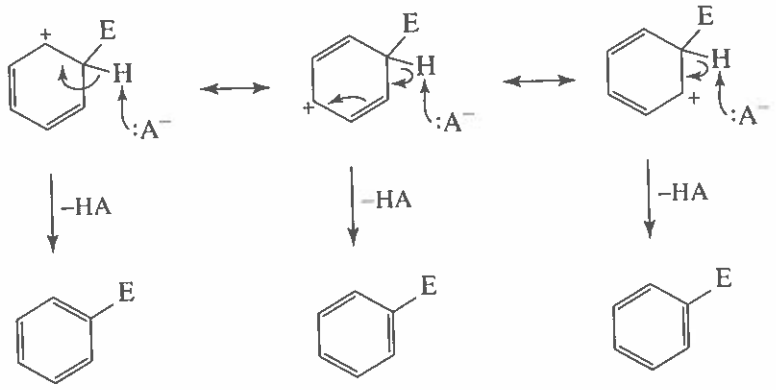
15 REACTIONS OF AROMATIC COMPOUNDS

SOLUTIONS TO PROBLEMS

15.1



15.2 The rate is dependent on the concentration of $^{+}NO_2$ ion formed from protonated nitric acid.

$$H-\overset{+}{O}(H)-NO_2 + HA \longrightarrow {}^{+}NO_2 + H_3O^{+} + A^{-}$$

(where HA = HNO_3 or $HOSO_3H$)

Because H_2SO_4 ($HOSO_3H$) is a stronger acid, a mixture of it and HNO_3 will contain a higher concentration of protonated nitric acid than will nitric acid alone.

That is, the reaction,

$$H-O-NO_2 + HOSO_3H \rightleftharpoons H-\overset{+}{O}(H)-NO_2 + HSO_4^{-}$$

Protonated nitric acid

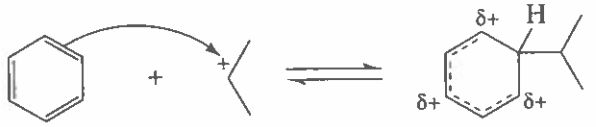
produces more protonated nitric acid than the reaction,

$$H-O-NO_2 + H-O-NO_2 \rightleftharpoons H-\overset{+}{O}(H)-NO_2 + NO_3^{-}$$

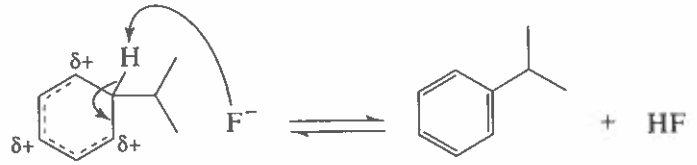
15.3 *Step 1*



Step 2



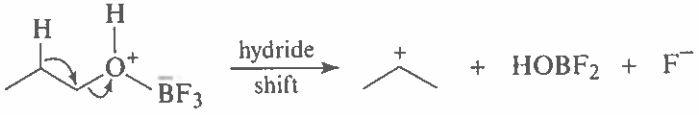
Step 3



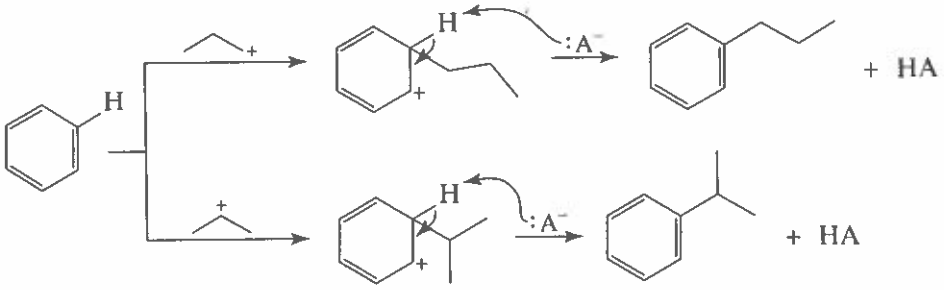
15.4



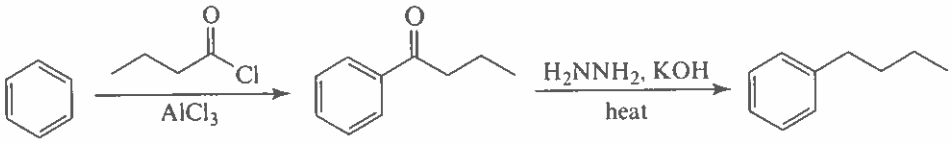
Rearrangement to the secondary carbocation occurs as the leaving group departs.



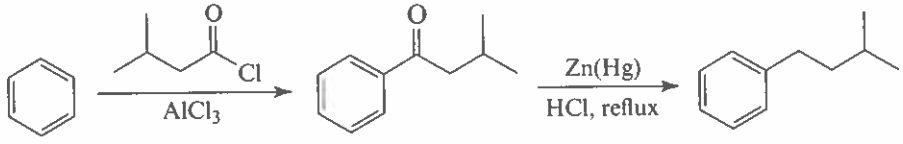
Both carbocations are then attacked by the ring.

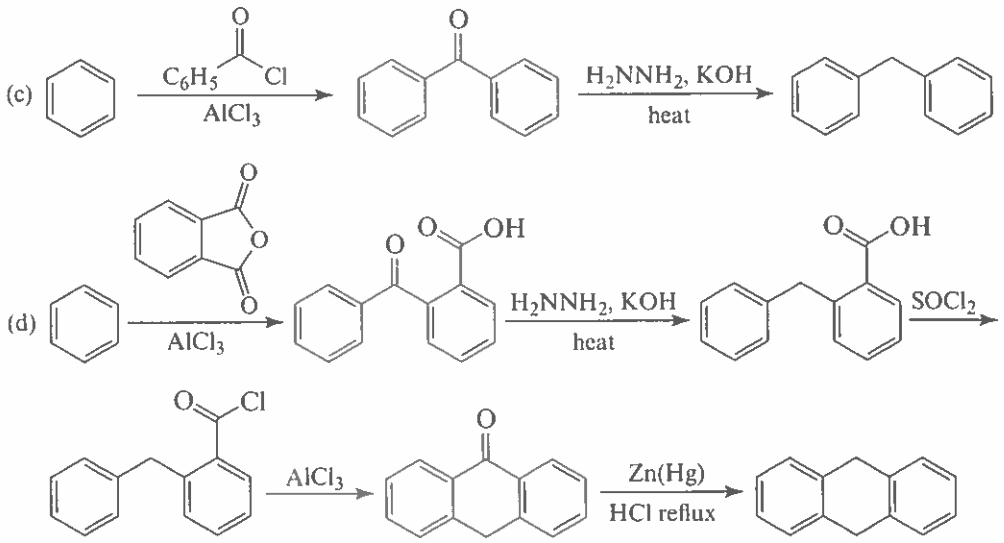


15.5 (a)



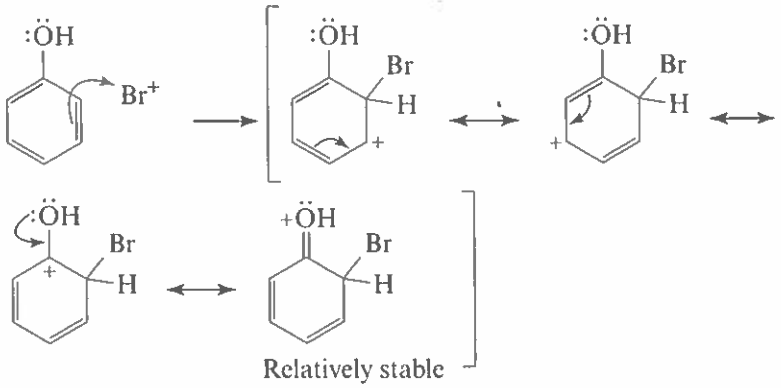
(b)



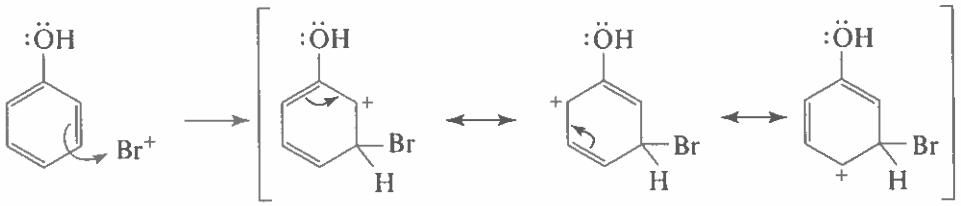


15.6 As the following structures show, attack at the ortho and para positions of phenol leads to arenium ions that are more stable (than the one resulting from meta attack) because they are hybrids of four resonance structures, one of which is relatively stable. Only three resonance structures are possible for the meta arenium ion, and none is relatively stable.

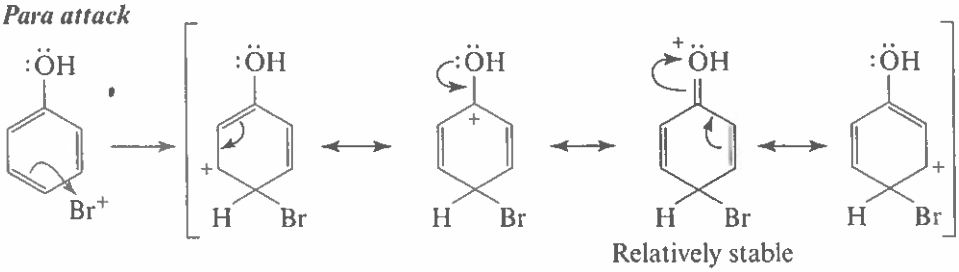
Ortho attack



Meta attack



Para attack



15.7 (a) The atom (an oxygen atom) attached to the benzene ring has an unshared electron pair that it can donate to the arenium ions formed from ortho and para attack, stabilizing them. (The arenium ions are analogous to the previous answer with a $-COCH_3$ group replacing the $-H$ of the phenolic hydroxyl).

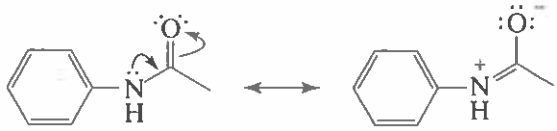
(b) Structures such as the following compete with the benzene ring for the oxygen electrons, making them less available to the benzene ring.



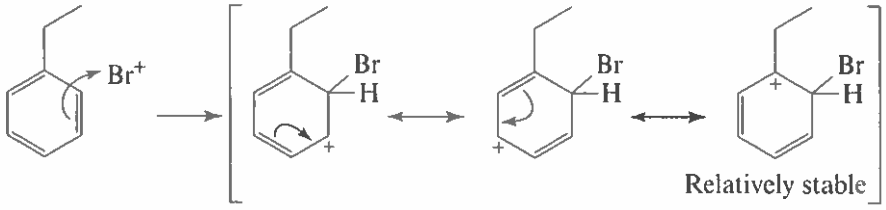
This effect makes the benzene ring of phenyl acetate less electron rich and, therefore, less reactive.

(c) Because the acetamido group has an unshared electron pair on the nitrogen atom that it can donate to the benzene ring, it is an ortho-para director.

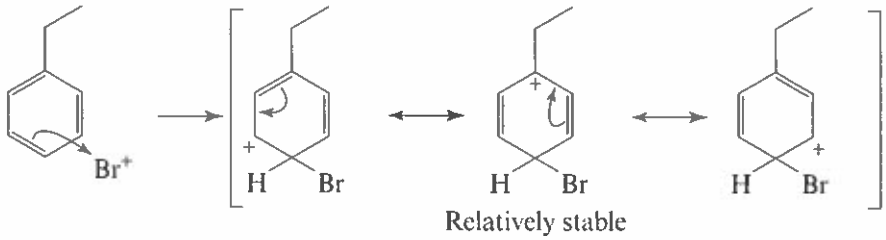
(d) Structures such as the following compete with the benzene ring for the nitrogen electrons, making them less available to the benzene ring.



15.8 ***Ortho attack***

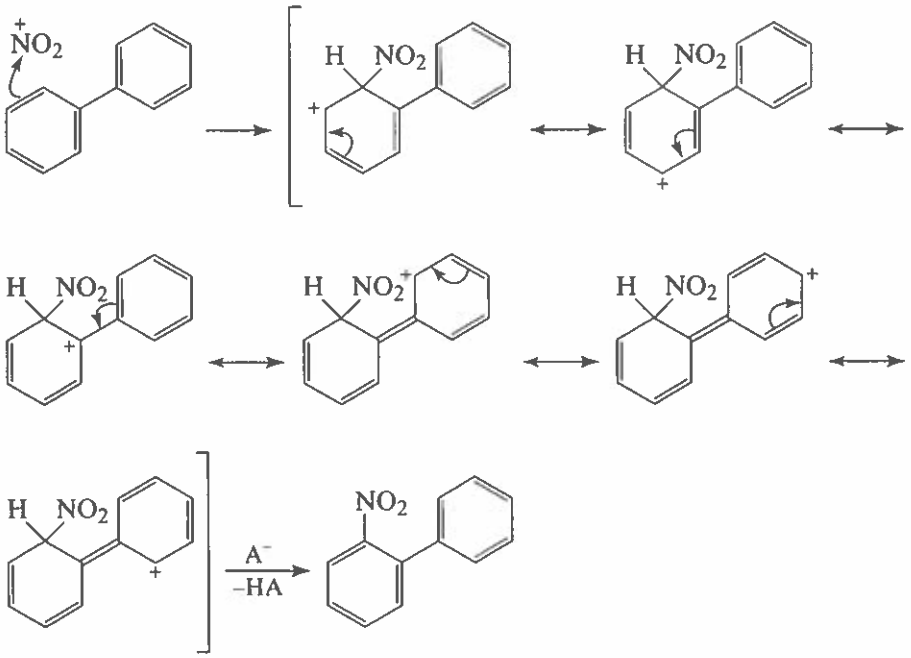


Para attack



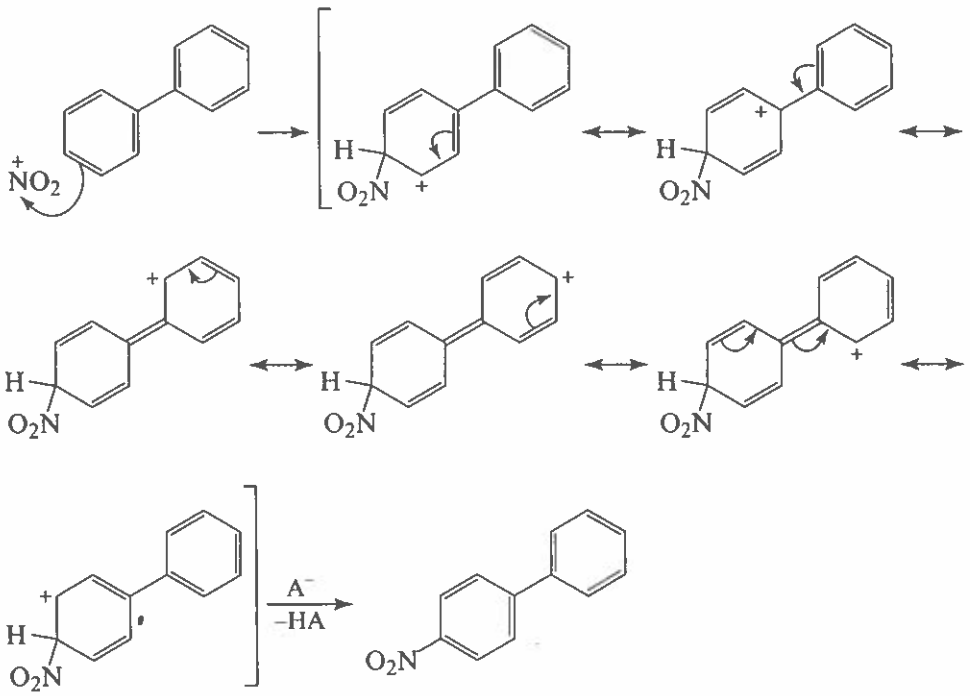
15.9 The phenyl group, as the following resonance structures show, can act as an electron-releasing group and can stabilize the arenium ions formed from ortho and para attack.

Ortho attack



In the case of the arenium ions above and following, the unsubstituted ring can also be shown in the alternative Kekulé structure.

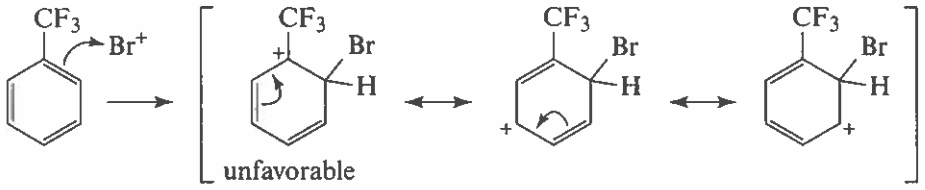
Para attack



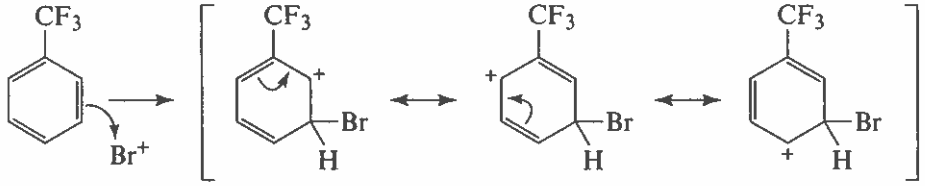
In the case of both ortho and para substitution, the phenyl group functions as an activating group, resulting in a faster reaction than in the case of benzene.

15.10 As the following resonance structures show, each mode of attack has three possible resonance forms. However, for both ortho and para attack, there is one resonance form which puts a positive charge next to the inductively withdrawing CF_3 group. That result is unfavorable, and renders meta attack the best possible option since such an unfavorable resonance from is avoided.

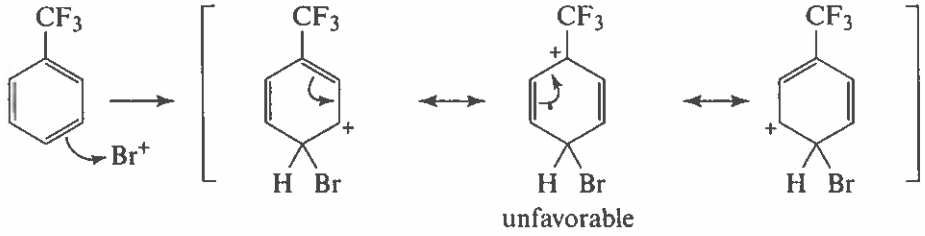
Ortho attack



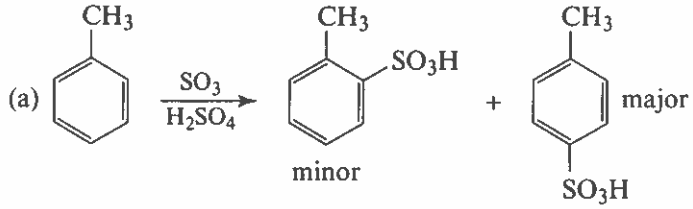
Meta attack



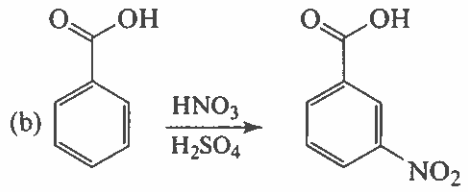
Para attack



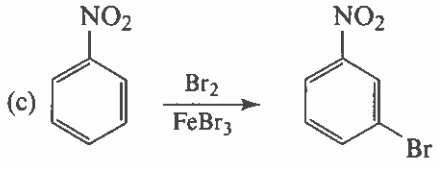
15.11 (a)

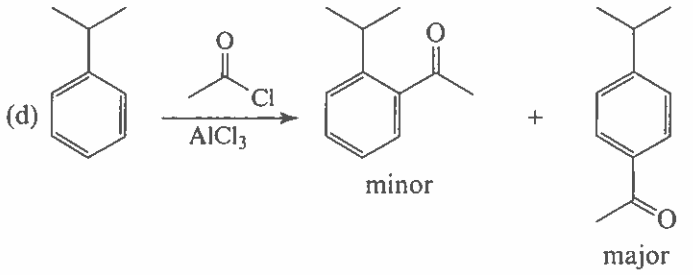


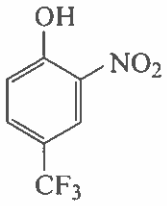
(b)

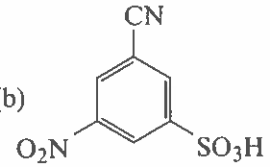


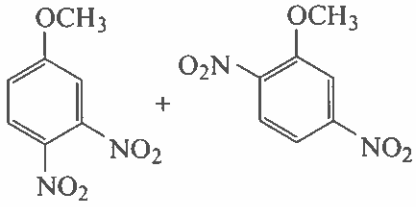
(c)



(d) 

15.12 (a) 

(b) 

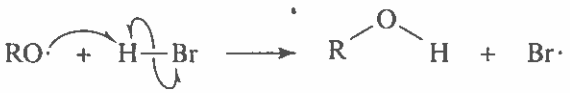
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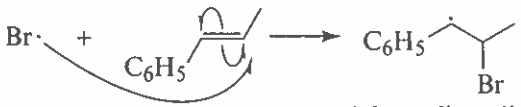
15.13 The addition of hydrogen bromide to 1-phenylpropene proceeds through a benzylic radical in the presence of peroxides, and through a benzylic cation in their absence (cf., a and b as follows).

(a) Hydrogen bromide addition in the presence of peroxides.

Chain Initiation

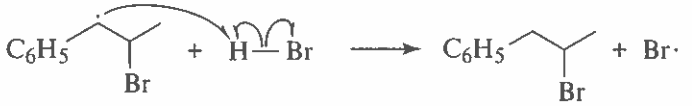
Step 1 

Step 2 

Step 3 

A benzylic radical

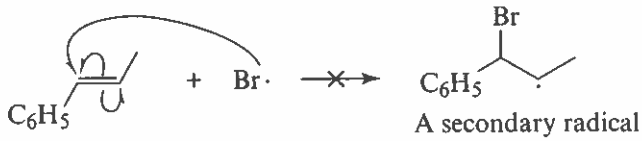
Chain Propagation

Step 4 

2-Bromo-1-phenylpropane

The mechanism for the addition of hydrogen bromide to 1-phenylpropene in the presence of peroxides is a chain mechanism analogous to the one we discussed when we described anti-Markovnikov addition in Section 10.9. The step that determines the orientation of the reaction is the first chain-propagating step. Bromine attacks the second carbon atom of the chain because by doing so the reaction produces a

more stable benzylic radical. Had the bromine atom attacked the double bond in the opposite way, a less stable secondary radical would have been formed.

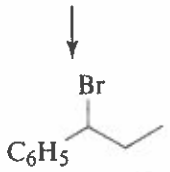


A secondary radical

(b) Hydrogen bromide addition in the absence of peroxides.

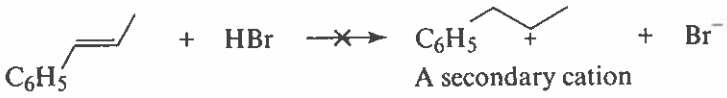


A benzylic cation

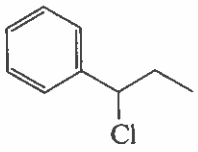


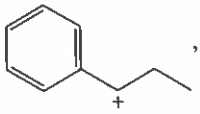
1-Bromo-1-phenylpropane

In the absence of peroxides, hydrogen bromide adds through an ionic mechanism. The step that determines the orientation in the ionic mechanism is the first, where the proton attacks the double bond to give the more stable benzylic cation. Had the proton attacked the double bond in the opposite way, a less stable secondary cation would have been formed.

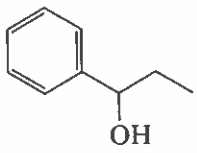


A secondary cation

15.14 (a) 

because the more stable carbocation intermediate is the benzylic carbocation, 

, which then reacts with a chloride ion.

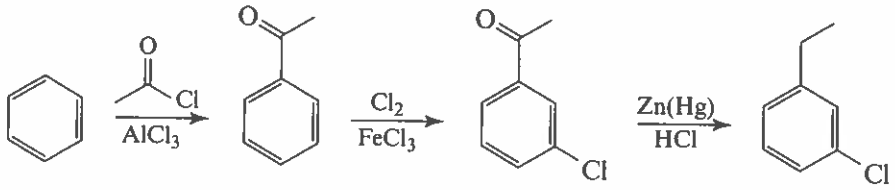
(b) 

because the more stable intermediate is a mercurinium ion in which a partial positive charge resides on the benzylic carbon, which then reacts with H_2O.

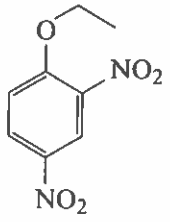
15.15 (a) The first method would fail because introducing the chlorine substituent first would introduce an ortho-para directing group. Consequently, the subsequent Friedel-Crafts reaction would not then take place at the desired meta position.

The second method would fail for essentially the same reasons. Introducing the ethyl group first would introduce an ortho-para director, and subsequent ring chlorination would not take place at the desired meta position.

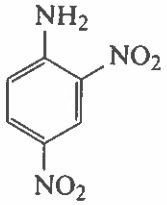
(b) If we introduce an acetyl group first, which we later convert to an ethyl group, we install a meta director. This allows us to put the chlorine atom in the desired position. Conversion of the acetyl group to an ethyl group is then carried out using the Clemmensen (or Wolff–Kishner) reduction.



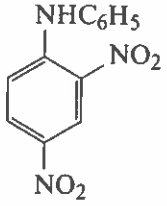
15.16 (a)



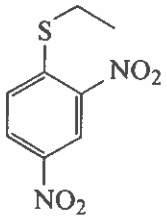
(b)



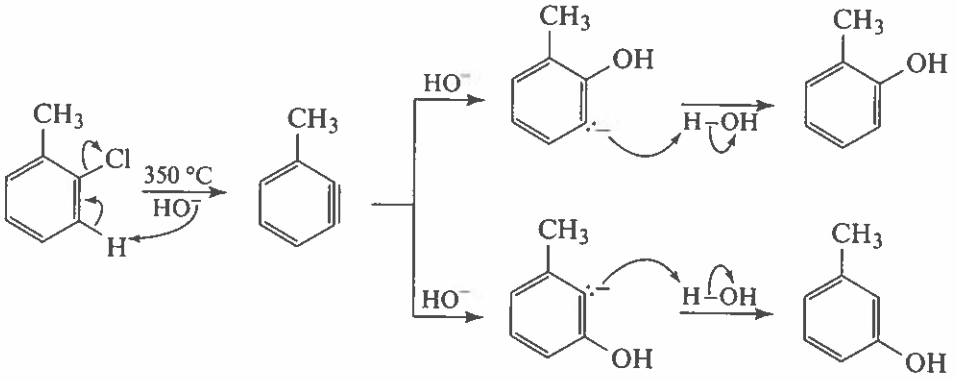
(c)



(d)



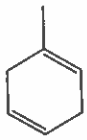
15.17 That *o*-chlorotoluene leads to the formation of two products (*o*-cresol and *m*-cresol) when submitted to the conditions used in the Dow process suggests that an elimination-addition mechanism takes place.



Inasmuch as chlorobenzene and *o*-chlorotoluene should have similar reactivities under these conditions, it is reasonable to assume that chlorobenzene also reacts by an elimination-addition mechanism in the Dow process.

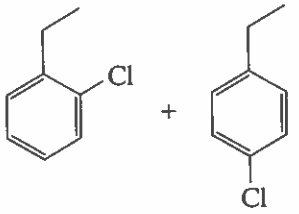
15.18 2-Bromo-1,3-dimethylbenzene, because it has no α-hydrogen, cannot undergo an elimination. Its lack of reactivity toward sodium amide in liquid ammonia suggests that those compounds (e.g., bromobenzene) that do react do so by a mechanism that begins with an elimination.

15.19

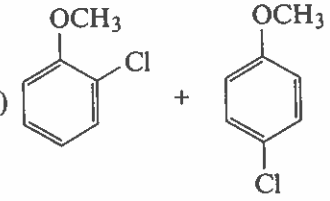


Reactions and Synthesis

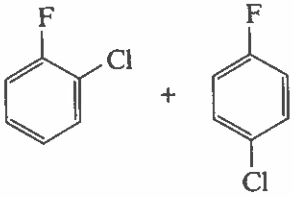
15.20 (a)



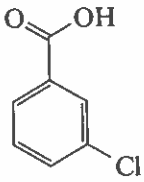
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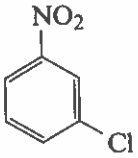
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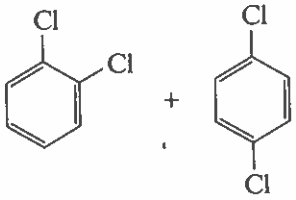
(d)



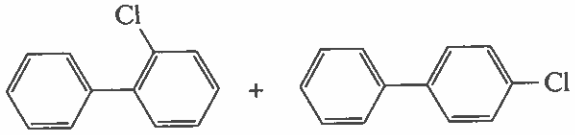
(e)



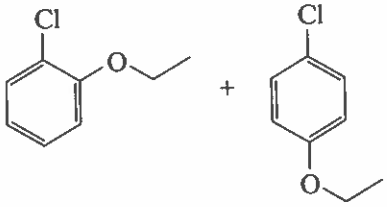
(f)



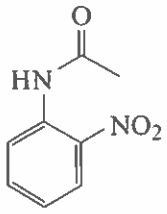
(g)



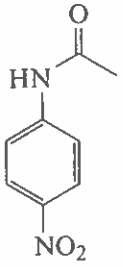
(h)



15.21 (a)

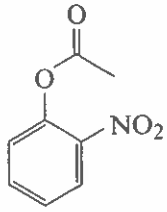


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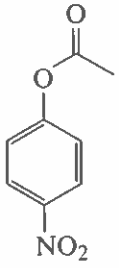


(mainly)

(b)

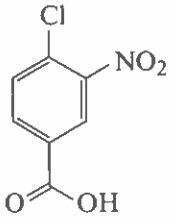


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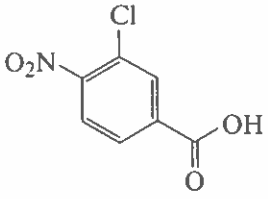


(mainly)

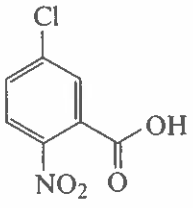
(c)



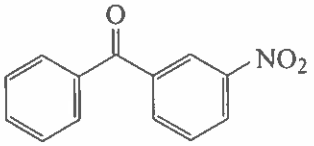
(d)



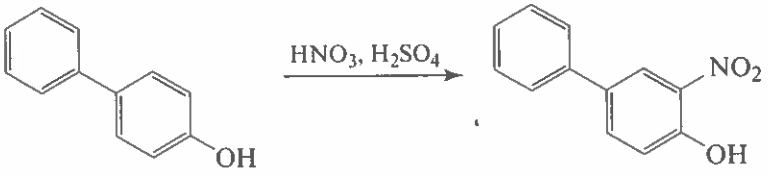
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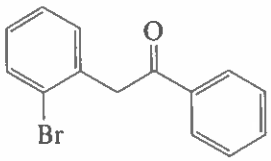
(e)



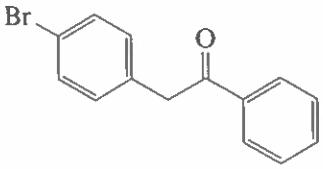
(f)



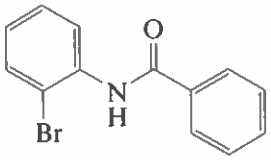
15.22 (a)



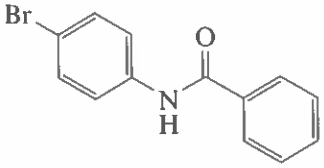
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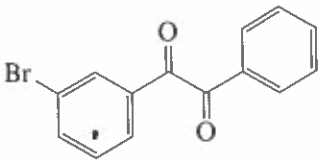
(b)

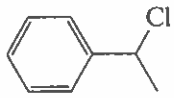


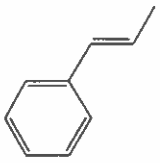
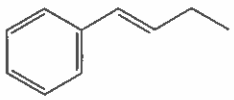
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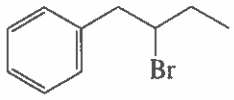


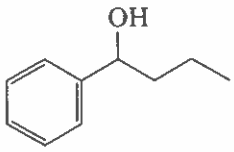
(c)

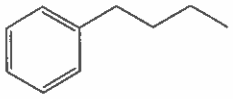


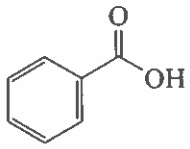
15.23 (a) 

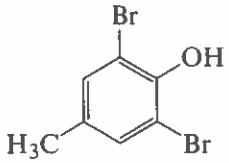
(b) 
(c) 

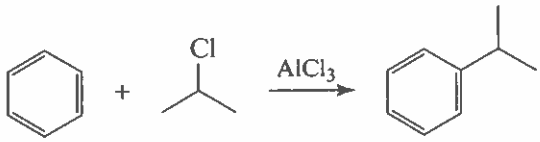
(d) 

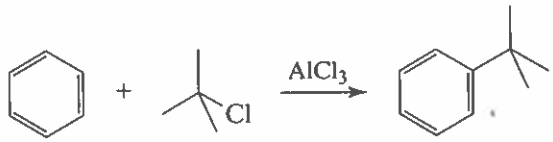
(e) 

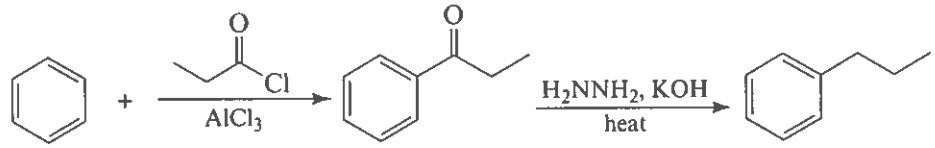
(f) 

(g) 

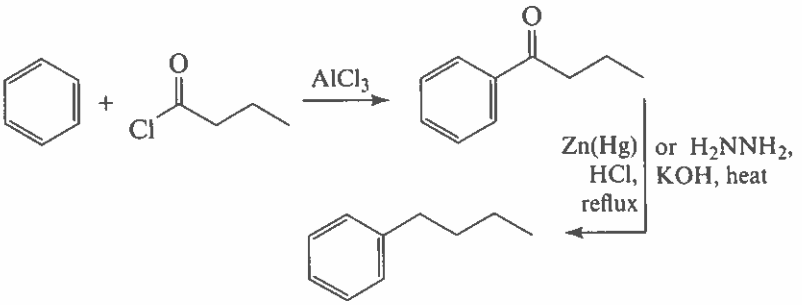
(h) 

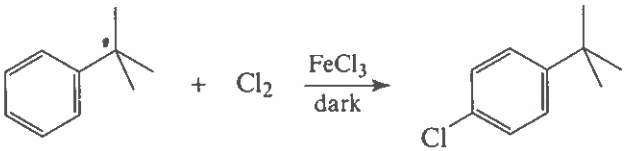
15.24 (a) 

(b) 

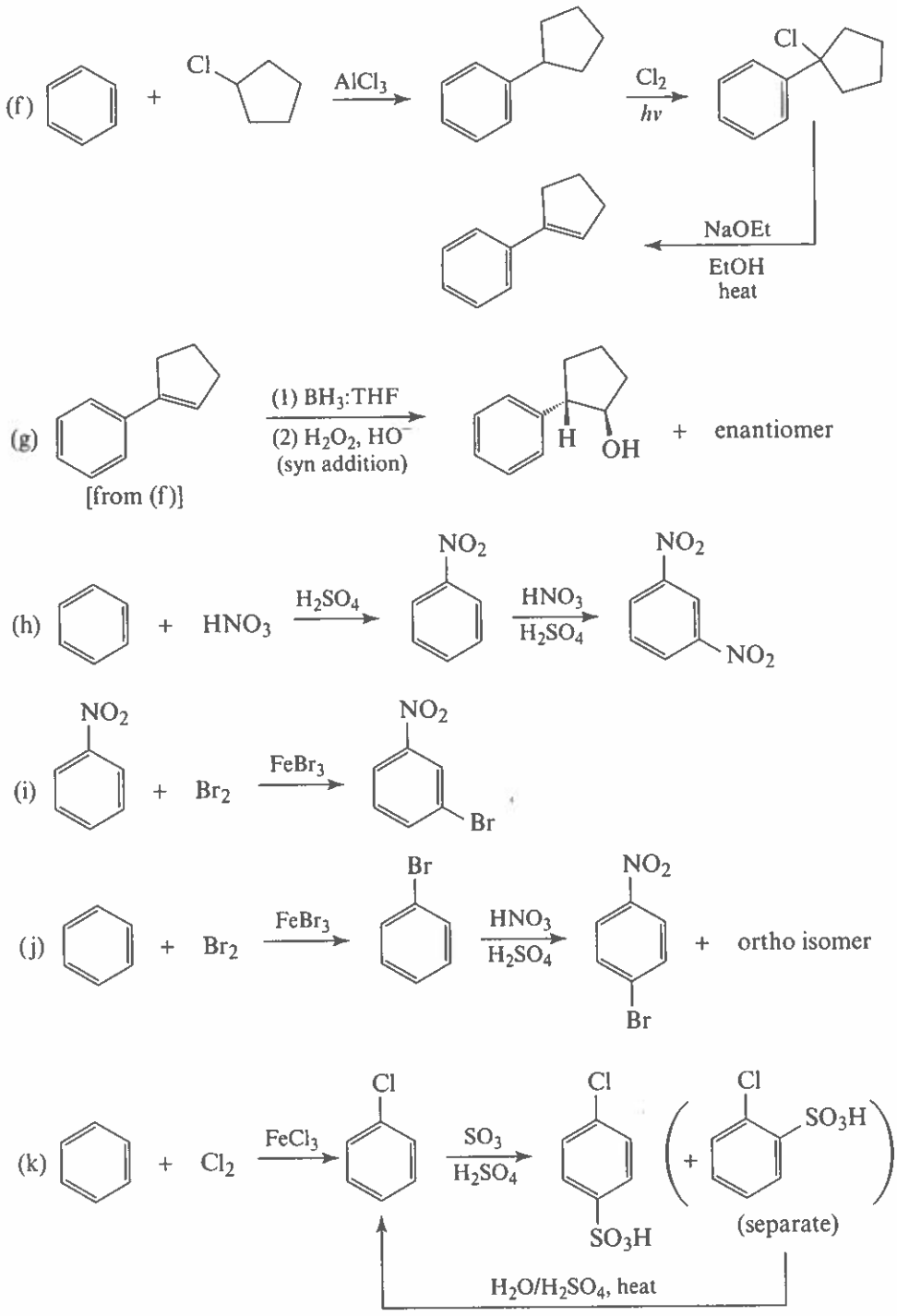
(c) 

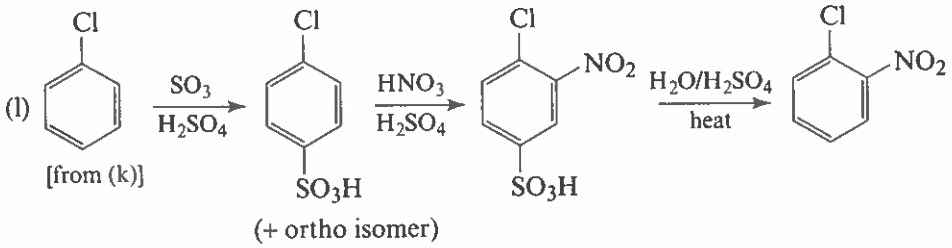
(*Note:* The use of Cl in a Friedel-Crafts synthesis gives mainly the rearranged product, isopropylbenzene.)

(d) 

(e) 

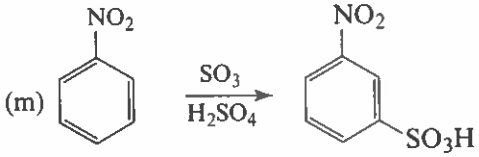
[from (b)]


(f)
Cl
AlCl3
Cl2
hv
Cl
NaOEt
EtOH
heat
(g)
(1) BH3:THF
(2) H2O2, HO−
(syn addition)
H
OH
+ enantiomer
[from (f)]
(h)
HNO3
H2SO4
NO2
HNO3
H2SO4
NO2
NO2
(i)
Br2
FeBr3
NO2
Br
(j)
Br2
FeBr3
Br
HNO3
H2SO4
NO2
Br
+ ortho isomer
(k)
Cl2
FeCl3
Cl
SO3
H2SO4
Cl
SO3H
Cl
SO3H
+
(separate)
H2O/H2SO4, heat

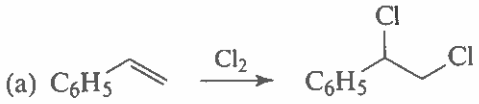
(l) 

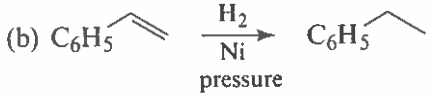
[from (k)]

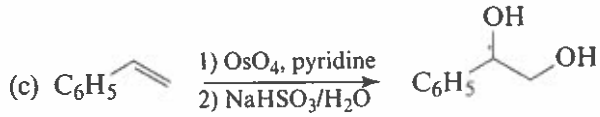
(+ ortho isomer)

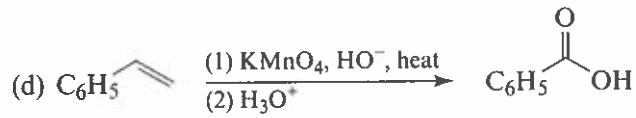
(m) 

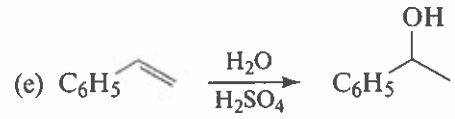
[from (h)]

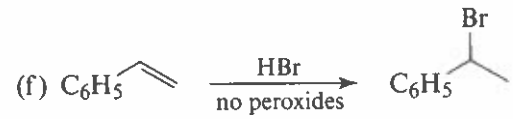
15.25 (a) 

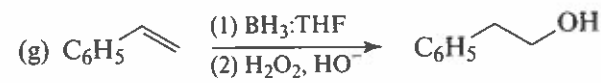
(b) 

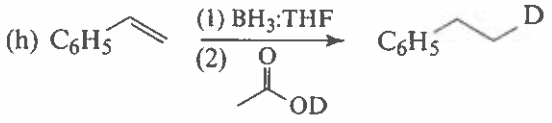
(c) 

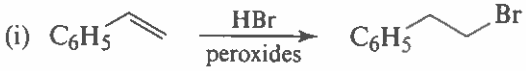
(d) 

(e) 

(f) 

(g) 

(h) 

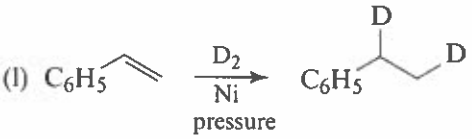
(i) 

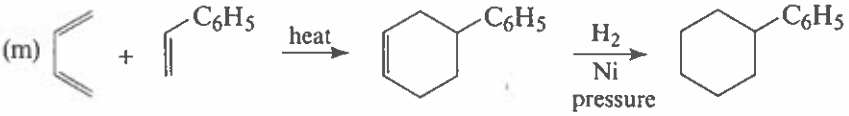
(j) 

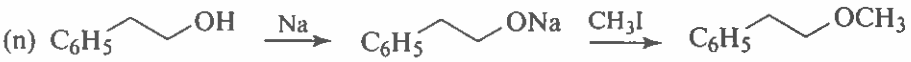
[from (i)]

(k) 

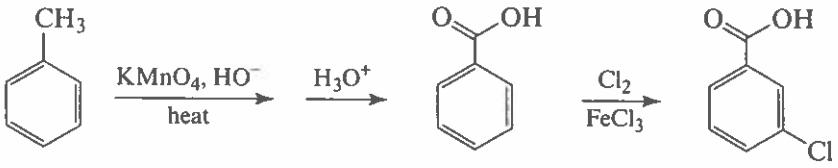
[from (i)]

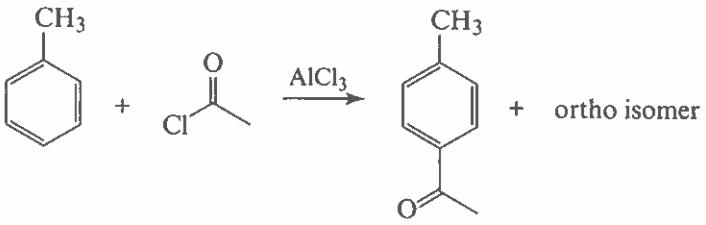
(l) 

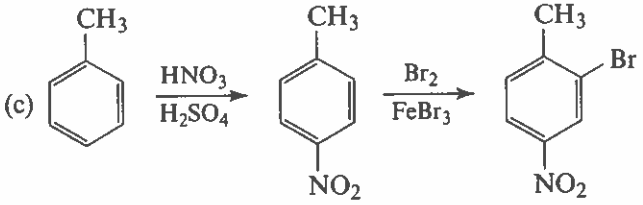
(m) 

(n) 

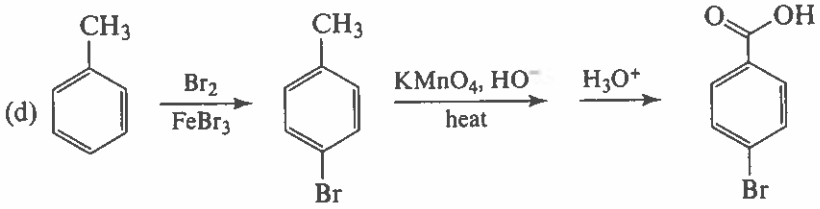
[from (g)]

15.26 (a) 

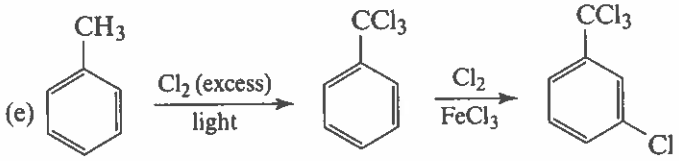
(b) 

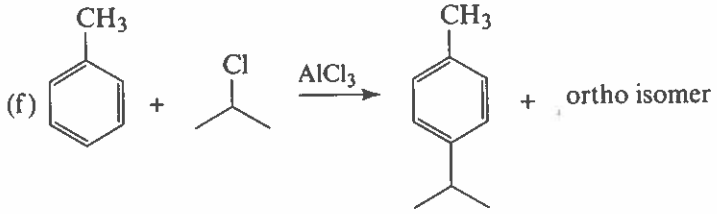


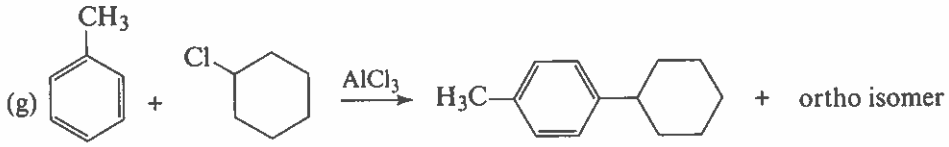
(+ ortho isomer)

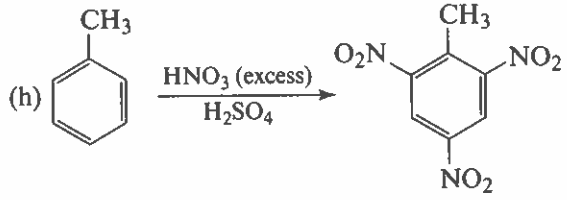


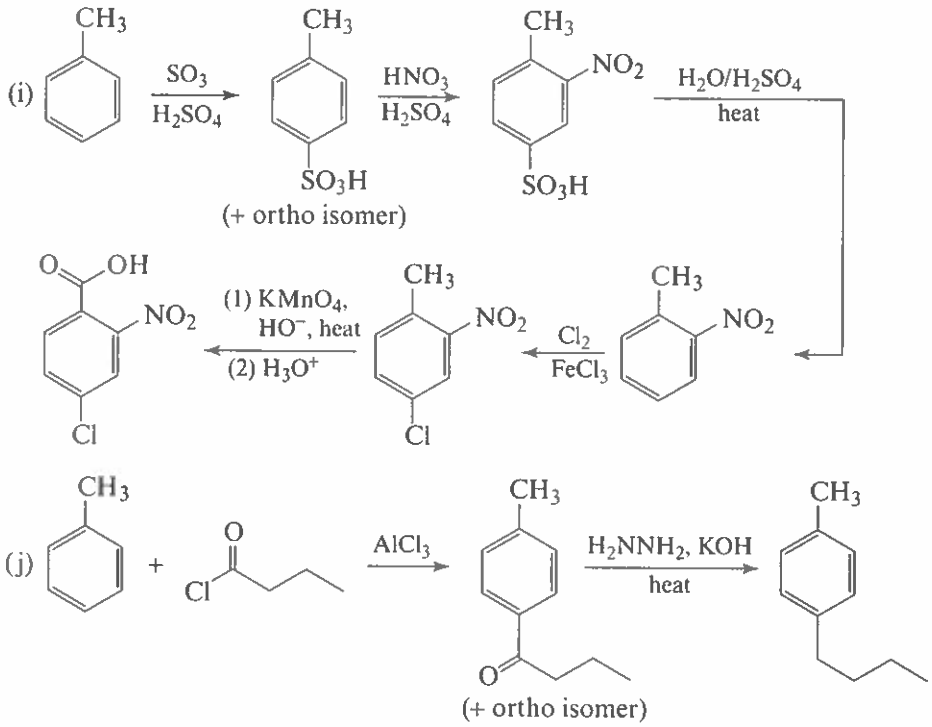
(+ ortho isomer)



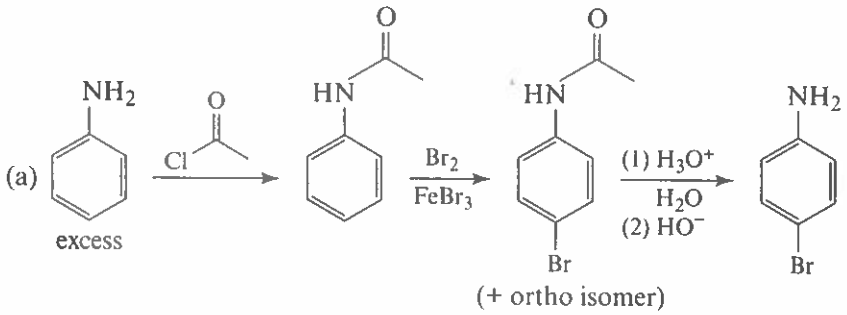


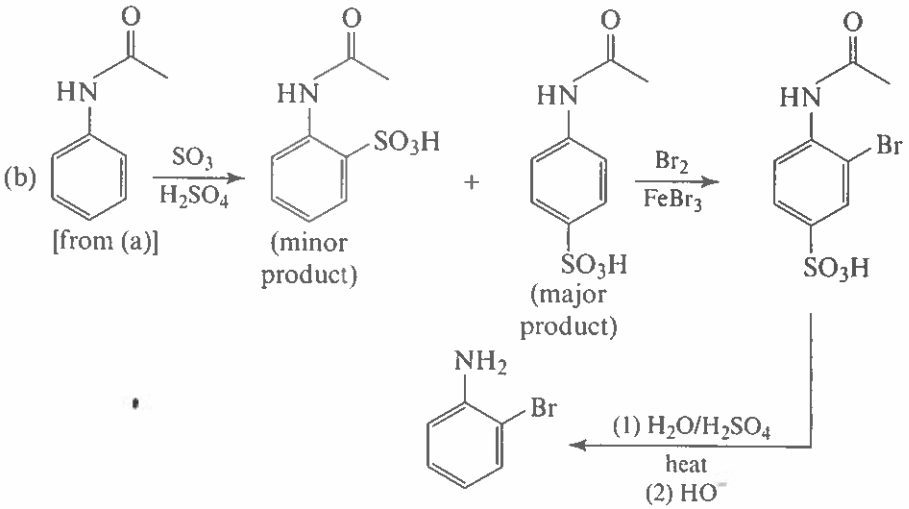


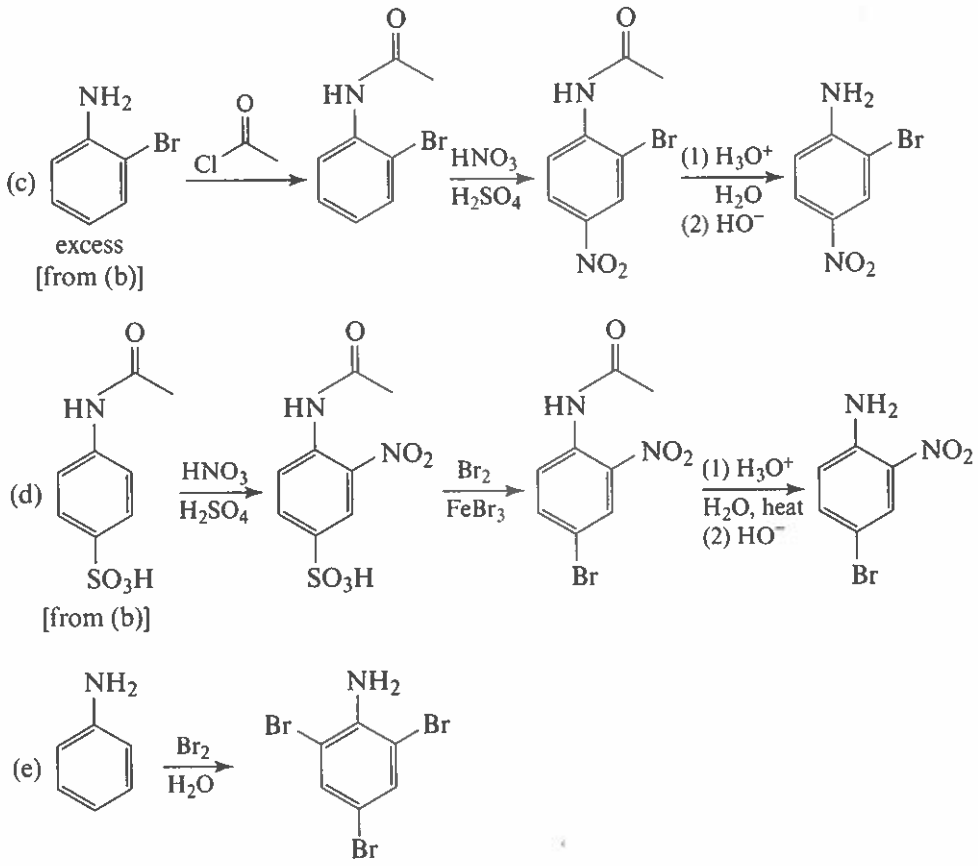



(i)
CH3
SO3
H2SO4
SO3H
HNO3
H2SO4
NO2
H2O/H2SO4
heat
(+ ortho isomer)
OH
O
NO2
Cl
(1) KMnO4,
HO−, heat
(2) H3O+
Cl2
FeCl3
(j)
AlCl3
H2NNH2, KOH
heat
(+ ortho isomer)

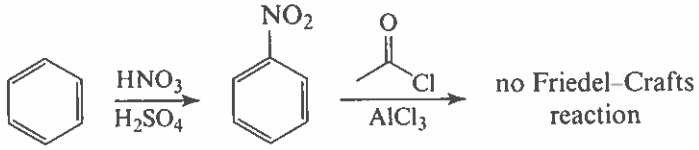
15.27


(a)
NH2
excess
Cl
HN
Br2
FeBr3
(1) H3O+
H2O
(2) HO−
Br
(+ ortho isomer)


(b)
[from (a)]
SO3
H2SO4
SO3H
(minor
product)
+
Br2
FeBr3
(major
product)
Br
(1) H2O/H2SO4
heat
(2) HO−



15.28 (a) Step (2) will fail because a Friedel–Crafts reaction will not take place on a ring that bears an $-NO_2$ group (or any meta director).



(b) The last step will first brominate the double bond.

