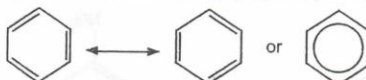


## Aromatic Compounds

### Chapter Summary

**Benzene** is the parent of the family of **aromatic hydrocarbons**. Its six carbons lie in a plane at the corners of a regular hexagon and each carbon has one hydrogen attached. Benzene is a resonance hybrid of two contributing Kekulé structures:



In orbital terms, each carbon is  $sp^2$ -hybridized. These orbitals form  $\sigma$  bonds to the hydrogen and the two neighboring carbons are all in the ring plane. A  $p$  orbital at each carbon is perpendicular to this plane, and the six electrons, one from each carbon, form an electron cloud of  $\pi$  bonds which lie above and below the ring plane.

The bond angles in benzene are  $120^\circ$ . All C–C bond distances are equal (1.39 Å). The compound is more stable than either of the contributing Kekulé structures and has a **resonance or stabilization energy** of about 36 kcal/mol.

The nomenclature of benzene derivatives is described in Sec. 4.6. Common names and structures to be memorized include those of **toluene**, **styrene**, **phenol**, **aniline**, and **xylene**. Monosubstituted benzenes are named as benzene derivatives (bromobenzene, nitrobenzene, and so on). Disubstituted benzenes are named as *ortho*- (1,2-), *meta*- (1,3-), or *para*- (1,4-), depending on the relative positions of the substituents on the ring. Two important groups are **phenyl** ( $C_6H_5-$ ) and **benzyl** ( $C_6H_5CH_2-$ ).

Aromatic compounds react mainly by **electrophilic aromatic substitution**, in which one or more ring hydrogens are replaced by various electrophiles. Typical reactions are **chlorination**, **bromination**, **nitration**, **sulfonation**, **alkylation**, and **acylation** (the last two are Friedel–Crafts reactions). The mechanism involves two steps: addition of the electrophile to a ring carbon, to produce an intermediate **benzenonium ion**, followed by proton loss to again achieve the (now substituted) aromatic system.

Substituents already present on the ring affect the rate of further substitution and the position taken by the next substituent. Most groups are either *meta*-directing and *ring-deactivating* or *ortho,para*-directing and *ring-activating* (Table 4.1). Exceptions are the halogens, which are *ortho,para*-directing but *ring-deactivating*. These effects must be taken into account in devising syntheses of aromatic compounds.

Benzene is a major commercial chemical—a source of styrene, phenol, other aromatics, acetone, and cyclohexane.

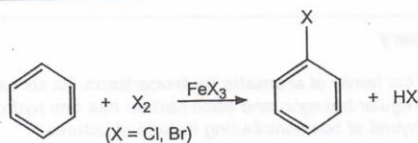
**Polycyclic aromatic hydrocarbons**, which are built of *fused* benzene rings, include **naphthalene**, **anthracene**, and **phenanthrene**. Some, such as benzo[a]pyrene, are

carcinogens. Graphite, a common allotrope of carbon, consists of layers of planar, hexagonal rings separated by 3.4 Å. The fullerenes are a recently discovered novel polycyclic form of carbon.

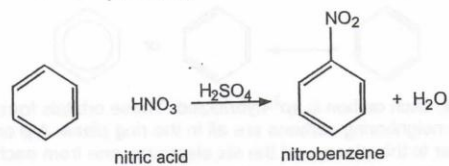
### Reaction Summary

#### Electrophilic Aromatic Substitution

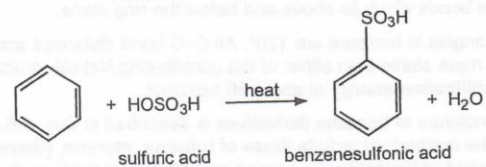
##### Halogenation



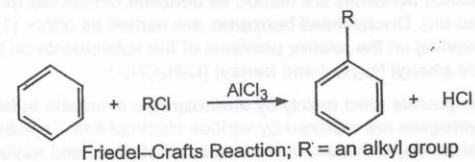
##### Nitration



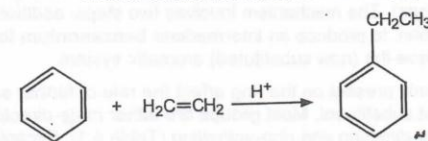
##### Sulfonation



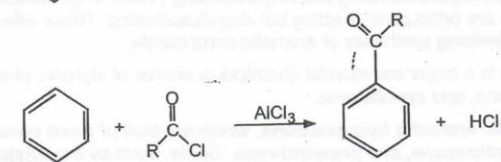
##### Alkylation

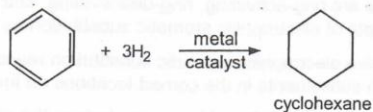
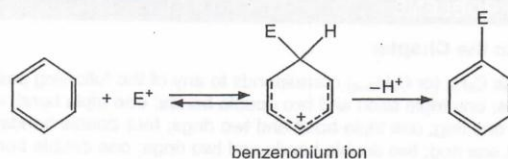


##### Alkylation



##### Acylation



Catalytic Hydrogenation**Mechanism Summary**Electrophilic Aromatic Substitution**Learning Objectives**

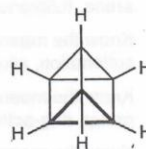
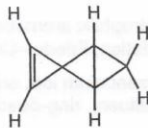
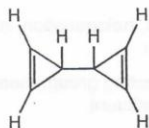
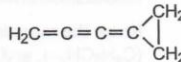
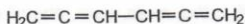
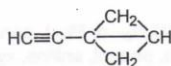
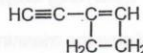
1. Know the meaning of: Kekulé structure, benzene resonance hybrid, resonance or stabilization energy.
2. Know the meaning of: *ortho*, *meta*, *para*, phenyl group (C<sub>6</sub>H<sub>5</sub>- or Ph-), benzyl group (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-), aryl group (Ar-), benzene, toluene, styrene, phenol, aniline, xylene, arene, fullerene.
3. Know the meaning of: electrophilic aromatic substitution, halogenation, nitration, sulfonation, alkylation, acylation, Friedel-Crafts reaction.
4. Know the meaning of: benzenonium ion, *ortho*, *para*-directing group, *meta*-directing group, ring-activating substituent, ring-deactivating substituent.
5. Know the meaning of: polycyclic aromatic hydrocarbon, naphthalene, anthracene, phenanthrene, carcinogenic, graphite, fullerene.
6. Name and write the structures for aromatic compounds, especially monosubstituted and disubstituted benzenes and toluenes.
7. Given the reactants, write the structures of the main organic products of the common electrophilic aromatic substitution reactions (halogenation, nitration, sulfonation, alkylation, and acylation).
8. Write the steps in the mechanism for an electrophilic aromatic substitution reaction.
9. Draw the structures of the main contributors to the benzenonium ion resonance hybrid.
10. Draw the structures of the main contributors to substituted benzenonium ions, and tell whether the substituent stabilizes or destabilizes the ion.
11. Know which groups are *ortho*, *para*-directing, which are *meta*-directing, and explain why each group directs the way it does.

12. Know which groups are ring-activating, ring-deactivating, and explain why each group affects the rate of electrophilic aromatic substitution as it does.
13. Given two successive electrophilic aromatic substitution reactions, write the structure of the product, with substituents in the correct locations on the ring.
14. Given a disubstituted or trisubstituted benzene, deduce the correct sequence in which to carry out electrophilic substitutions to give the product with the desired orientation.

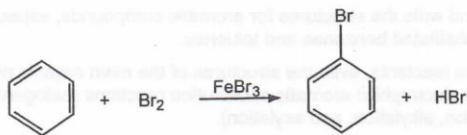
### ANSWERS TO PROBLEMS

#### Problems Within the Chapter

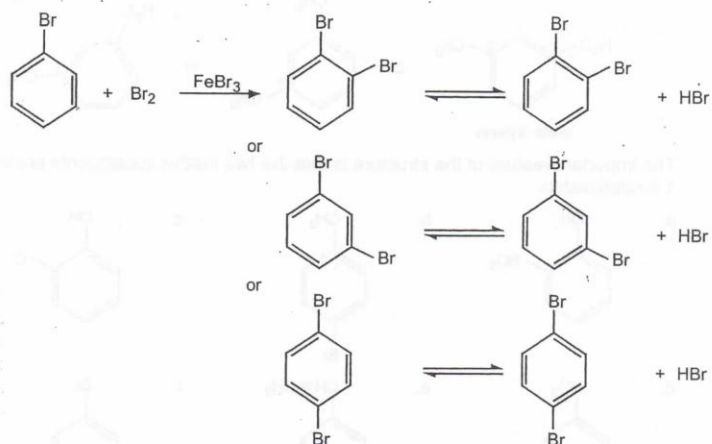
- 4.1 The formula  $C_6H_6$  (or  $C_7H_{2n-6}$ ) corresponds to any of the following possibilities: two triple bonds; one triple bond and two double bonds; one triple bond, one double bond, and one ring; one triple bond and two rings; four double bonds; three double bonds and one ring; two double bonds and two rings; one double bond and three rings; four rings. Obviously there are very many possibilities. One example from each of the above categories is shown below.



- 4.2 eq. 4.2:

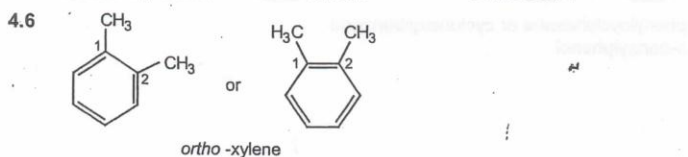
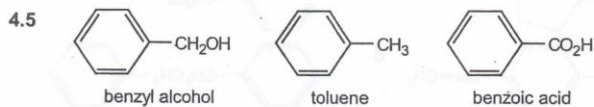


eq. 4.4:



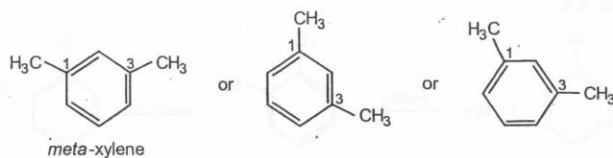
Yes, Kekulé's explanation accounts for one monobromobenzene and three dibromobenzenes, if the equilibrium between the two Kekulé structures for each dibromo isomer is taken into account. As you will see in Sec. 4.3, however, this picture is not quite correct.

- 4.3 Kekulé would have said that the structures are in such rapid equilibrium with one another that they cannot be separated. We know now, however, that there is only one such structure, which is not accurately represented by either Kekulé formula.
- 4.4 Although *two* Kekulé structures can be drawn for each of the *three* dibromobenzenes (see the  $2 \times 3 = 6$  structures shown in the answer to Problem 4.2), each pair of structures represents only *one* dibromobenzene. The structure of each dibromobenzene is actually a resonance hybrid of the two contributing resonance structures.



It does not matter whether we write the benzene ring standing on one corner or lying on a side.



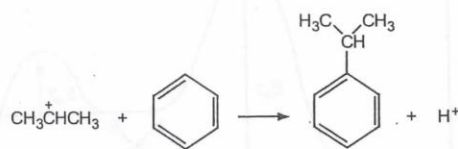
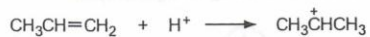


The important feature of the structure is that the two methyl substituents are in a 1,3-relationship.

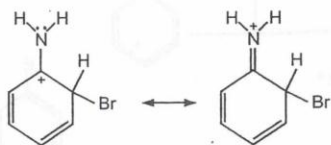
- 4.7 a. b. c.
- d. e. f.
- 4.8 a. b.
- 4.9 a. b.
- c. d.
- 4.10 a. phenylcyclohexane or cyclohexylbenzene  
b. o-benzylphenol



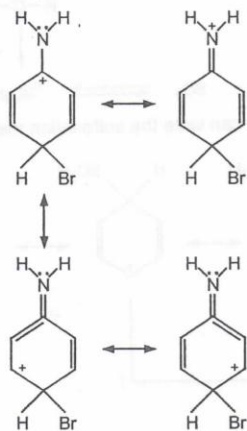
- 4.13 The product would be isopropylbenzene because the proton of the acid catalyst would add to propene according to Markovnikov's rule to give the isopropyl cation:



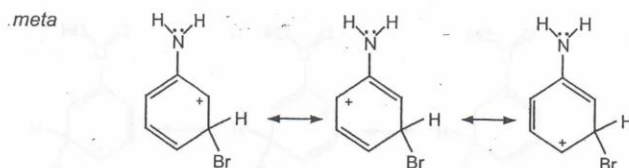
4.14 *ortho*



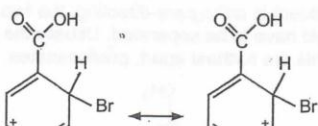
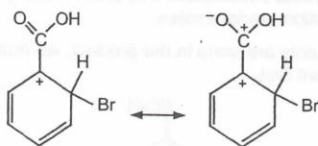
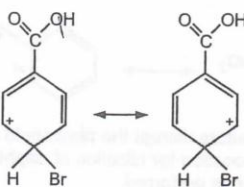
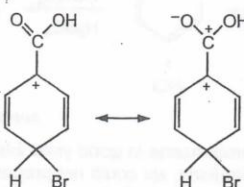
*para*

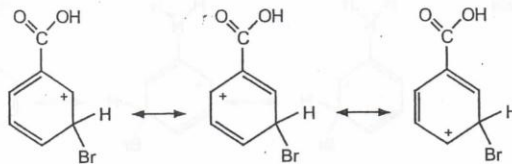






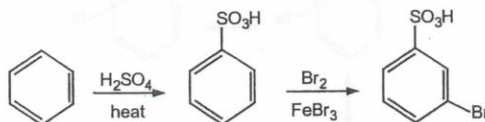
Note that in *ortho* or *para* substitution the carbocation can be stabilized by delocalization of the positive charge to the nitrogen atom. This is not possible for *meta* substitution. Therefore, *ortho* and *para* substitution are preferred.

4.15 *ortho**para*

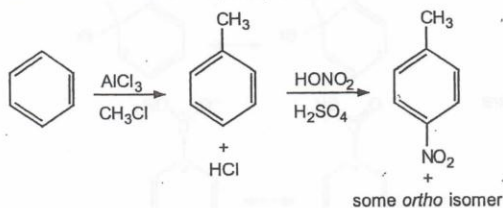
*meta*

In *ortho* or *para* substitution, the positive charge of the benzenonium ion is adjacent to the partially positive carboxyl carbon. It is energetically unfavorable to have two adjacent like charges. In *meta* substitution, this unfavorable possibility does not exist. Thus, *meta* substitution predominates.

- 4.16 a. Since the substituents are *meta* in the product, we must introduce the *meta*-directing substituent first:

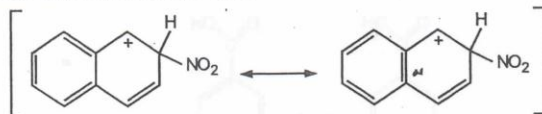


- b. The methyl substituent is *ortho,para*-directing; the two isomers obtained in the final step would have to be separated. Usually the *para* isomer, in which the two substituents are furthest apart, predominates.



- 4.17 We could not make *m*-bromochlorobenzene in good yield this way because both Br and Cl are *ortho,para*-directing. Similarly, we could not prepare *p*-nitrobenzenesulfonic acid directly because both the nitro and sulfonic acid substituents are *meta*-directing.

- 4.18 Only two such contributors are possible:

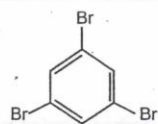


Any additional resonance contributors disrupt the benzenoid structure in the "left" ring. Since the intermediate carbocation for nitration of naphthalene at C-1 is more stable, substitution at that position is preferred.

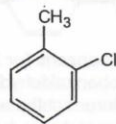
- 4.19 The carbon-to-hydrogen ratios are: benzene = 1; naphthalene = 1.25; anthracene = 1.40; pyrene = 1.60. The percentage of carbon in a structure increases with the number of fused aromatic rings.

**ADDITIONAL PROBLEMS**

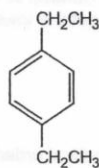
4.20 a.



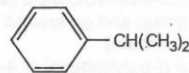
b.



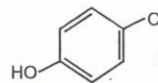
c.



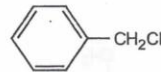
d.



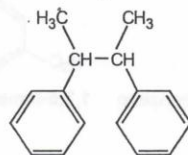
e.



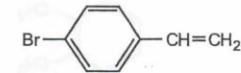
f.



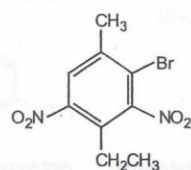
g.



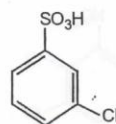
h.



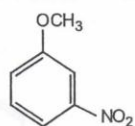
i.



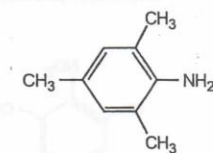
j.



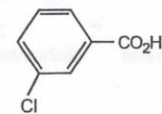
k.



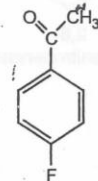
l.

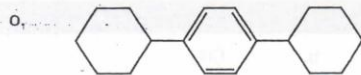


m.



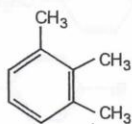
n.



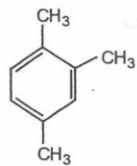


- 4.21 a. isopropylbenzene (or 2-phenylpropane)  
 b. *m*-bromobenzaldehyde  
 c. 1,8-dichloronaphthalene  
 d. 2,5-dichlorotoluene (start numbering with the carbon bonded to the methyl group and go around the ring such that substituents get the lowest possible numbers)  
 e. *p*-(*t*-butyl)phenol or 4-(1,1-dimethylethyl)phenol  
 f. *o*-nitrotoluene  
 g. hexafluorobenzene  
 h. 3,5-dibromostyrene  
 i. 1-ethyl-1-phenylcyclopropane (substituents in alphabetical order)

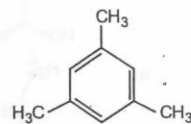
4.22 a.



1,2,3-trimethylbenzene

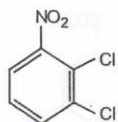
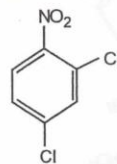
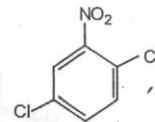
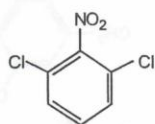
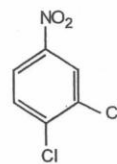
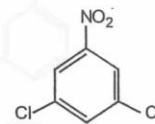


1,2,4-trimethylbenzene



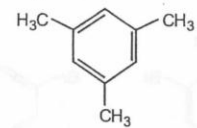
1,3,5-trimethylbenzene

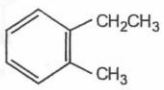
b.

2,3-  
dichloronitrobenzene2,4-  
dichloronitrobenzene2,5-  
dichloronitrobenzene2,6-  
dichloronitrobenzene3,4-  
dichloronitrobenzene3,5-  
dichloronitrobenzene

4.23 In each case six carbons are required for the benzene ring; the remaining carbons must be present as alkyl substituents:

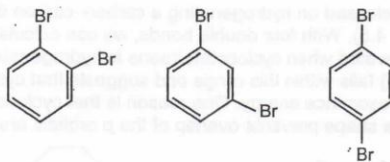
a.  Only *o*-xylene gives two monobromo derivatives, as shown by the arrows.

b.  The structure is symmetrical, and all three positions for aromatic substitution are equivalent.

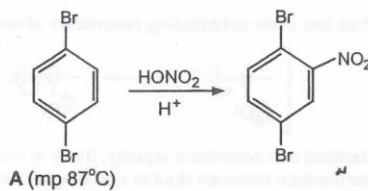
c.  Substitution at each unoccupied ring position gives a different product.

The compound in part b is 1,3,5-trimethylbenzene and that in part c is *o*-ethyltoluene or 2-ethyltoluene.

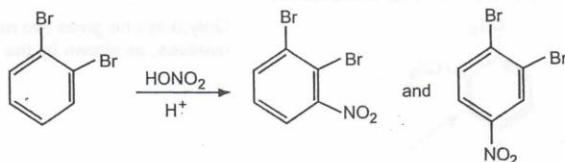
4.24 The three possible structures are:



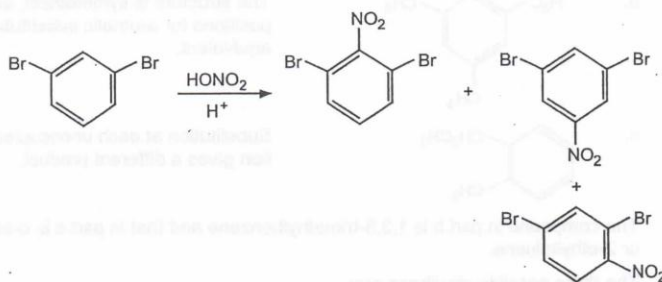
Only in the *para* isomer are all four remaining hydrogens equivalent. Therefore, it can give only *one* mononitro derivative and must be A:



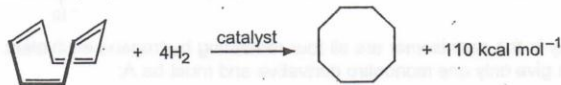
The *ortho* isomer can give only two mononitration products and must be B:



The *meta* isomer is therefore C:



- 4.25 The energy released on hydrogenating a carbon-carbon double bond is 26–30 kcal/mol (eq. 4.5). With four double bonds, we can calculate that 104–120 kcal/mol should be liberated when cyclooctatetraene is hydrogenated. The observed value (110 kcal/mol) falls within this range and suggests that cyclooctatetraene has no appreciable resonance energy. One reason is that cyclooctatetraene is not planar, and its tublike shape prevents overlap of the  $p$  orbitals around the ring.



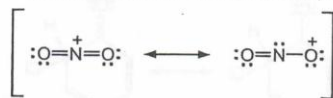
- 4.26 The nitro group has two main contributing resonance structures:



Since they are identical and contribute equally, there is only one type of nitrogen-oxygen bond, intermediate between double and single in length.

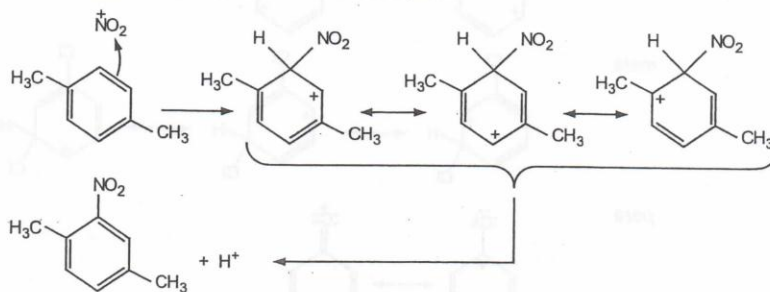


- 4.27  $\text{NO}_2^+$  There are 16 valence electrons available ( $\text{N} = 5$ , and  $2 \times \text{O} = 2 \times 6 = 12$  for a total of 17, but we must subtract 1 electron since the ion is positive).



The structure with the positive charge on the nitrogen is preferred because each atom has an octet of electrons. In the structure with the positive charge on the oxygen, the oxygen atom has only six electrons around it. Note that in aromatic nitrations, it is the nitrogen atom of  $\text{NO}_2^+$  that is attacked and becomes attached to the aromatic ring.

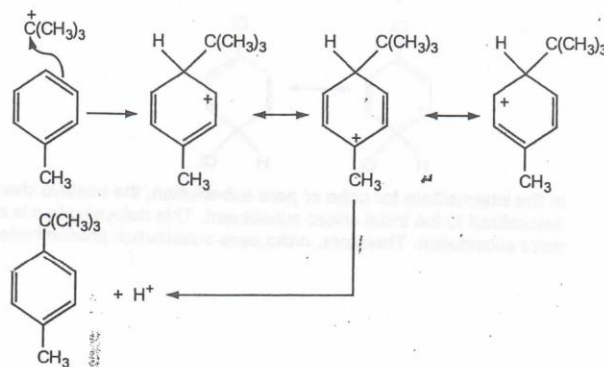
- 4.28 a. The electrophile,  $\text{NO}_2^+$ , is formed as in eq. 4.18. Then the mechanism follows the same steps as the solution to Example 4.2.

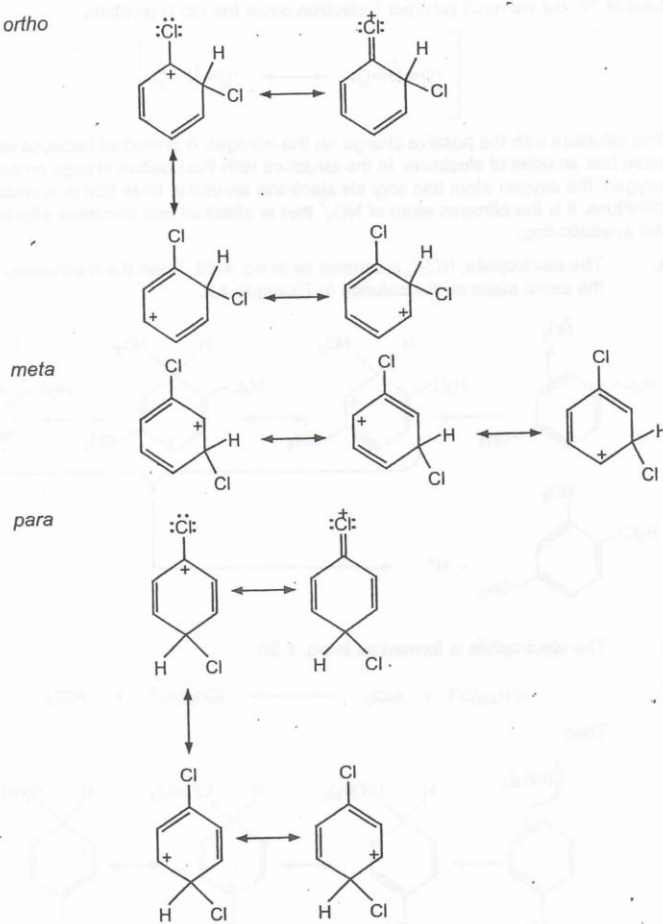


- b. The electrophile is formed as in eq. 4.20:



Then

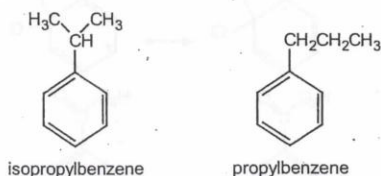


4.29 *ortho*

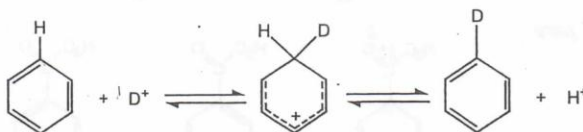
In the intermediate for *ortho* or *para* substitution, the positive charge can be delocalized to the initial chloro substituent. This delocalization is not possible with *meta* substitution. Therefore, *ortho,para*-substitution predominates.



- 4.32 The major product is isopropylbenzene. Protonation of propene gives the 2-propyl cation, a secondary carbocation, rather than the less stable 1-propyl cation, a primary carbocation.

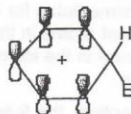


- 4.33  $D_2SO_4$  is a strong acid and a source of the electrophile  $D^+$  (analogous to  $H^+$  from  $H_2SO_4$ ).



Loss of  $H^+$  from the intermediate benzenonium results in replacement of H by D. With a large excess of  $D_2SO_4$ , these equilibria are shifted to the right, eventually resulting in fully deuterated benzene,  $C_6D_6$ .

- 4.34 The carbon bonded to the electrophile (E) is  $sp^3$ -hybridized. The remaining carbons are  $sp^2$ -hybridized.



- 4.35 a. *Meta*-directing and ring-deactivating because of the positive charge on the nitrogen (electron-withdrawing).
- $-\overset{+}{N}(CH_3)_2$
- b. *Meta*-directing and ring-deactivating because of the partial positive charge on the carbonyl carbon, due to contributors such as



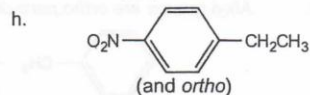
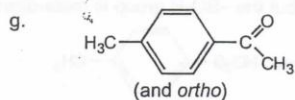
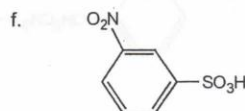
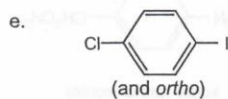
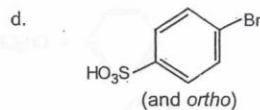
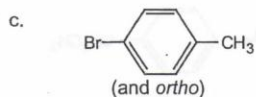
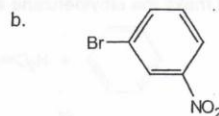
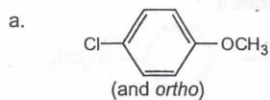
- c. *Ortho,para*-directing and ring-activating because of the unshared electron pairs on the oxygen.



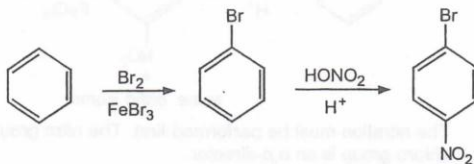
- d. *Ortho,para*-directing and ring-activating because of the unshared electron pairs on the sulfur.



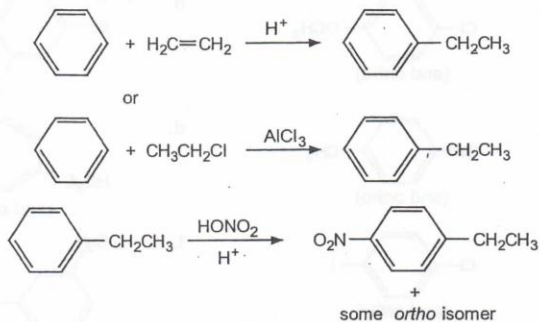
4.36 See Sec. 4.11 for a discussion of the orienting influence of substituents.



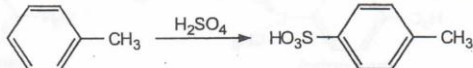
- 4.37 a. Anisole; the  $-\text{OCH}_3$  group is ring-activating, whereas the  $-\text{CO}_2\text{H}$  group is ring-deactivating.  
 b. Ethylbenzene; although both substituents ( $-\text{CH}_2\text{CH}_3$  and  $-\text{Cl}$ ) are *ortho,para*-directing, the ethyl group is ring-activating, whereas the chlorine is ring-deactivating.
- 4.38 Nitro groups are ring-deactivating. Thus, as we substitute nitro groups for hydrogens, we make the ring less and less reactive toward further electrophilic substitution and, therefore, must increase the severity of the reaction conditions.
- 4.39 a. Since the two substituents must end up in a *para* relationship, the first one introduced into the benzene ring must be *para*-directing. Therefore, brominate first and then nitrate.



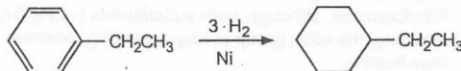
- b. First make the ethylbenzene and then nitrate it:



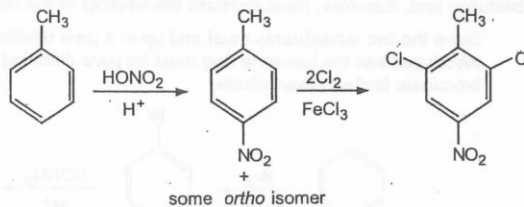
- c. Alkyl groups are *ortho,para*-directing but the  $-\text{SO}_3\text{H}$  group is *meta*-directing.



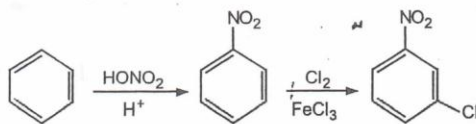
- d. Arenes can be converted to substituted cyclohexanes by catalytic hydrogenation.



- 4.40 a. The nitro substituent must be introduced first, to block the *para* position from the chlorination.

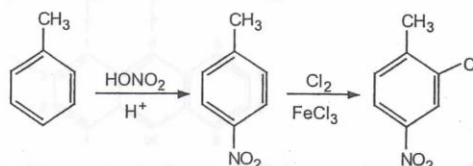


- b. The nitration must be performed first. The nitro group is a *m*-director while a chloro group is an *o,p*-director.

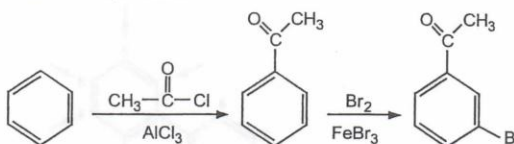




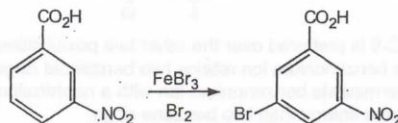
- c. If the chlorination were performed first, a considerable portion of product would have the chlorine *para* to the methyl group. Also, note that in the second step, both substituents direct the chlorine to the desired position ( $-\text{CH}_3$  is *o,p*-directing,  $-\text{NO}_2$  is *m*-directing).



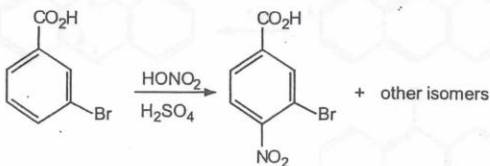
- d. If the bromination were performed first, the Friedel-Crafts acylation would occur at the 2 and 4 positions.



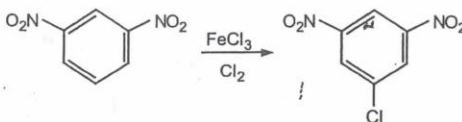
- 4.41 3-Nitrobenzoic acid is better because both substituents are *meta*-directing:



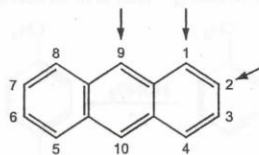
On the other hand, 3-bromobenzoic acid has an *ortho,para*-directing and a *meta*-directing substituent and, on nitration, would give a mixture of isomers:



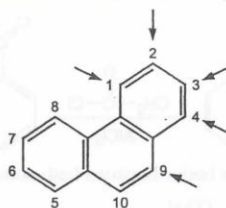
- 4.42 The *meta*-directing effect on both nitro groups reinforces substitution in the position shown.



- 4.43 a. Three different monosubstitution products are possible: at C-1 (equivalent to C-4, C-5, and C-8); at C-2 (equivalent to C-3, C-6, and C-7); and at C-9 (equivalent to C-10).



- b. Five different monosubstitution products are possible: at C-1 (equivalent to C-8); at C-2 (equivalent to C-7); at C-3 (equivalent to C-6); at C-4 (equivalent to C-5); and at C-9 (equivalent to C-10).



- 4.44 Bromination at C-9 is preferred over the other two possibilities (C-1 or C-2) because the intermediate benzenonium ion retains two benzenoid rings. Substitution at C-1 or C-2 gives an intermediate benzenonium ion with a naphthalene substructure, which has less resonance energy than two benzene rings.

