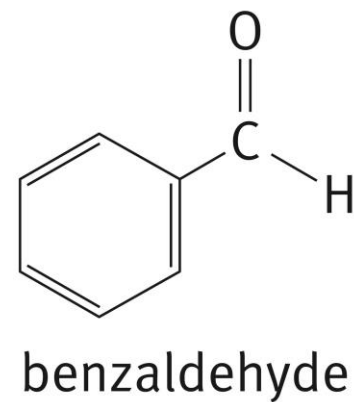
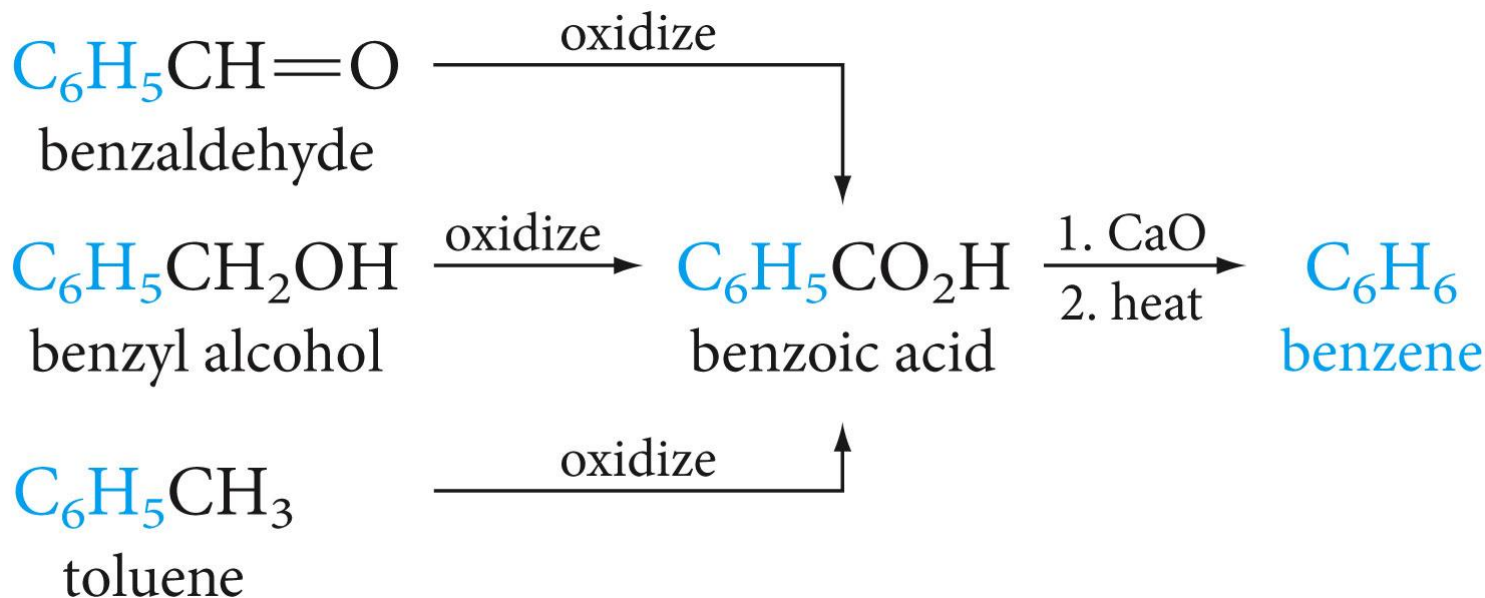


Chapter 4: Aromatic Compounds



Bitter almonds are the source of the aromatic compound benzaldehyde

Sources of Benzene

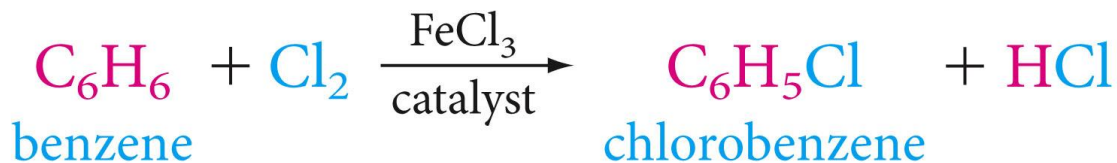
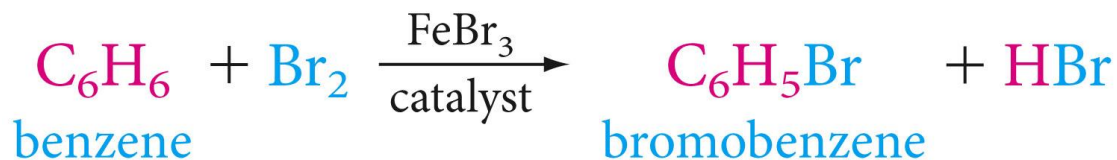


Benzene, C_6H_6 , is the parent hydrocarbon of the especially stable compounds known as **aromatic compounds**.

4.1 Some Facts About Benzene

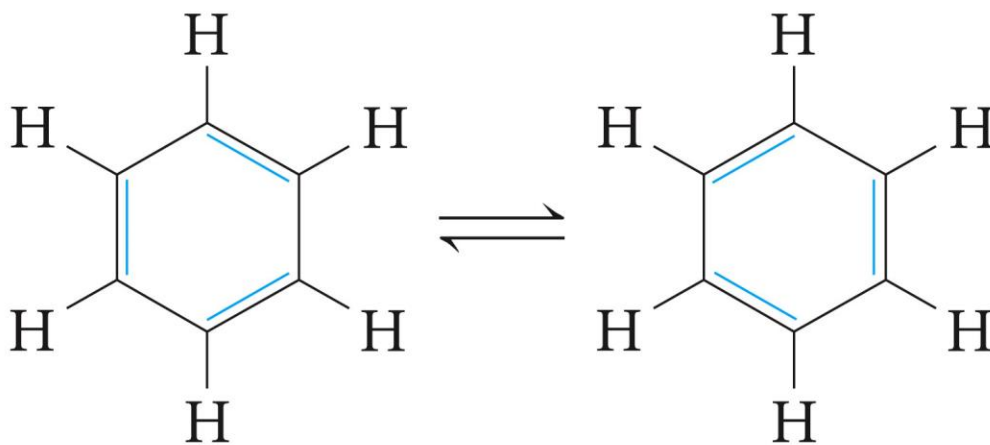
- The carbon-to-hydrogen ratio in benzene, C_6H_6 , suggests a highly unsaturated structure.
- Despite its molecular formula, benzene for the most part does not behave as if it were unsaturated.
- it does not decolorize bromine solutions .
- it not easily oxidized by potassium permanganate.

Reacts *mainly* by substitution



4.2 The Kekulé Structure for Benzene

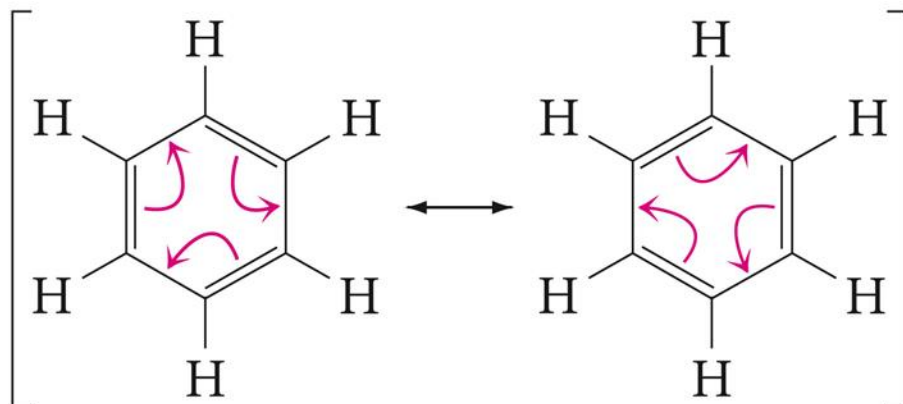
In 1865, Kekulé proposed a reasonable structure for benzene



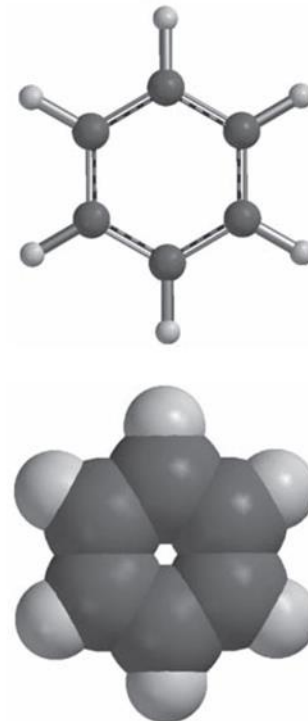
the Kekulé structures for benzene

Kekulé's two structures for benzene *differ only* in the arrangement of the electrons; all of the atoms occupy the same positions in both structures.

4.3 The Resonance Structure of Benzene



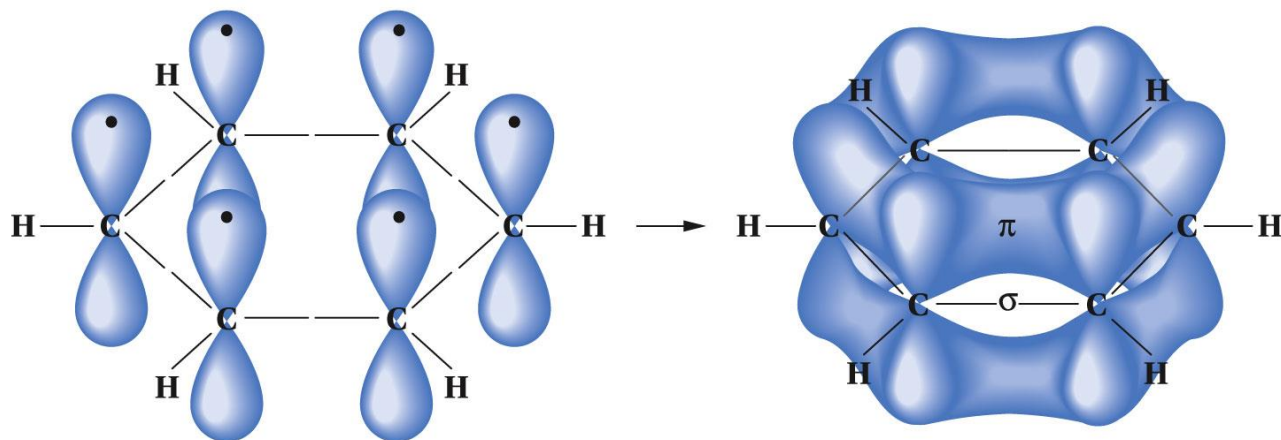
Benzene is a resonance hybrid of these two contributing structures.



Modern physical measurements support this model for the benzene structure:

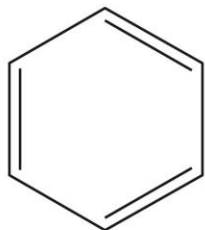
- Benzene is planar.
- Each carbon atom is at the corner of a regular hexagon.
- All of the carbon-carbon bond lengths are identical: 1.39 Å, intermediate between typical single (1.54 Å) and double (1.34 Å) carbon-carbon bond lengths.

4.4 The Orbital Model for Benzene

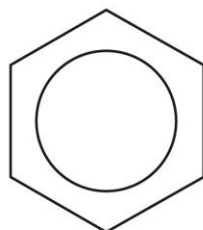


The p orbitals on all six carbon atoms can overlap laterally to form pi orbitals that create a ring or cloud of electrons above and below the plane of the ring.

4.5 Symbols for Benzene



Kekulé



delocalized pi cloud

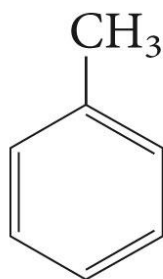
4.6 Nomenclature of Aromatic Compounds

Common names have acquired historic respectability and are accepted by IUPAC.

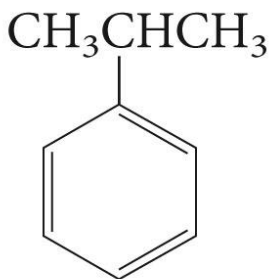
Monosubstituted benzenes with common names



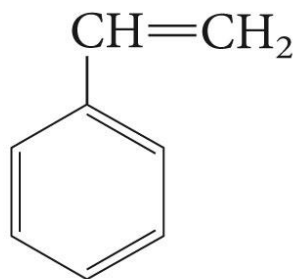
benzene



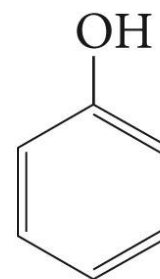
toluene



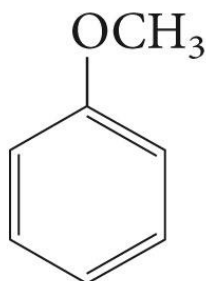
cumene



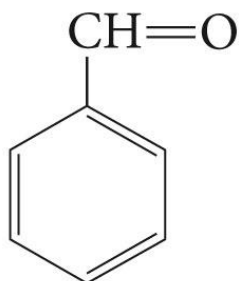
styrene



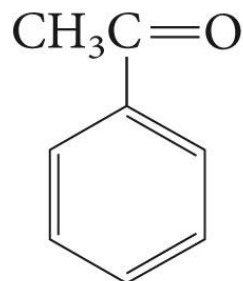
phenol



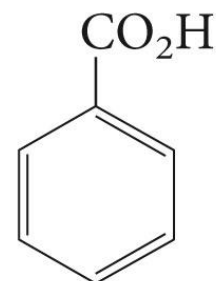
anisole



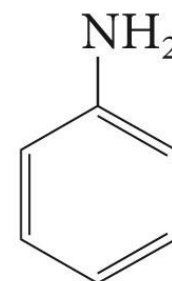
benzaldehyde



acetophenone

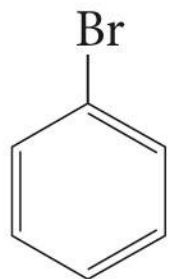


benzoic acid

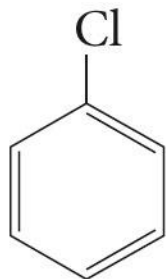


aniline

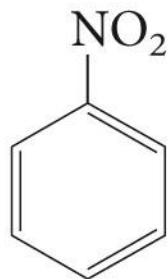
Monosubstituted benzenes that do not have common names



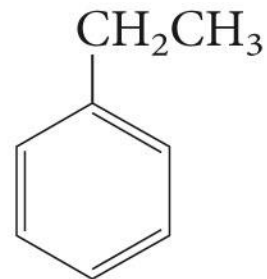
bromobenzene



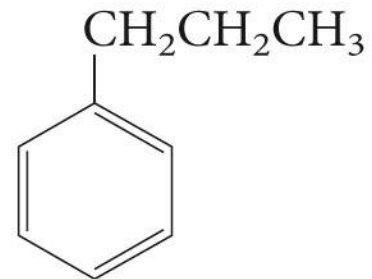
chlorobenzene



nitrobenzene

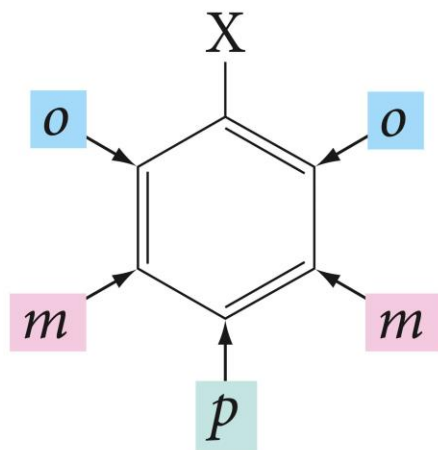


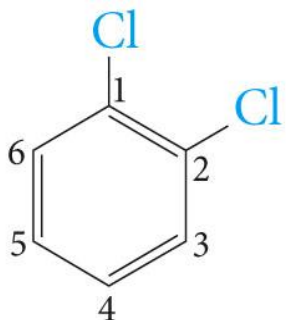
ethylbenzene



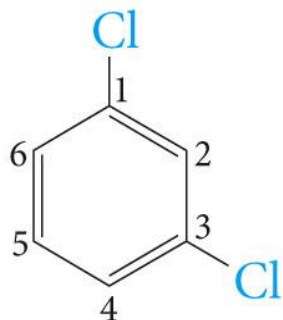
propylbenzene

When two substituents are present, we use prefixes *ortho-*, *meta-*, and *para-*, usually abbreviated as o-, m-, and p-, respectively.

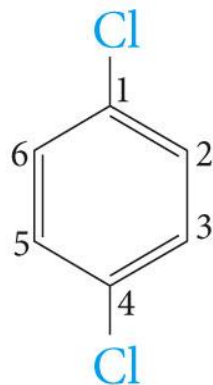




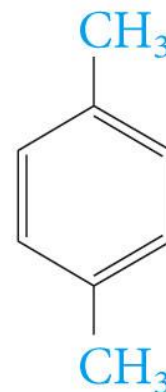
ortho-dichloro-
benzene



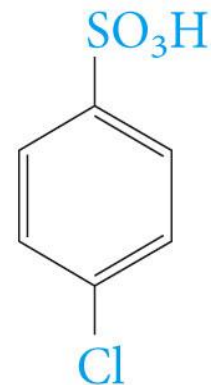
meta-dichloro-
benzene



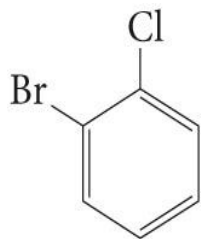
para-dichloro-
benzene



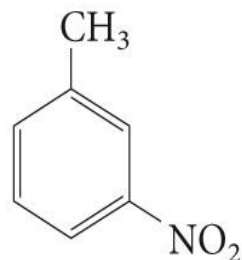
para-xylene**



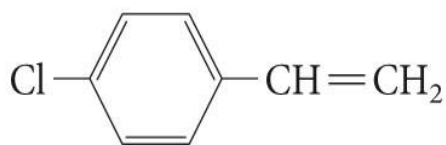
para-chlorobenzenesulfonic acid



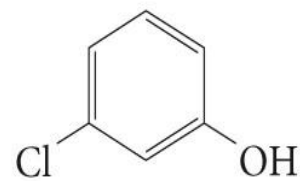
o-bromochlorobenzene
(note alphabetical order)



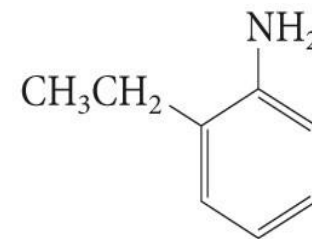
m-nitrotoluene



p-chlorostyrene

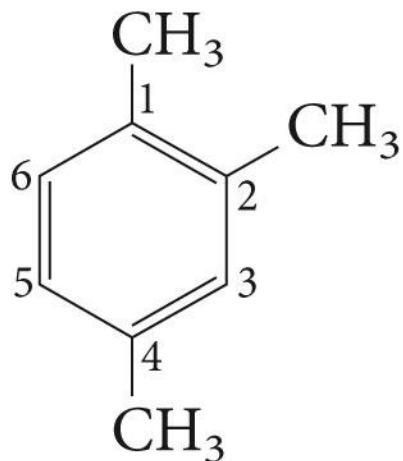


m-chlorophenol

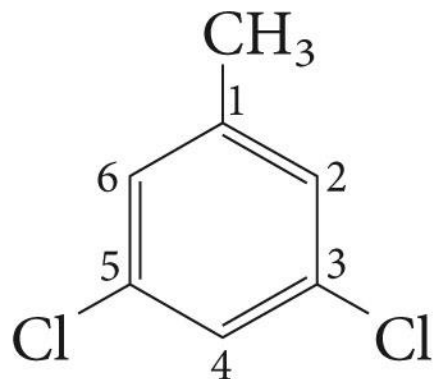


o-ethylaniline

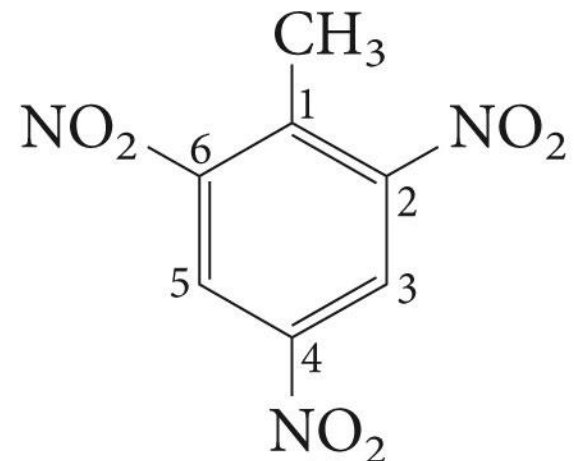
For more than two substituents, their positions are designated by numbering the ring.



1,2,4-tri-
methylbenzene

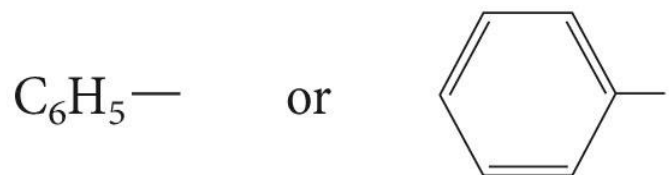


3,5-dichlorotoluene

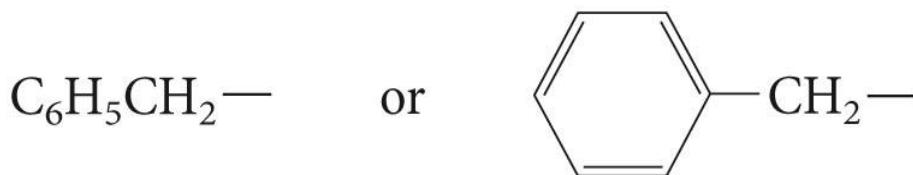


2,4,6-trinitrotoluene
(TNT)

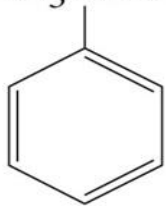
Aromatic hydrocarbons, as a class called Arenes (Ar) the aryl groups are therefore aromatic substituents.



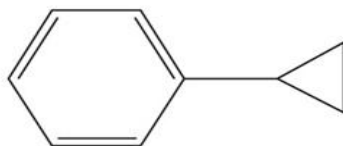
phenyl group



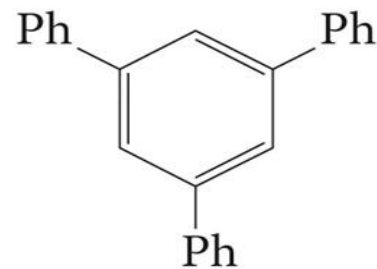
benzyl group



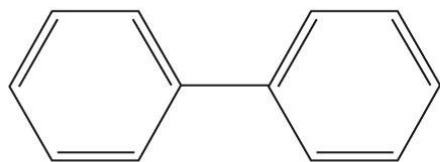
2-phenylpentane
(or 2-pentylbenzene)



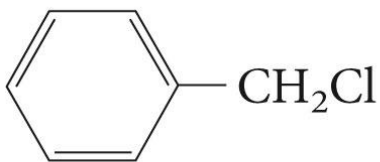
phenylcyclopropane
(or cyclopropylbenzene)



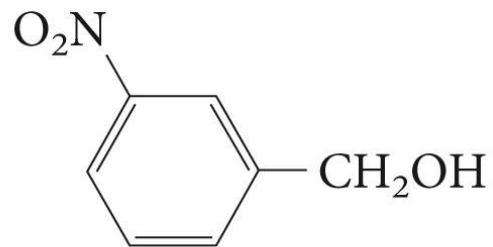
1,3,5-triphenylbenzene



biphenyl



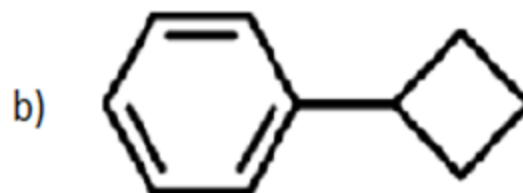
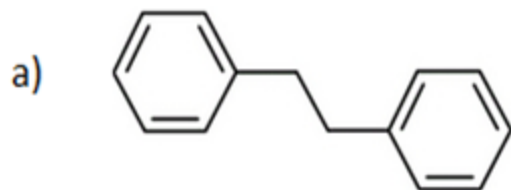
benzyl chloride

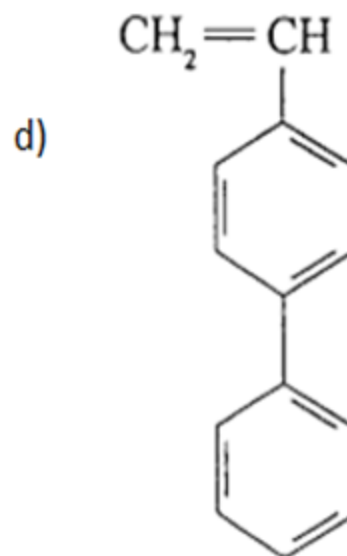
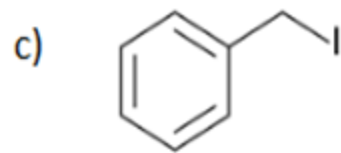


m-nitrobenzyl alcohol

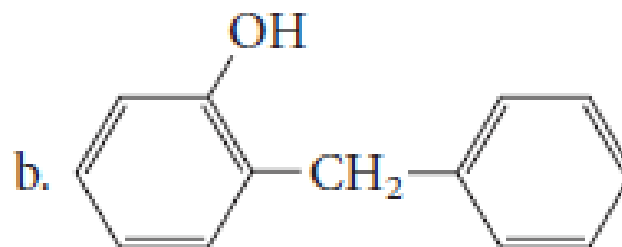
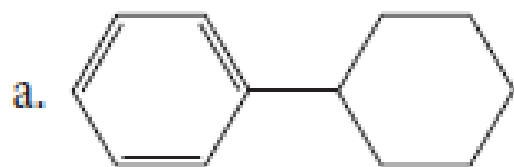
PROBLEM 4.9 Draw the structure of

- a. dibenzyl b. cyclobutylbenzene
c. benzyl iodide d. *p*-phenylstyrene





PROBLEM 4.10 Name the following structures:



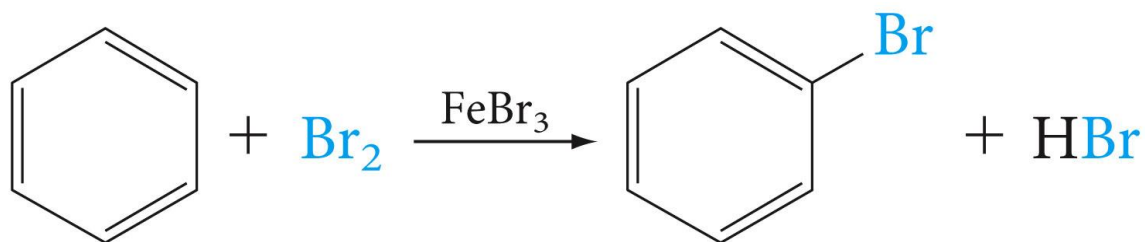
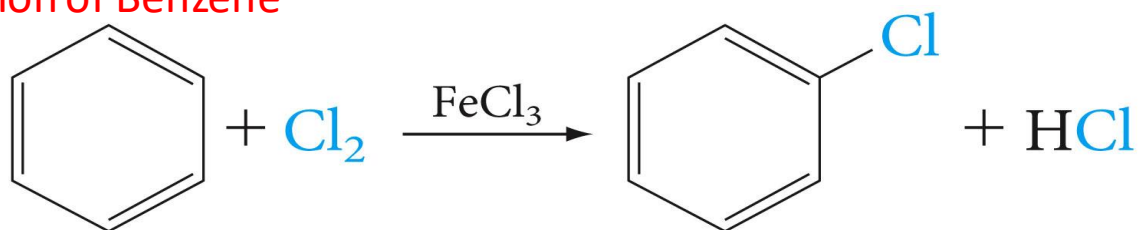
a. phenylcyclohexane or cyclohexylbenzene

b. o-benzylphenol

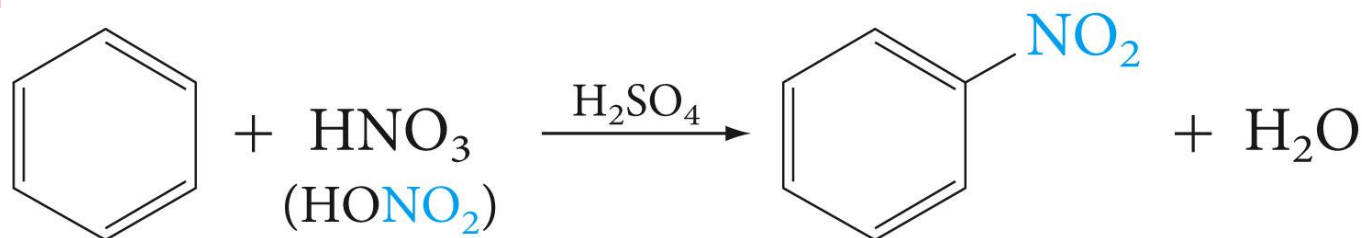
4.8 Electrophilic Aromatic Substitution

The most common reactions of aromatic compounds involve substitution of other atoms or groups for a ring hydrogen on the aromatic unit.

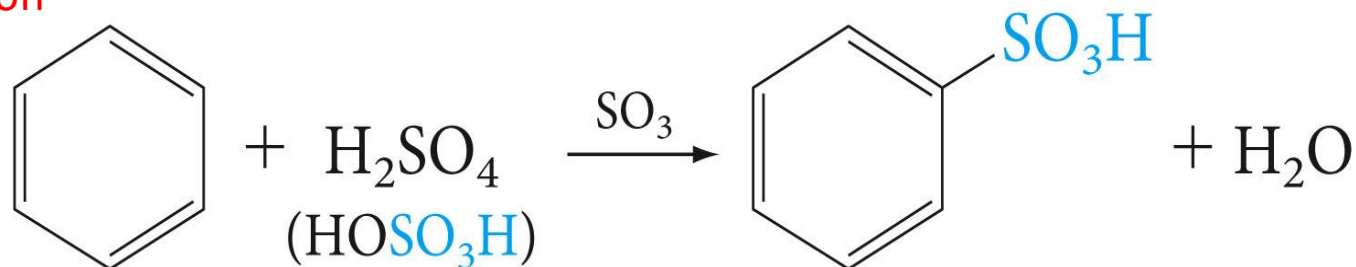
A- halogenation of Benzene



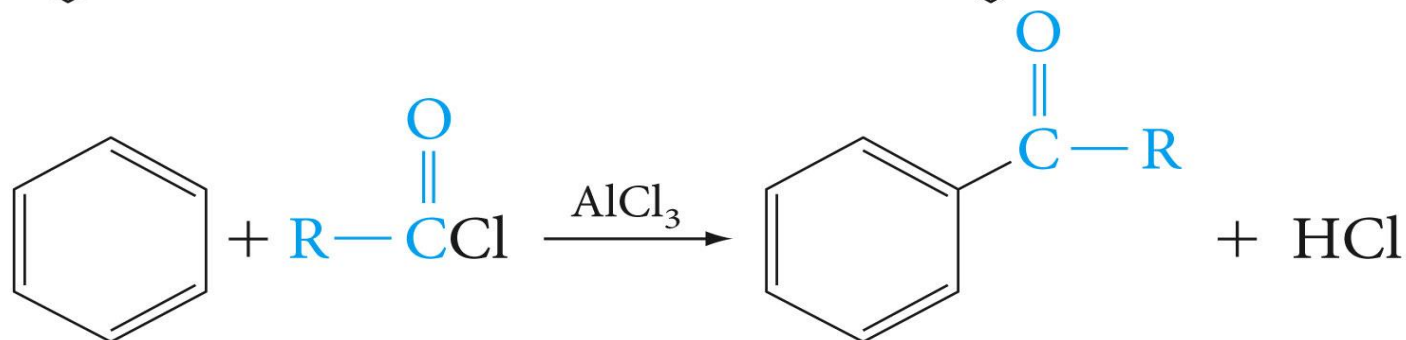
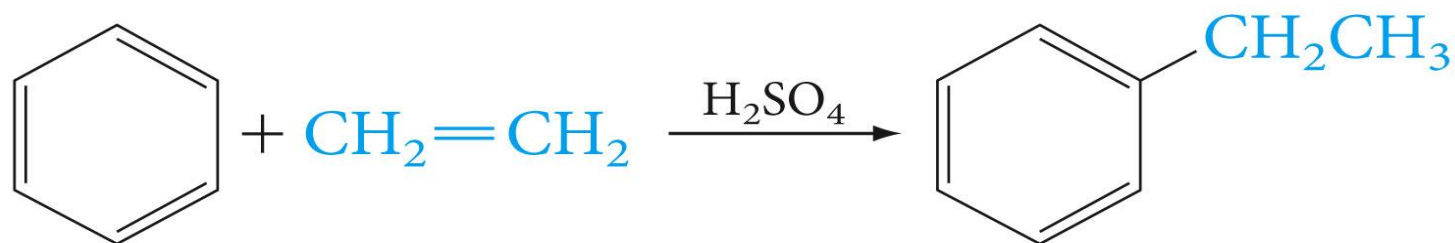
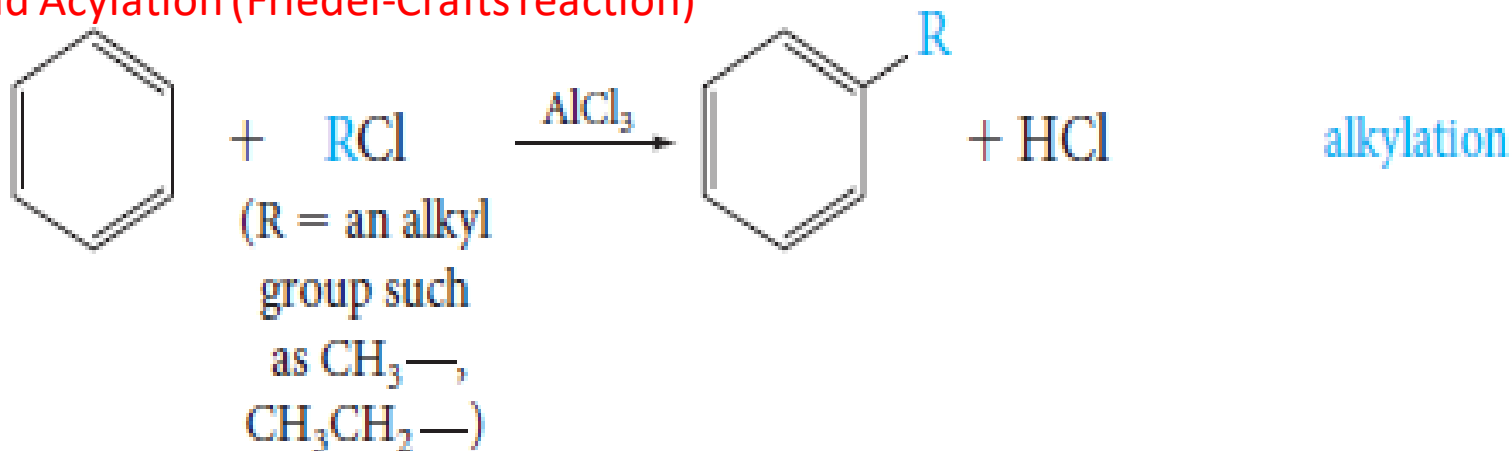
b. Nitration



c. sulfonation

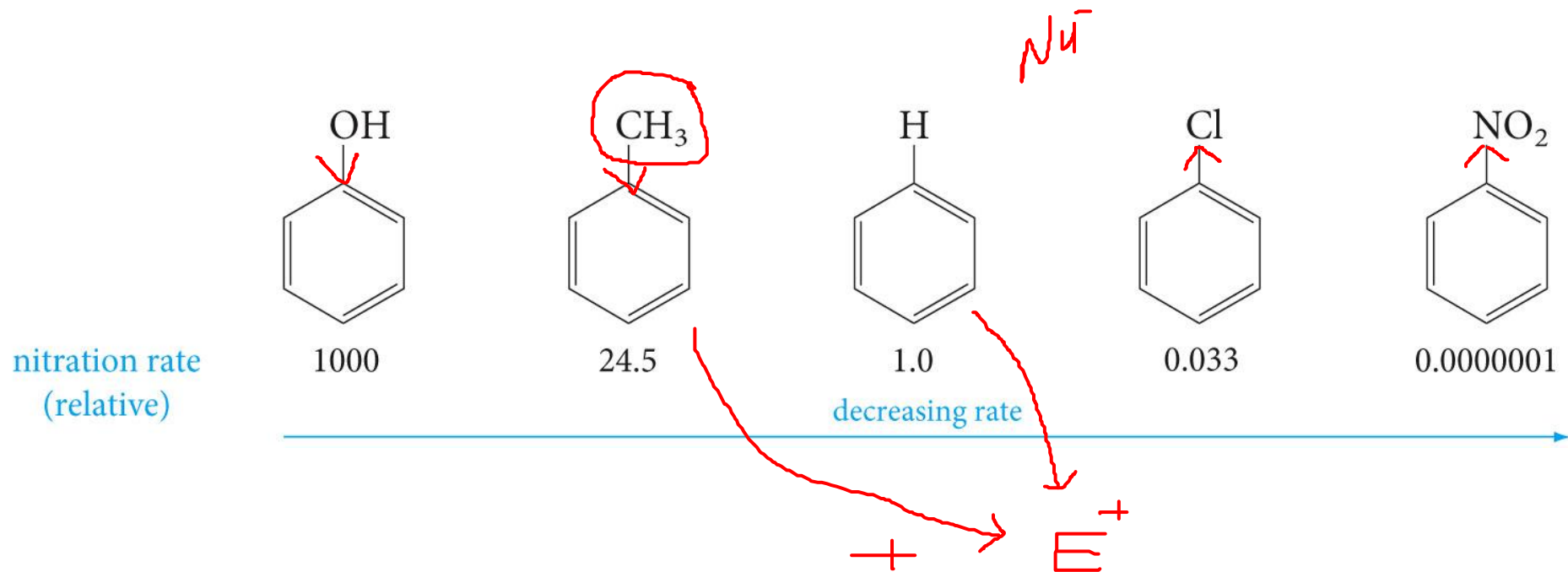


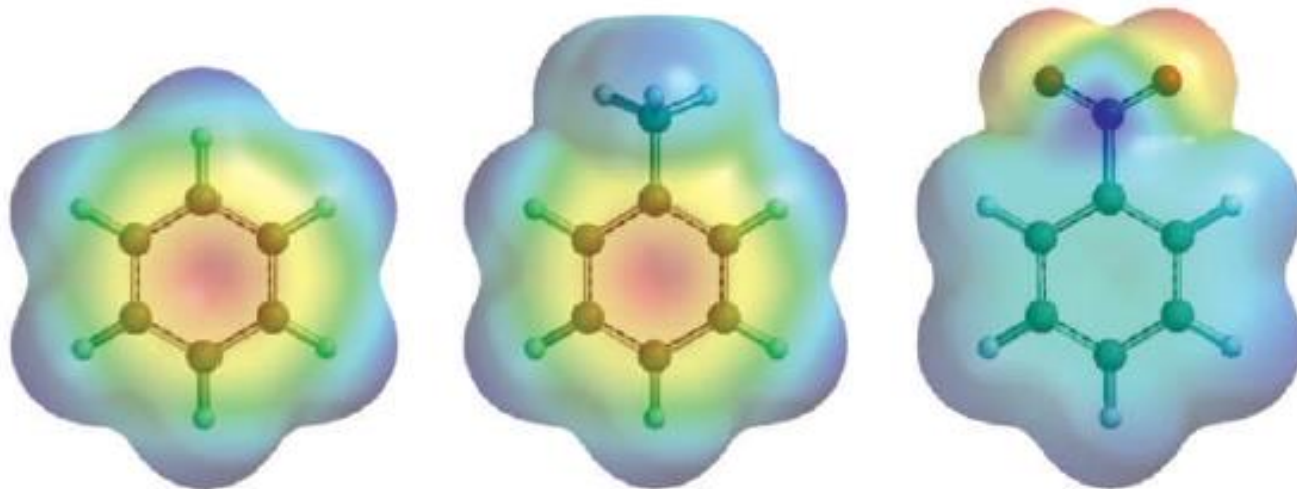
d. Alkylation and Acylation (Friedel-Crafts reaction)



4.10 Ring-Activating and ring-Deactivating Substituents

Consider the relative nitration rates of the following compounds, all under the same reaction conditions:





In the electrophilic mechanism for substitution:

Substituents that donate electrons to the ring will increase its electron density and, hence, speed up the reaction.

Substituents that withdraw electrons from the ring will decrease electron density in the ring and therefore slow down the reaction.

4.11 Ortho, Para-Directing and Meta-Directing Groups

Substituents already present on an aromatic ring determine the position taken by a new substituent.

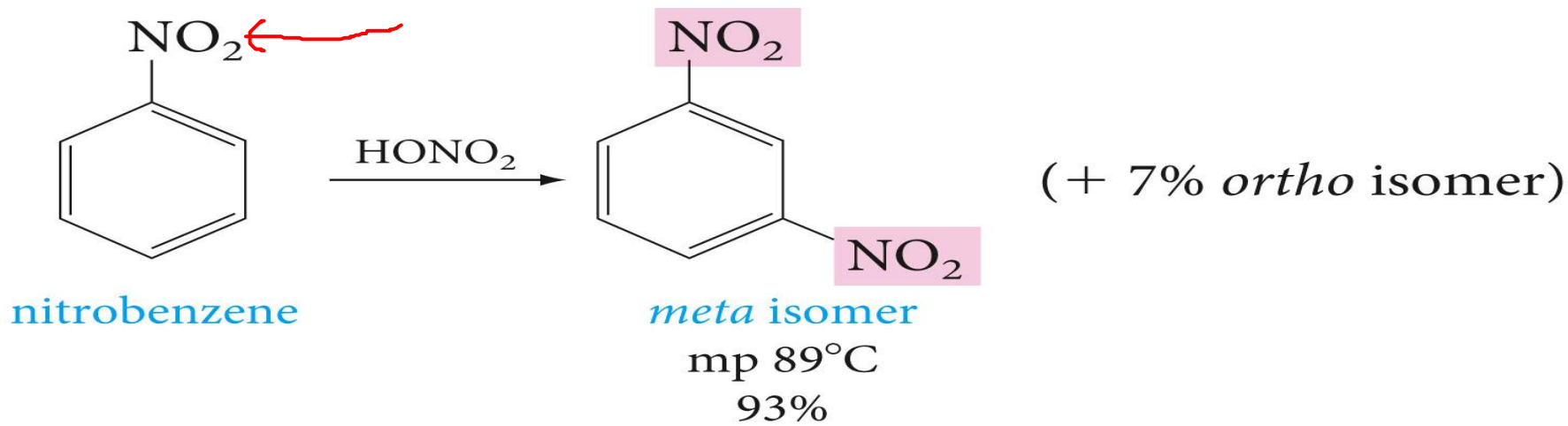
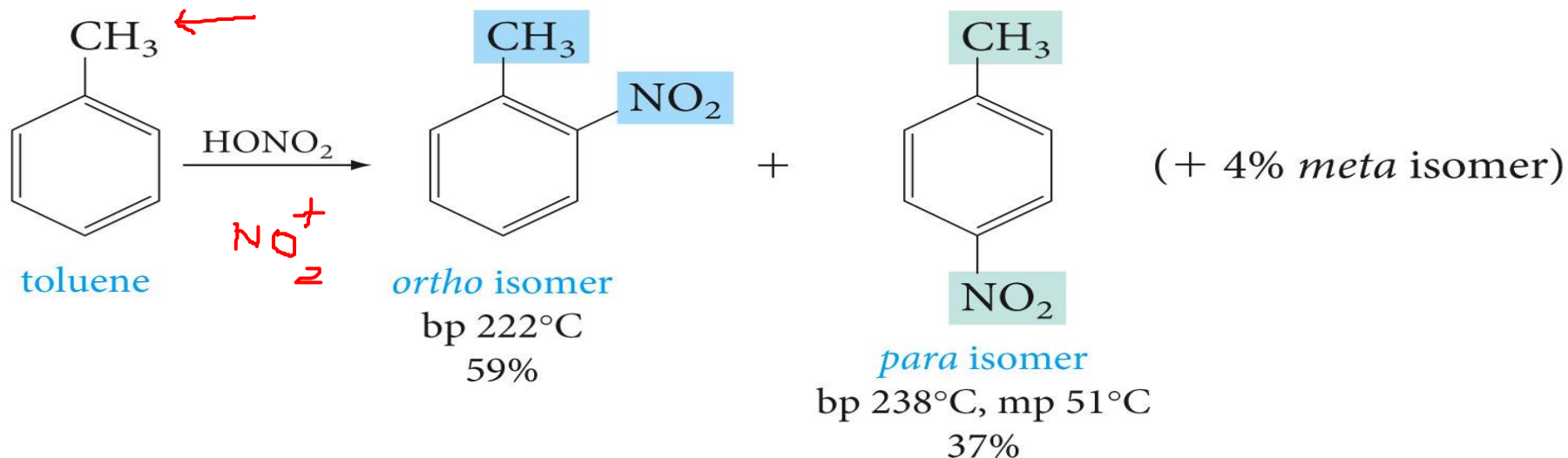


Table 4.1 Directing and Activating Effects of Common Functional Groups (Groups are Listed in Decreasing Order of Activation)

	<i>Substituent group</i>	<i>Name of group</i>	
<i>Ortho, Para-Directing</i>	$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{HR}, -\ddot{\text{N}}\text{R}_2$	amino	<i>Activating</i>
	$-\ddot{\text{O}}\text{H}, -\ddot{\text{O}}\text{CH}_3, -\ddot{\text{O}}\text{R}$	hydroxy, alkoxy	
	$-\ddot{\text{N}}\overset{\text{O}}{\parallel}\text{C}-\text{R}$	acylamino	
	$-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$ ✓	alkyl	
	$-\ddot{\text{F}}:, -\ddot{\text{Cl}}:, -\ddot{\text{Br}}:, -\ddot{\text{I}}:$	halo	
<i>Meta-Directing</i>	$\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{C}-\text{R} \end{array}$ $\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{C}-\ddot{\text{O}}\text{H} \end{array}$	acyl, carboxy	<i>Deactivating</i>
	$\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$ $\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{C}-\ddot{\text{O}}\text{R} \end{array}$	carboxamido, carboalkoxy	
	$\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{S}-\ddot{\text{O}}\text{H} \\ \parallel \\ \text{:O:} \end{array}$ ✓	sulfonic acid	
	$-\text{C}\equiv\text{N}:$	cyano	
	$\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{N}^+ \\ \diagdown \\ \text{:O:}^- \end{array}$	nitro	

c. Substituent Effect on Reactivity

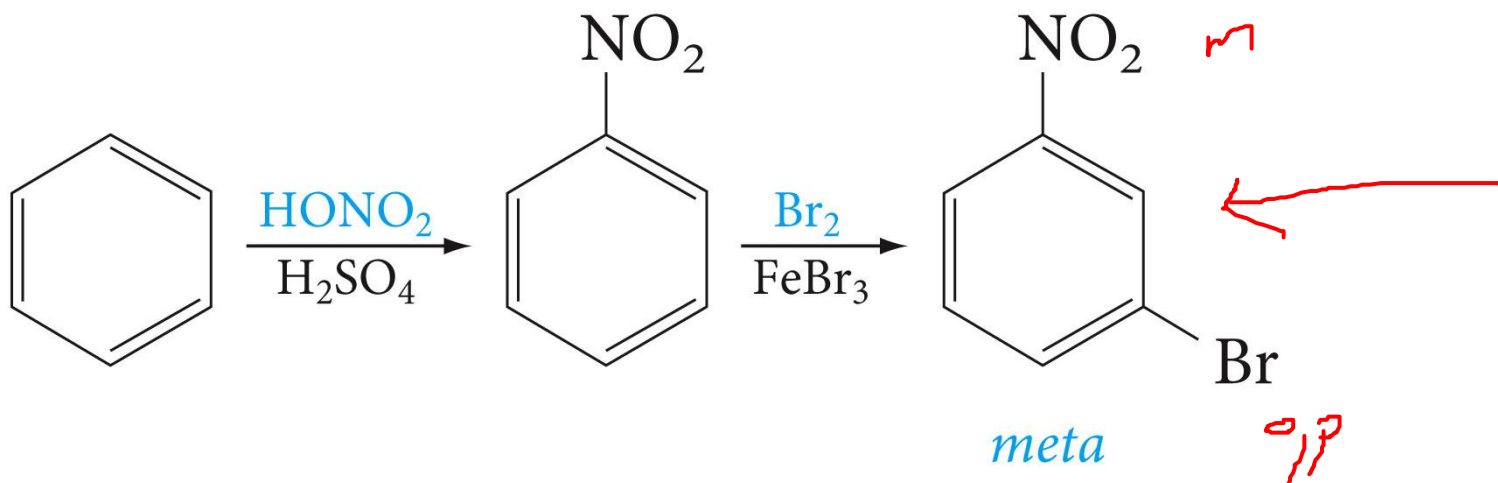
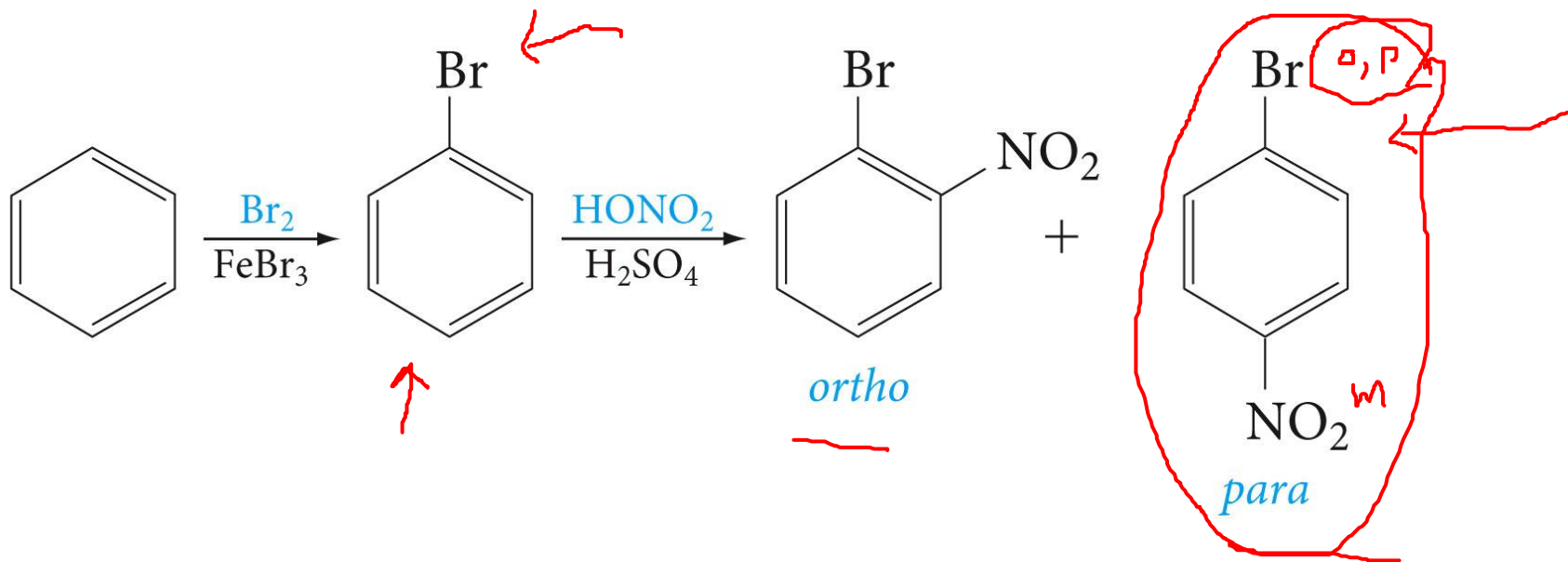
In all *meta*-directing groups, the atom connected to the ring carries a full or partial positive charge and will therefore withdraw electrons from the ring.

All meta-directing groups are therefore ring-deactivating groups.

On the other hand, *ortho,para*-directing groups in general supply electrons to the ring and are therefore ring activating.

With the halogens (F, Cl, Br, and I), two opposing effects bring about the only important exception to these rules. *Because they are strongly electron withdrawing, the halogens are ring deactivating; but because they have unshared electron pairs, they are ortho,para-directing.*

4.12 Importance of Directing Effects in Synthesis



PROBLEM 4.16

Devise a synthesis for each of the following, starting with benzene:

a. *m*-bromobenzenesulfonic acid

b. *p*-nitrotoluene

