 151 kJ/mol

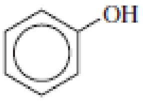
The huge 151 kJ mol (36 kcal mol) resonance energy of benzene cannot be explained by conjugation effects alone. The heat of hydrogenation for benzene is actually smaller than that for cyclohexa-1,3-diene. The hydrogenation of the *first* double bond of benzene is endothermic, the first endothermic hydrogenation we have encountered.In practice, this reaction is difficult to stop after the addition of 1 mole of because the product (cyclohexa-1,3-diene) hydrogenates more easily than benzene itself. Clearly,the benzene ring is exceptionally unreactive.



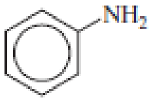
	$\Delta H^\circ_{\text{hydrogenation}}$	
benzene:	-208 kJ	(-49.8 kcal)
cyclohexa-1,3-diene:	-232 kJ	(-55.4 kcal)
$\Delta H^\circ =$	$+24$ kJ	($+5.6$ kcal)

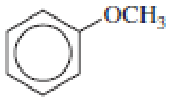
Nomenclature of Benzene Derivatives

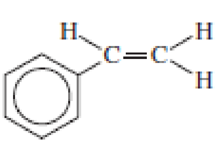
IUPAC names:

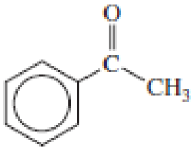

common name: phenol
(benzenol)

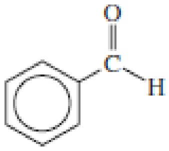

toluene
(methylbenzene)

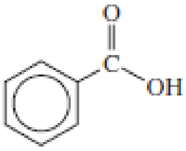

aniline
(benzenamine)


anisole
(methoxybenzene)

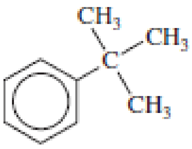

common name: styrene
(vinylbenzene)

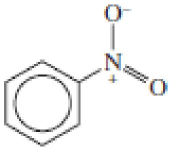

acetophenone
(methyl phenyl ketone)

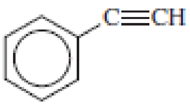

benzaldehyde

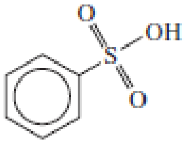

benzoic acid

Many compounds are named as derivatives of benzene, with their substituents named just as though they were attached to an alkane.

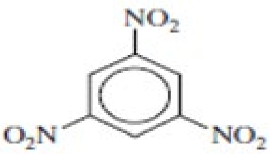

tert-butylbenzene


nitrobenzene

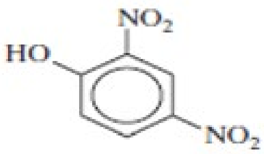

ethynylbenzene
(phenylacetylene)


benzenesulfonic acid

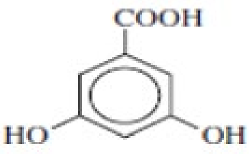
Disubstituted benzenes are named using the prefixes **ortho-, meta-,** and **para-** to specify the substitution patterns. These terms are abbreviated *o*-, *m*-, and *p*-. Numbers can also be used to specify the substitution in disubstituted benzenes.



1,3,5-trinitrobenzene

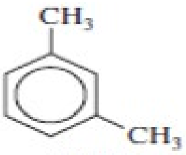


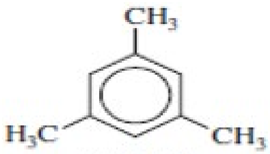
2,4-dinitrophenol

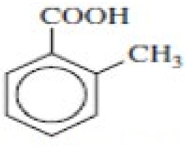


3,5-dihydroxybenzoic acid

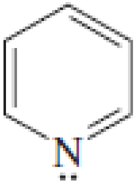
Many disubstituted benzenes (and polysubstituted benzenes) have historical names. Some of these are obscure, with no obvious connection to the structure of the molecule.





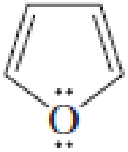


common name:	*m*-xylene	mesitylene	*o*-toluic acid
IUPAC name:	1,3-dimethylbenzene	1,3,5-trimethylbenzene	2-methylbenzoic acid

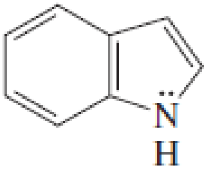


pyridine

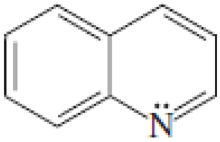
pyrrole



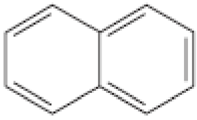
furan



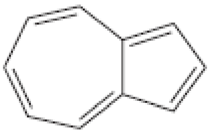
indole



quinoline



naphthalene



azulene

Physical Properties of Benzene and Its Derivatives

1. Benzene derivatives tend to be more symmetrical than similar aliphatic compounds, so they pack better into crystals and have higher melting points.

2. Benzene and other aromatic hydrocarbons are slightly denser than the nonaromatic analogues, but they are still less dense than water. The halogenated benzenes are denser than water.

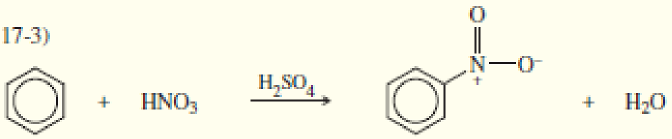
3. Aromatic hydrocarbons and halogenated aromatics are generally insoluble in water, although some derivatives with strongly polar functional groups (phenol, benzoic acid, etc.) are moderately soluble in water.

Reactions of Aromatic Compounds

1. *Electrophilic aromatic substitution*
   a. *Halogenation* (Section 17-2)

bromobenzene

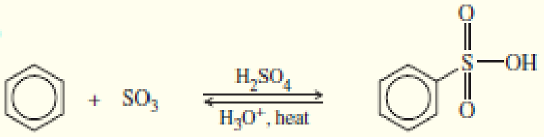
   b. *Nitration* (Section 17-3)



nitrobenzene

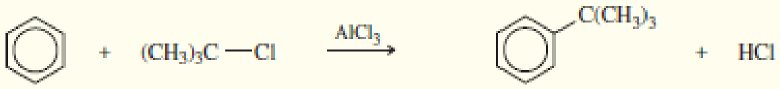
Nitration followed by reduction gives anilines.

   c. *Sulfonation* (Section 17-4)



benzenesulfonic acid

   d. *Friedel–Crafts alkylation* (Section 17-10)

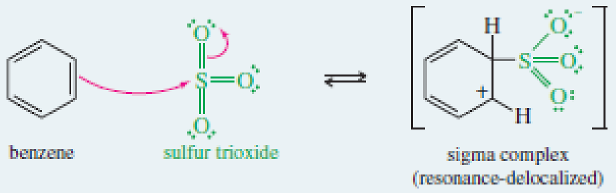


tert-butylbenzene

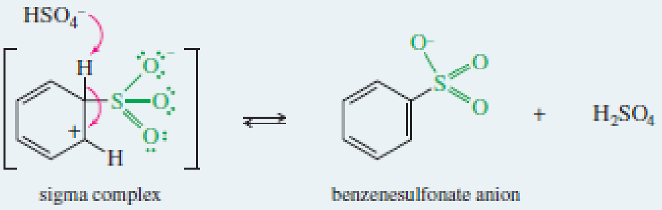
(Continued)

Sulfur trioxide is a powerful electrophile.

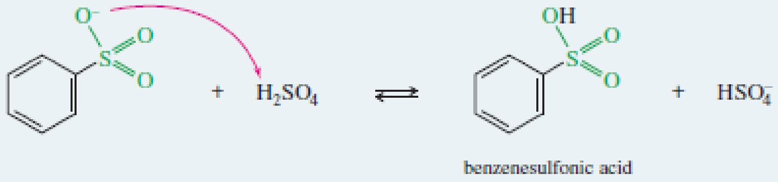
Step 1: Attack on the electrophile forms the sigma complex.



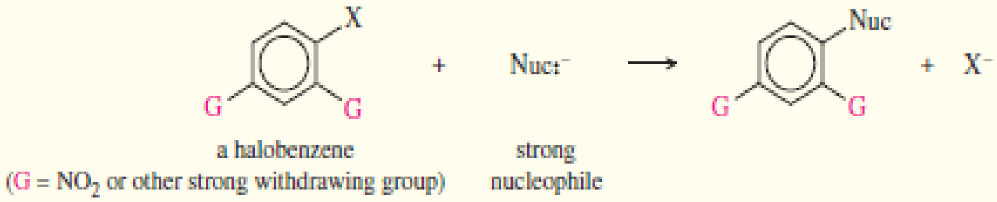
Step 2: Loss of a proton regenerates an aromatic ring.



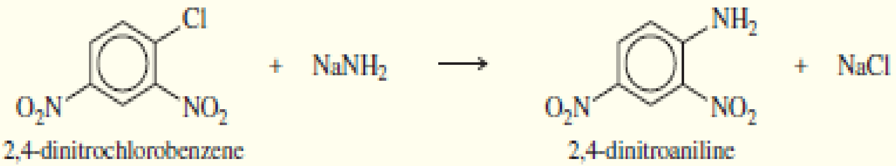
Step 3: The sulfonate group may become protonated in strong acid.



2. *Nucleophilic aromatic substitution* (Section 17-12)



Example



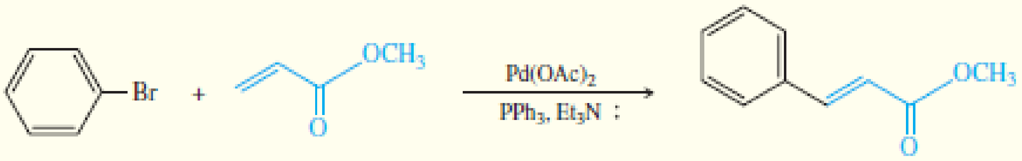
If G is not a strong electron-withdrawing group, severe conditions are required, and a benzyne mechanism is involved (Section 17–12B).

3. *Organometallic Couplings*

a. *Organocuprate couplings* (Section 17-13A)

iodobenzene lithium divinylcuprate styrene

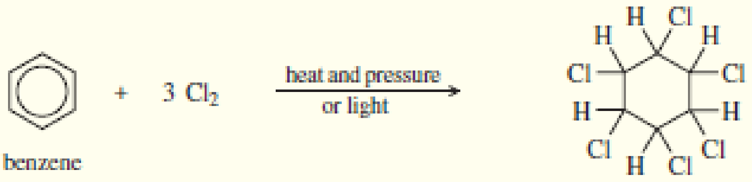
b. *Heck coupling* (Section 17-13B)



bromobenzene methyl acrylate methyl cinnamate

4. *Addition reactions*

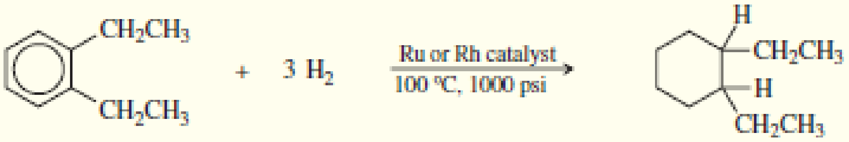
a. *Chlorination* (Section 17-14A)



benzene

benzene hexachloride (BHC)

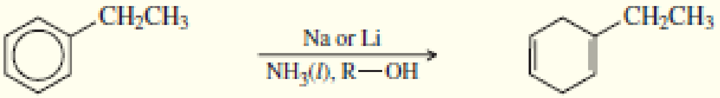
b. *Catalytic hydrogenation* (Section 17-14B)



o-diethylbenzene

1,2-diethylcyclohexane
(mixture of cis and trans)

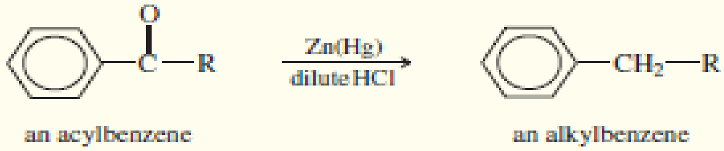
c. *Birch reduction* (Section 17-14C)



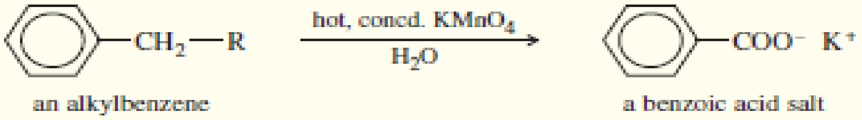
ethylbenzene 1-ethylcyclohexa-1,4-diene

5. ***Side-chain reactions***

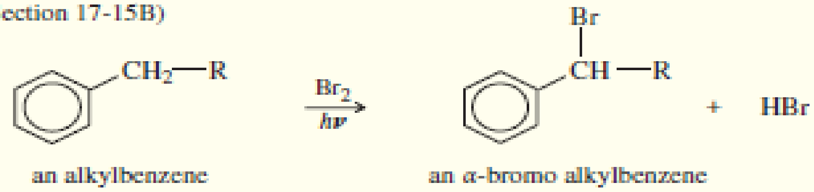
a. *The Clemmensen reduction* (converts acylbenzenes to alkylbenzenes, Section 17-11B)



b. *Permanganate oxidation* (Section 17-15A)



c. *Side-chain halogenation* (Section 17-15B)



6. ***Oxidation of phenols to quinones*** (Section 17-16A)