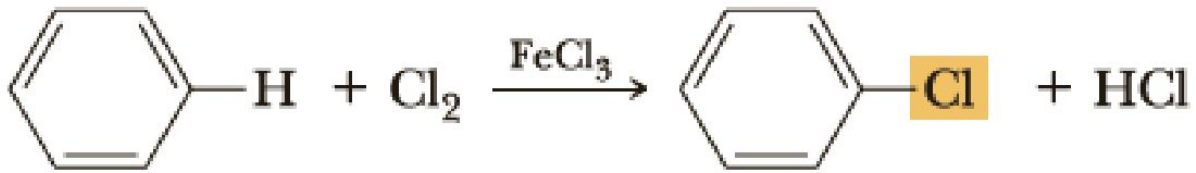
Свойства аренов

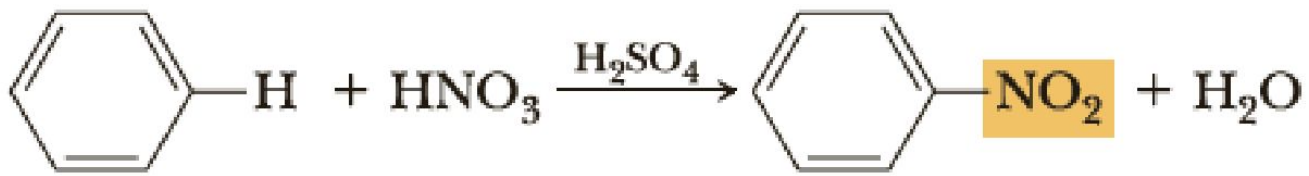
Реакции электрофильного замещения S_E

Halogenation:



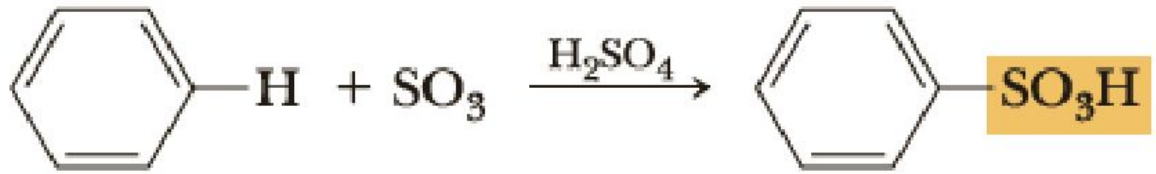
Chlorobenzene

Nitration:



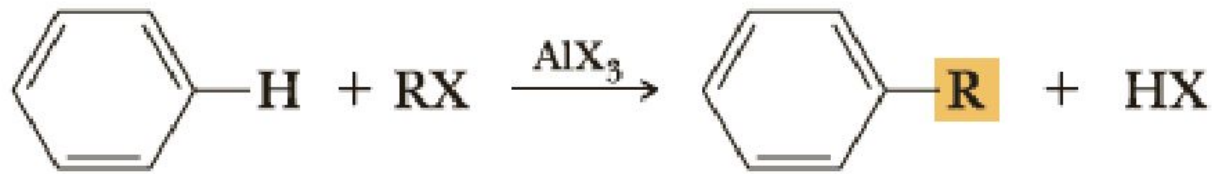
Nitrobenzene

Sulfonation:



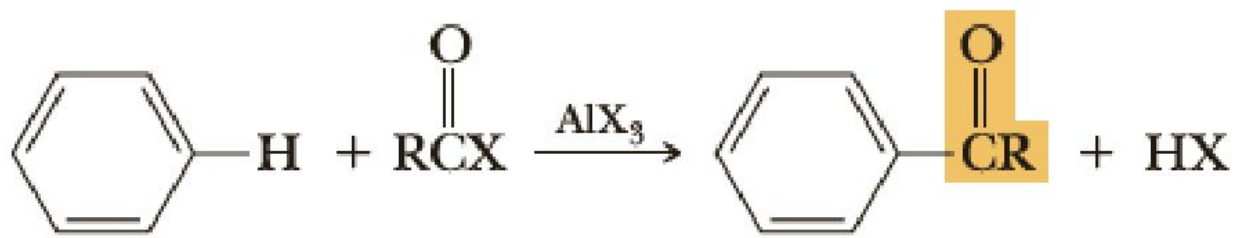
Benzenesulfonic acid

Alkylation:

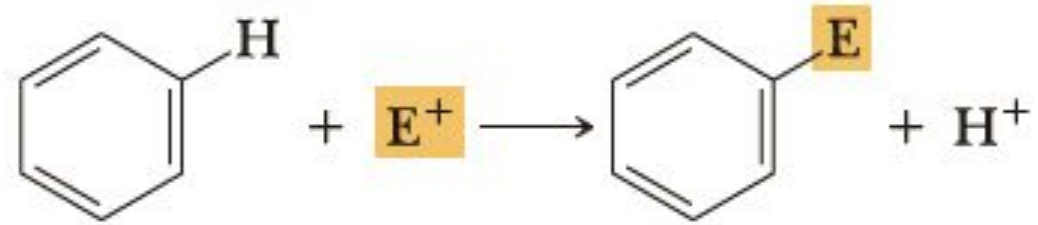


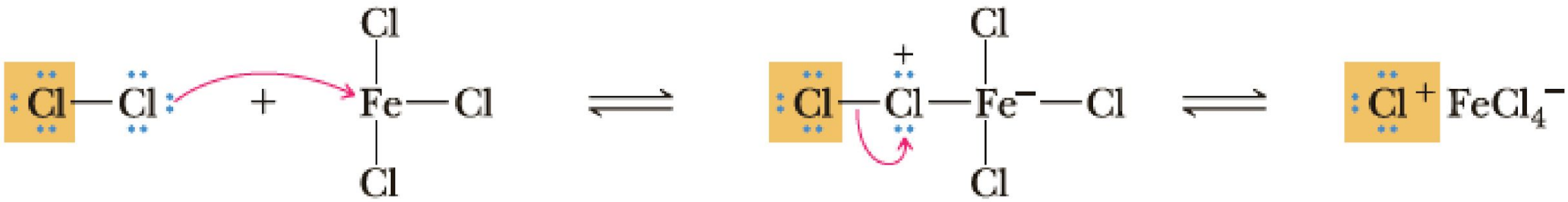
An alkylbenzene

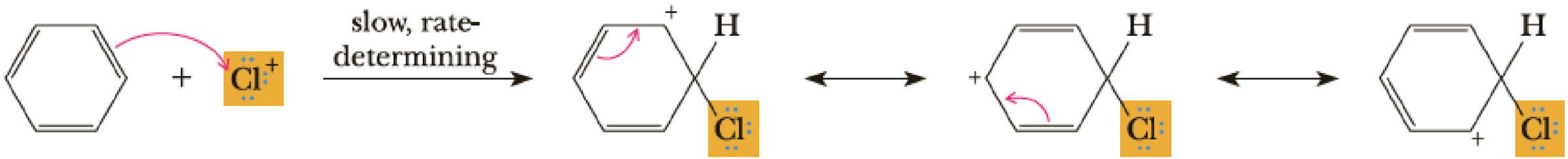
Acylation:

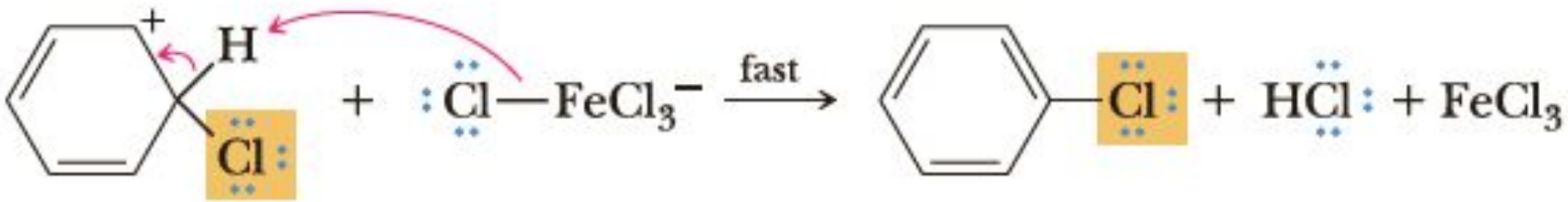


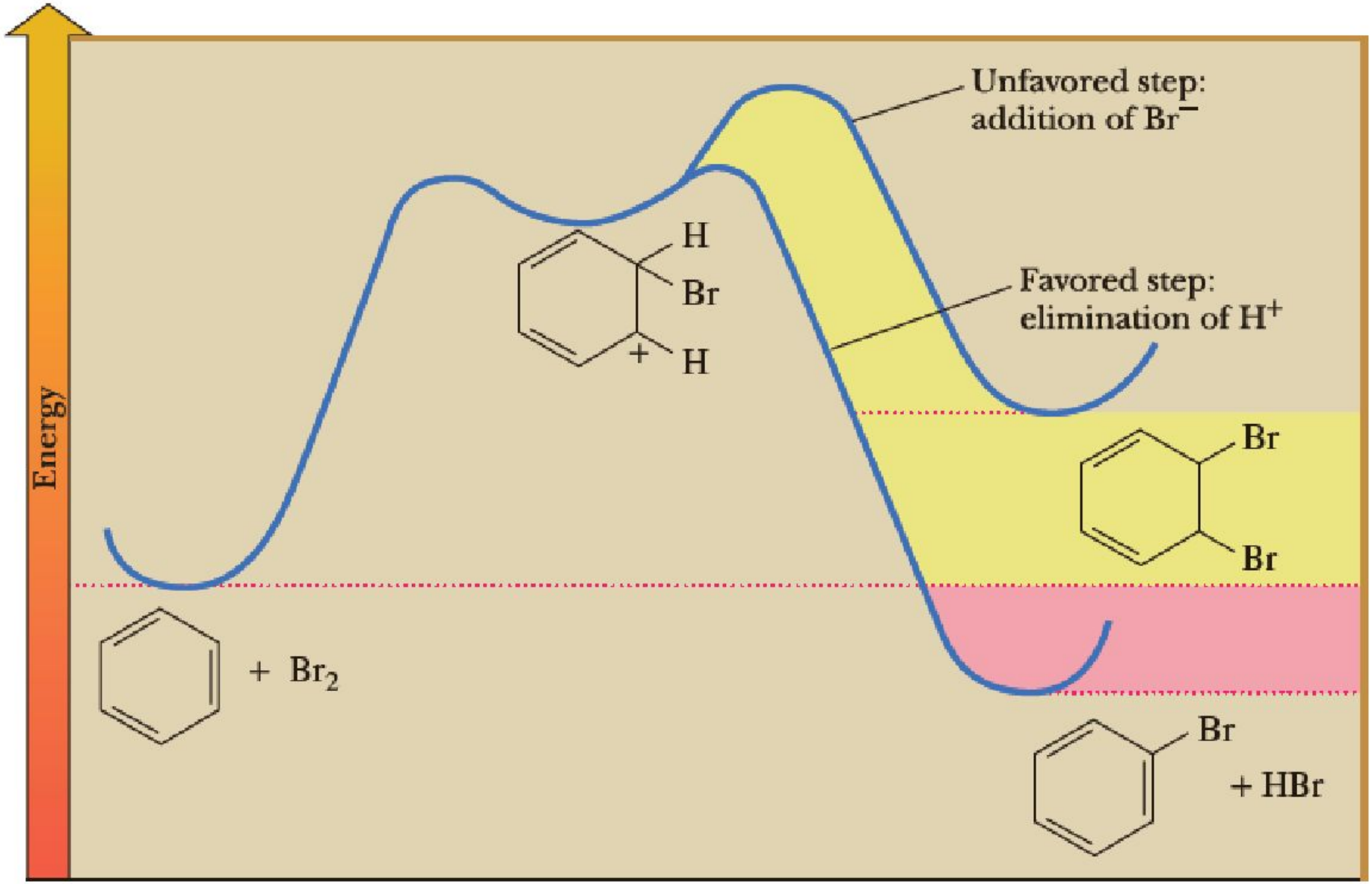
An acylbenzene


H
E
+ E+
+ H+

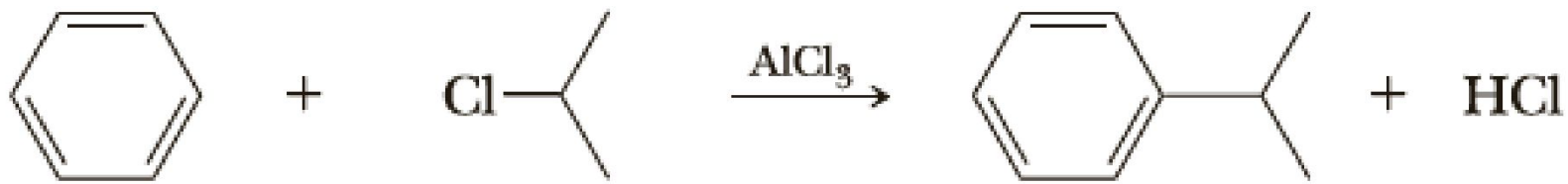

Cl
Cl
Fe
Cl
Cl
Cl
Cl
Fe−
Cl
Cl
Cl
Cl+ FeCl4−


+ Cl+
slow, rate-determining
H
Cl
H
Cl
H
Cl

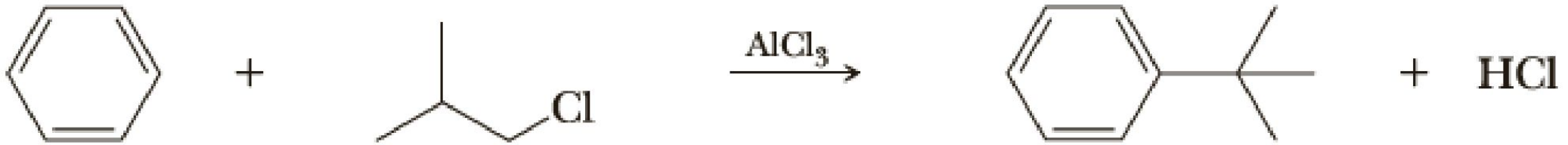

H
Cl
+ Cl—FeCl3−
fast
Cl
+ HCl + FeCl3


Energy
Unfavored step:
addition of Br⁻
Favored step:
elimination of H⁺
H
Br
H
+
Br
Br
+ Br2
Br
+ HBr
Reaction coordinate

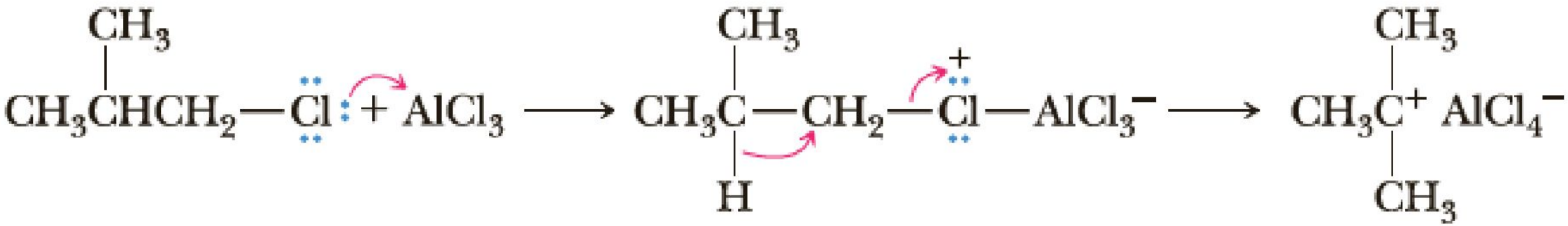
Алкилирование по Фриделю-Крафтсу



Benzene **2-Chloropropane (Isopropyl chloride)** **Cumene (Isopropylbenzene)**



1-Chloro-2-methylpropane (Isobutyl chloride) **2-Methyl-2-phenylpropane (*tert*-Butylbenzene)**

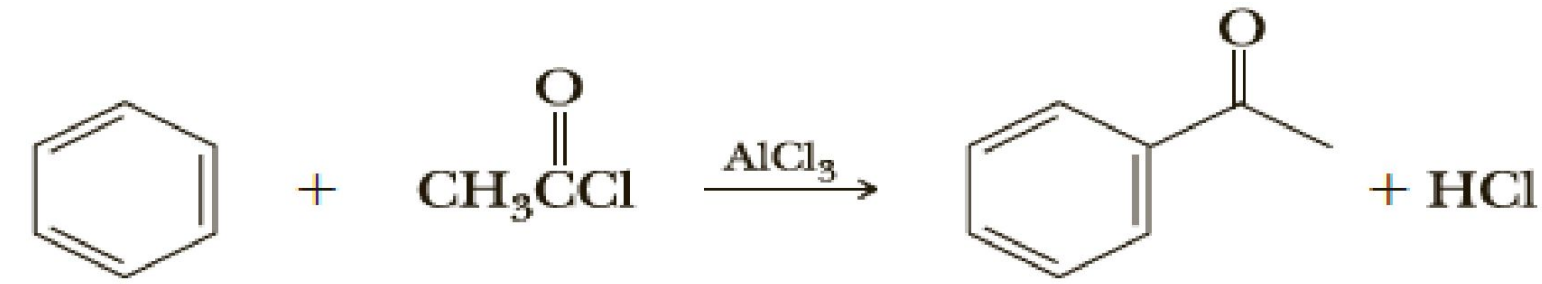


Isobutyl chloride

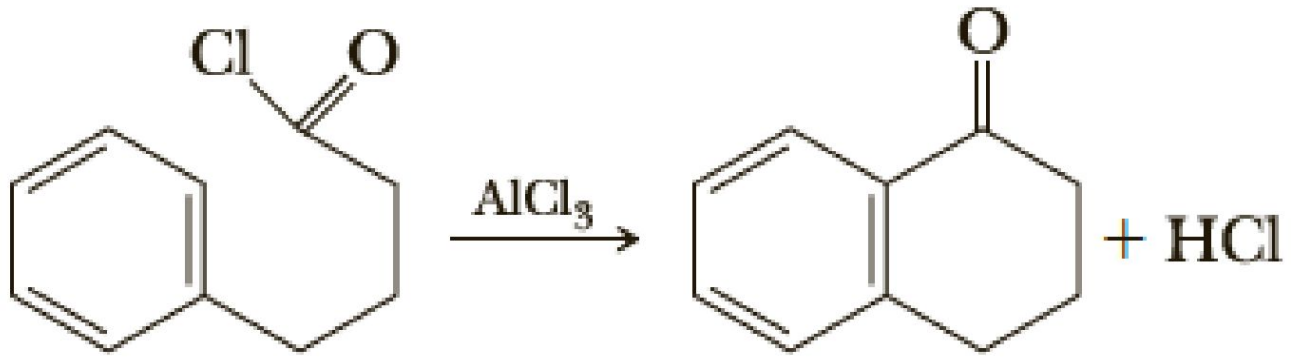
Isobutyl chloride/aluminum chloride complex

***tert*-Butyl cation/ $AlCl_4^-$ ion pair**

Ацилирование по Фриделю-Крафтсу

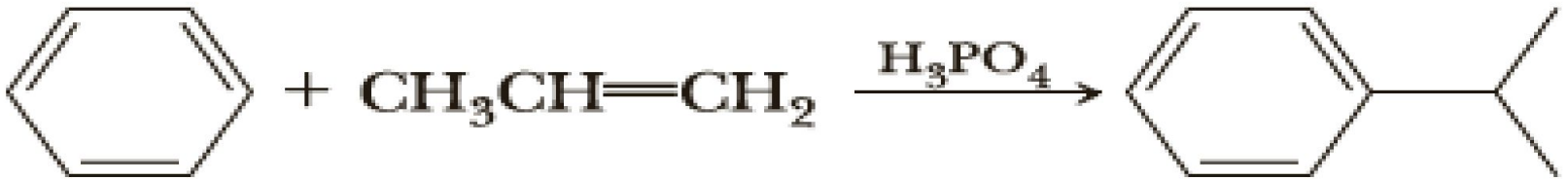


Benzene **Acetyl chloride (an acyl halide)** **Acetophenone (a ketone)**

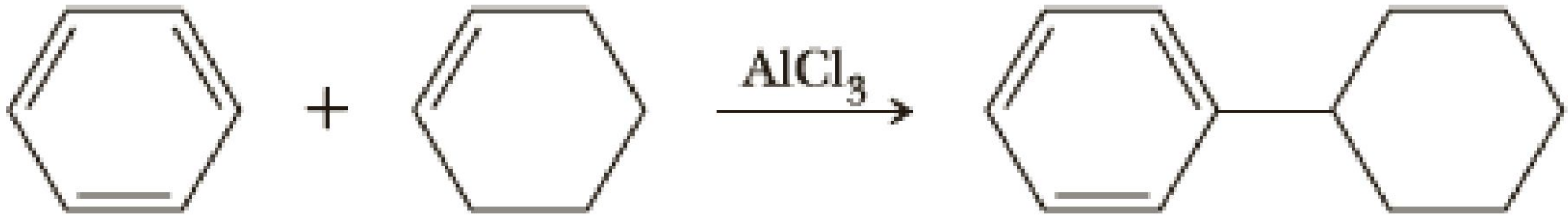


4-Phenylbutanoyl chloride **α-Tetralone**

Присоединение алкенов



Benzene **Propene** **Cumene**



Benzene **Cyclohexene** **Phenylcyclohexane**

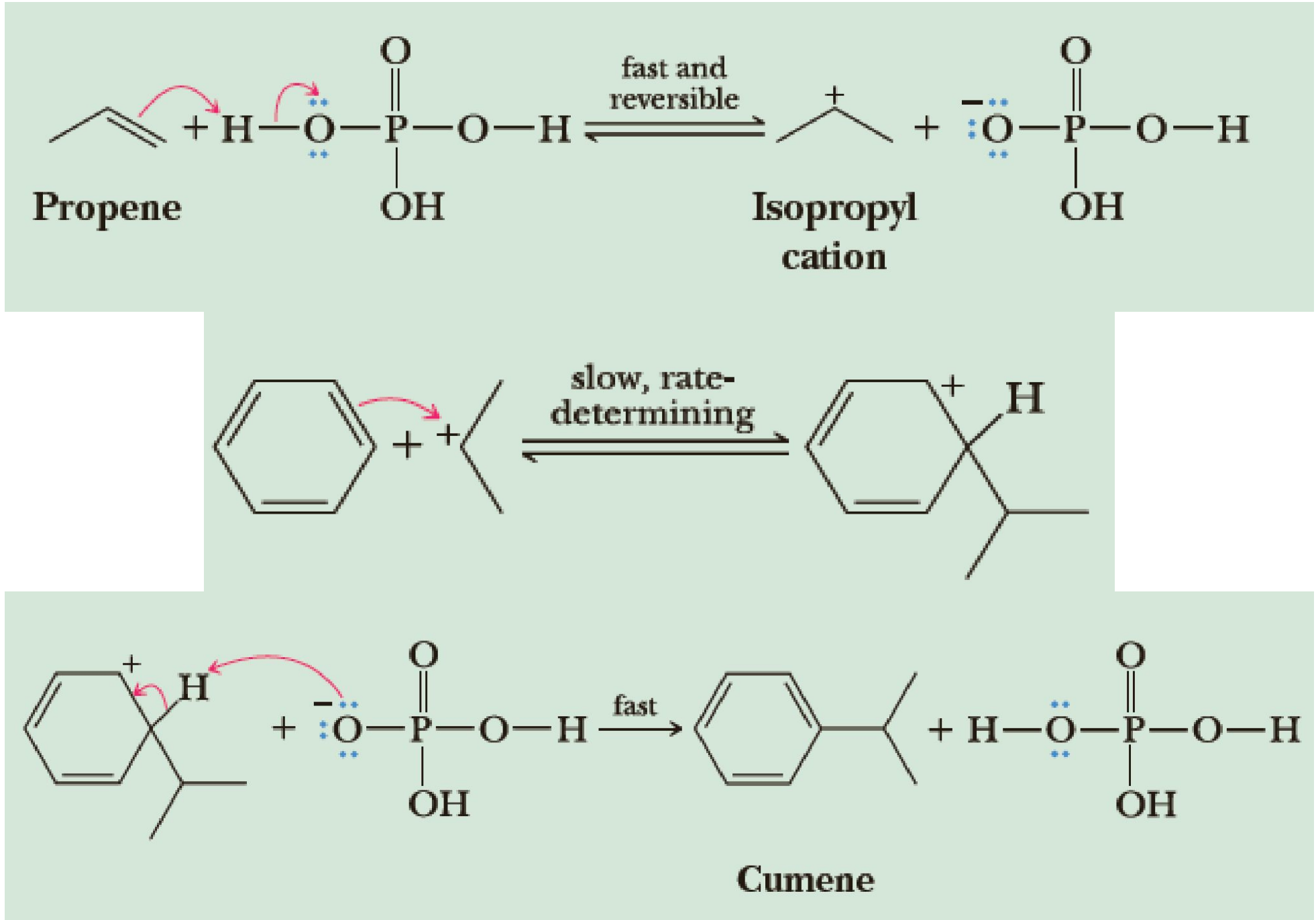
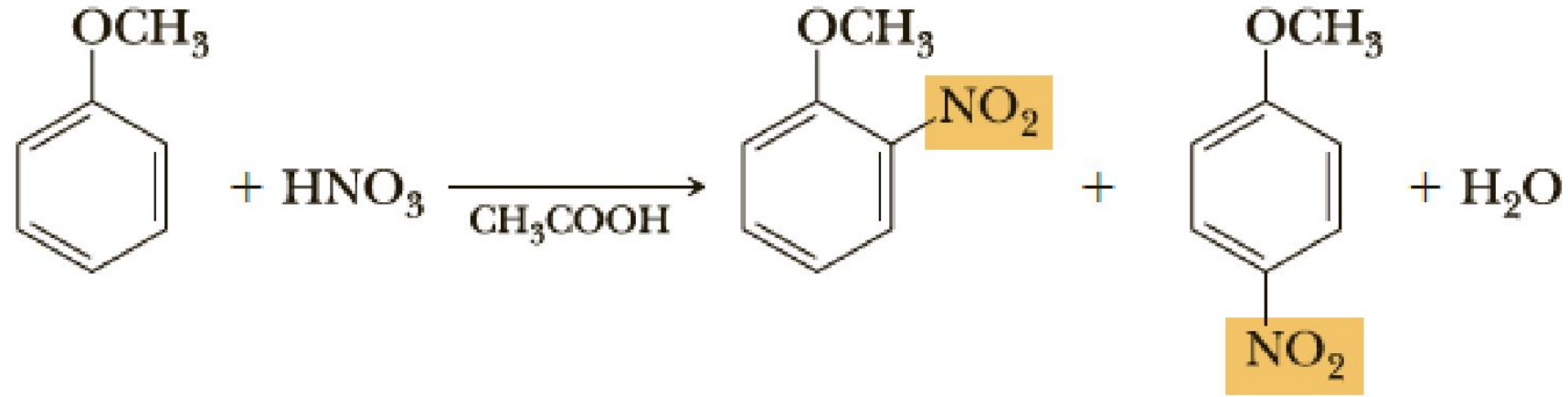

fast and
reversible
Propene
Isopropyl
cation
slow, rate-
determining
fast
Cumene

Table 22.1 Orientation on Nitration of Monosubstituted Benzenes

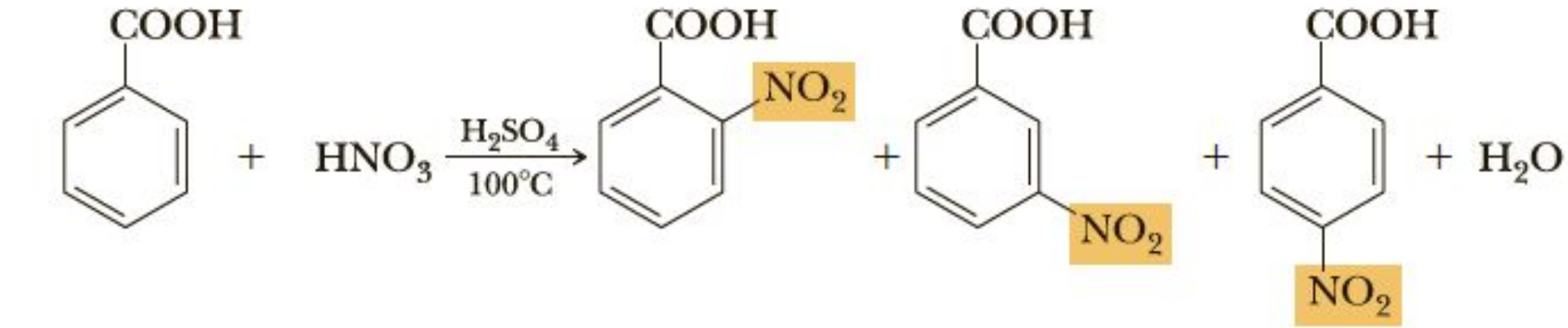
Substituent	ortho	meta	para	ortho + para	meta
—OCH_3	44	—	55	99	trace
—CH_3	58	4	38	96	4
—Cl	70	—	30	100	trace
—Br	37	1	62	99	1
—COOH	18	80	2	20	80
—CN	19	80	1	20	80
—NO_2	6.4	93.2	0.3	6.7	93.2



Anisole

***o*-Nitroanisole**
(44%)

***p*-Nitroanisole**
(55%)

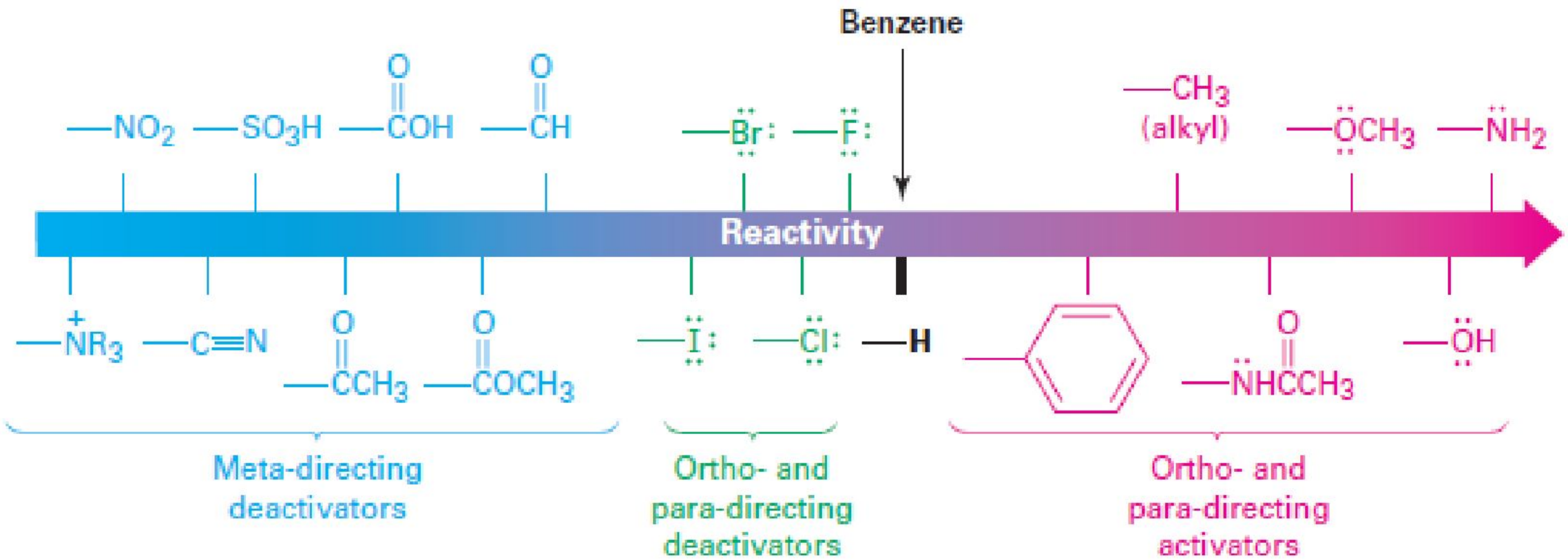


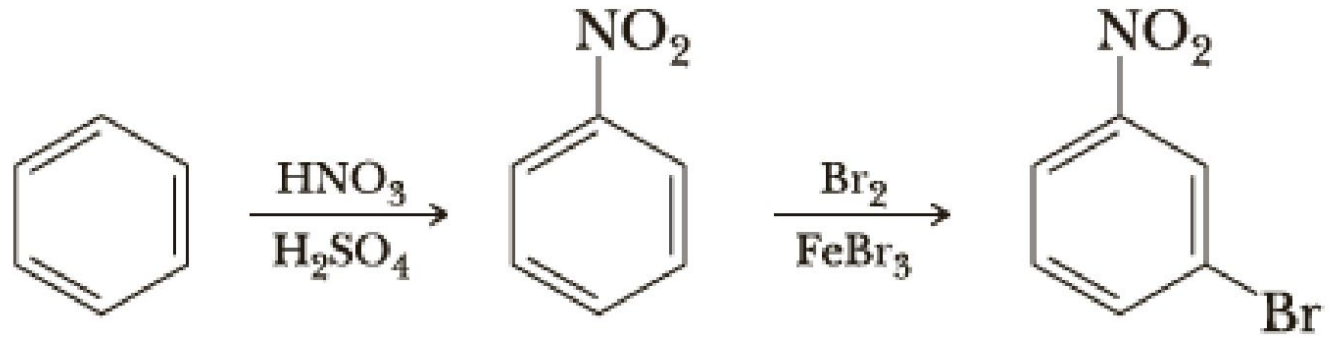
Benzoic acid

***o*-Nitro-benzoic acid**
(18%)

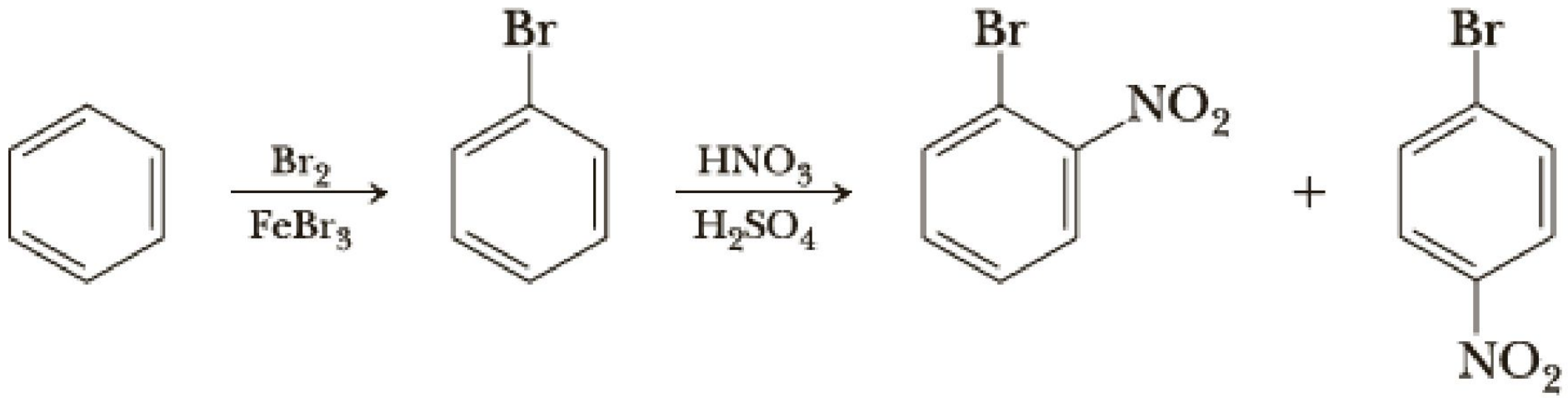
***m*-Nitro-benzoic acid**
(80%)

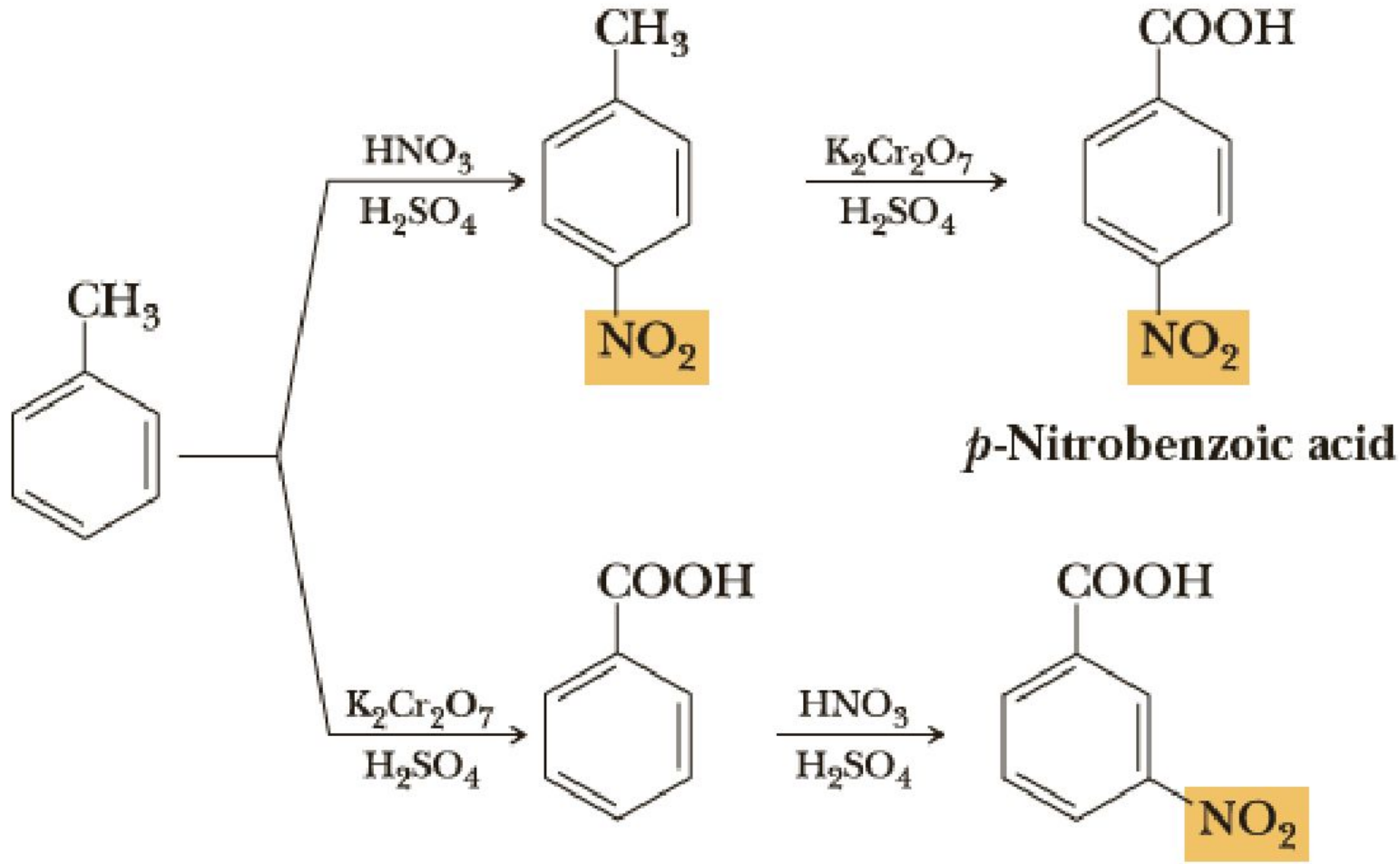
***p*-Nitro-benzoic acid**
(2%)

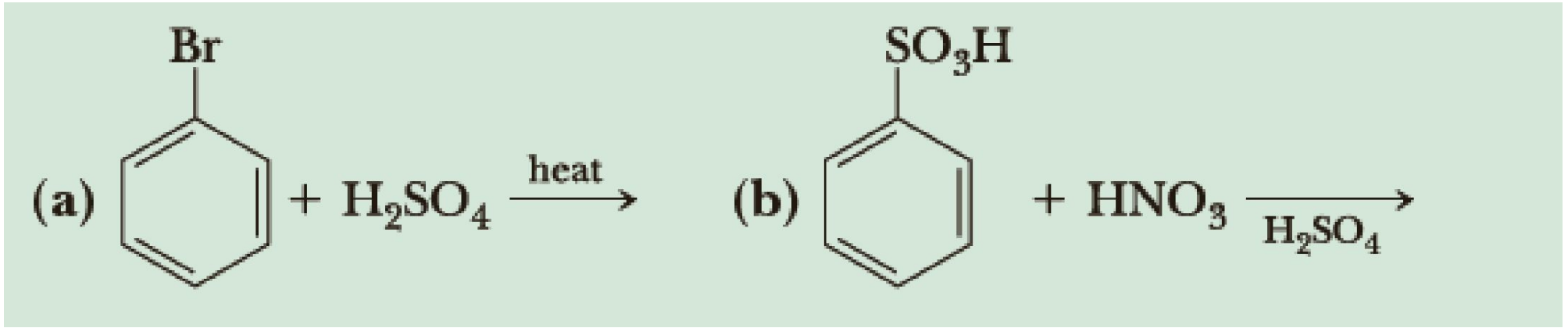

Benzene
—NO2
—SO3H
—COH
—CH
—Br:
—F:
—CH3
(alkyl)
—OCH3
—NH2
Reactivity
—NR3
—C≡N
—CCH3
—COCH3
—I:
—Cl:
—H
—NHCCH3
—OH
Meta-directing
deactivators
Ortho- and
para-directing
deactivators
Ortho- and
para-directing
activators

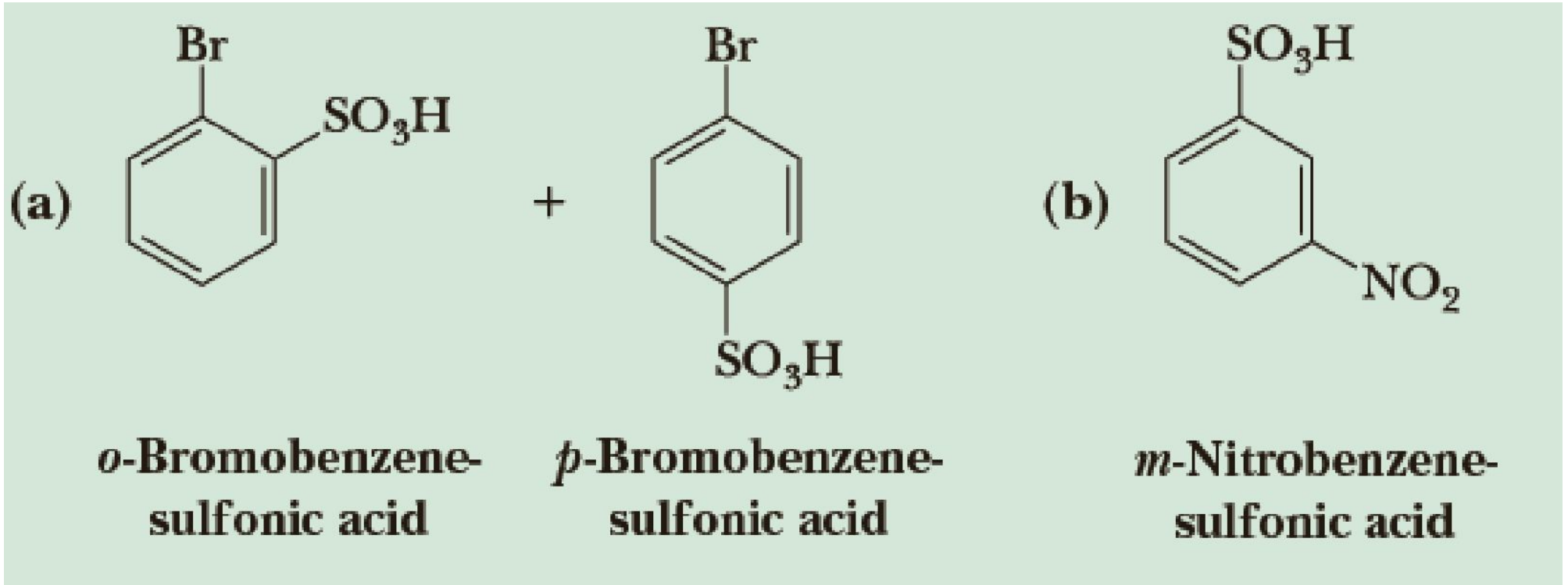


Nitrobenzene **_m_-Bromonitro-benzene**




CH3
HNO3
H2SO4
NO2
K2Cr2O7
H2SO4
COOH
NO2
p-Nitrobenzoic acid
CH3
K2Cr2O7
H2SO4
COOH
HNO3
H2SO4
COOH
NO2
m-Nitrobenzoic acid

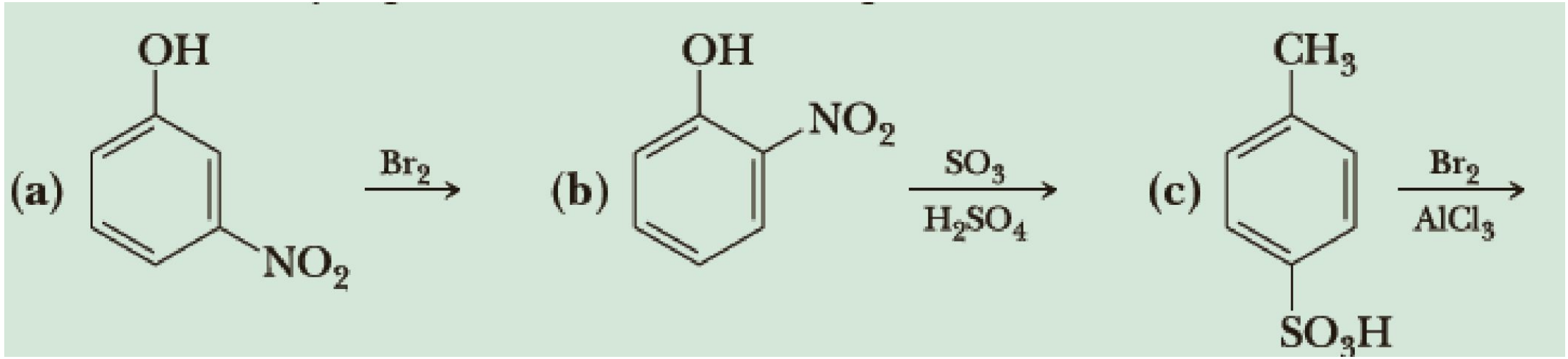


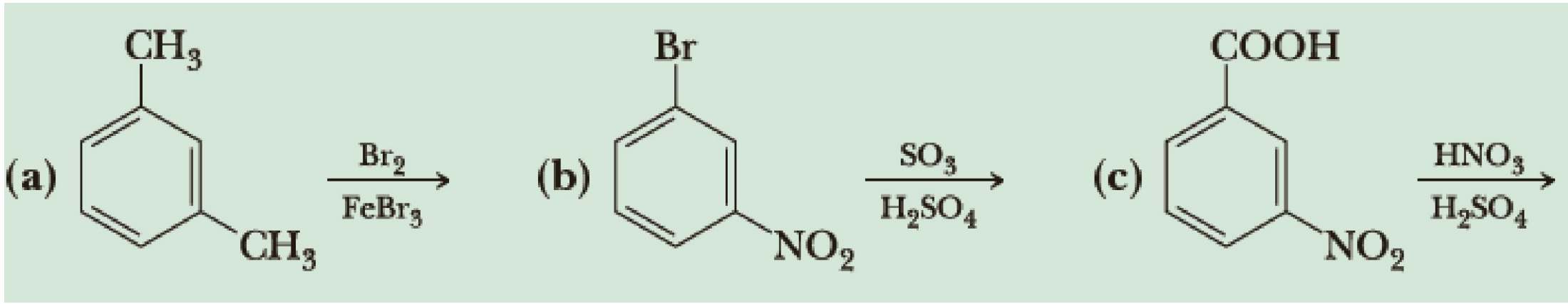


o-Bromobenzene-sulfonic acid

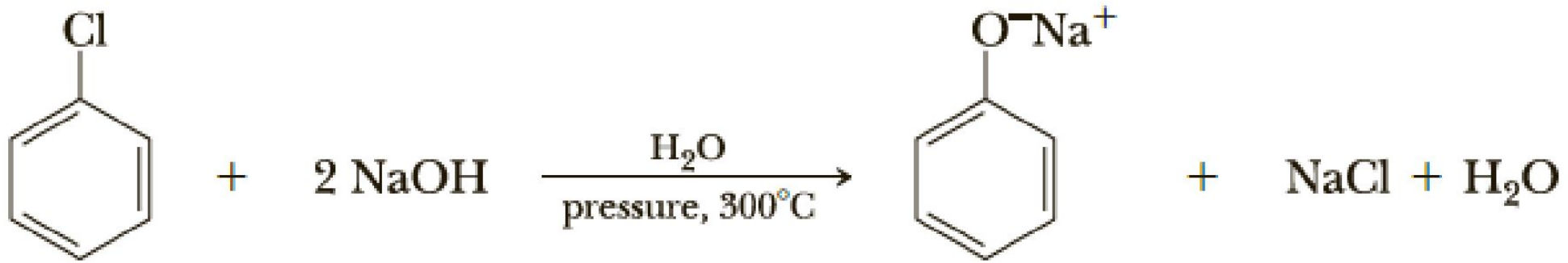
p-Bromobenzene-sulfonic acid

m-Nitrobenzene-sulfonic acid

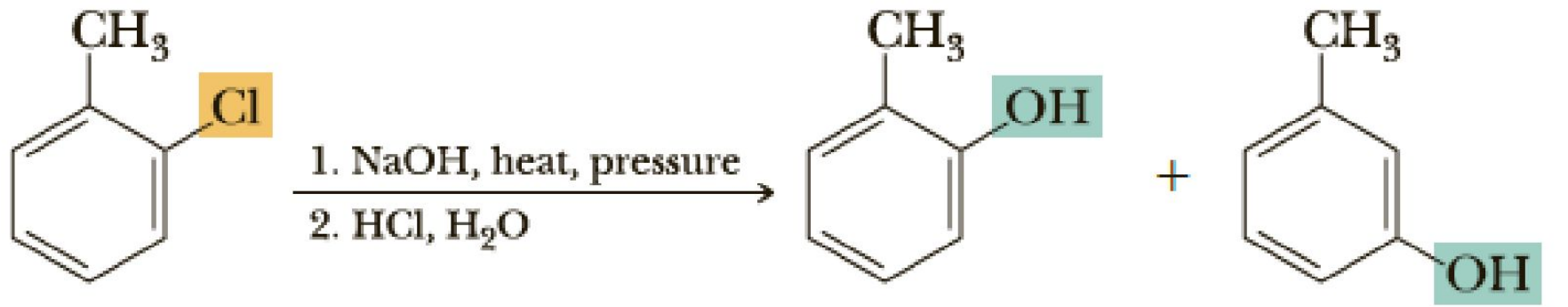

(a)
OH
NO2
Br2
(b)
OH
NO2
SO3
H2SO4
(c)
CH3
SO3H
Br2
AlCl3


(a)
CH3
CH3
Br2
FeBr3
(b)
Br
NO2
SO3
H2SO4
(c)
COOH
NO2
HNO3
H2SO4

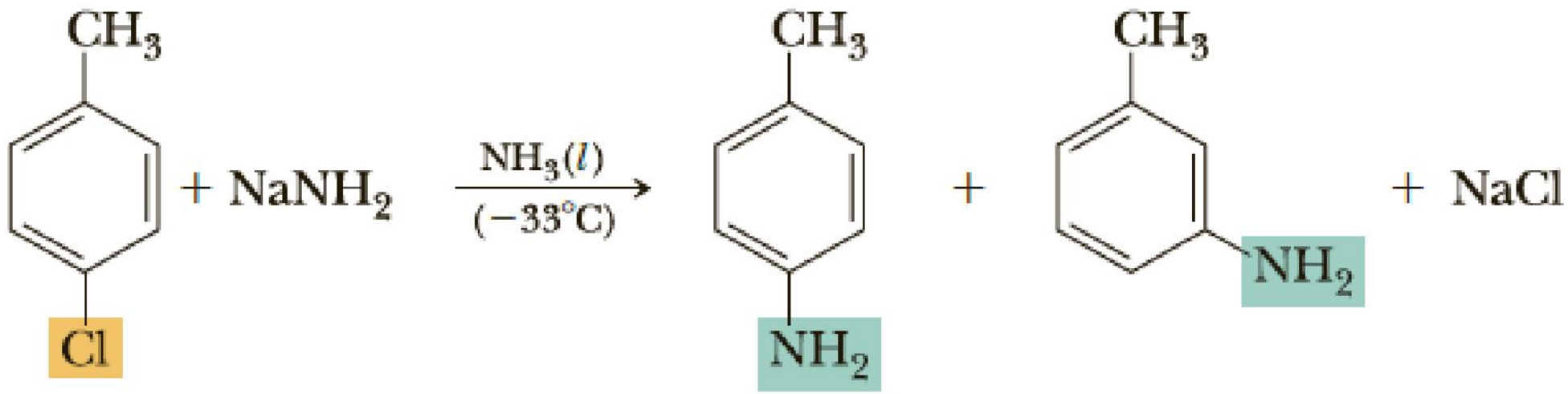
Нуклеофильное замещение S_N



Chlorobenzene **Sodium phenoxide**

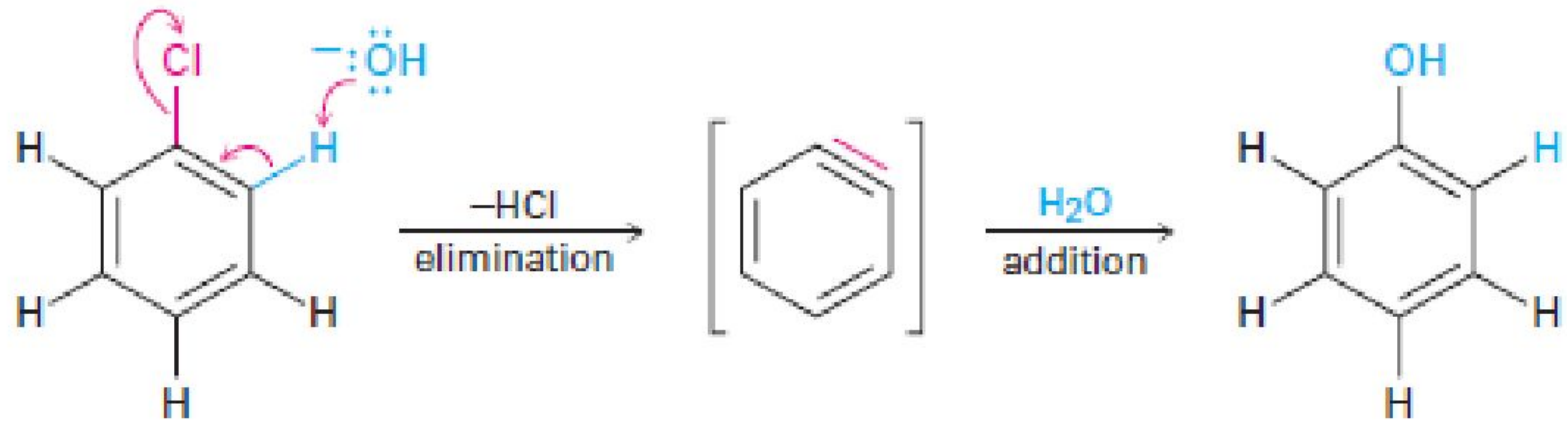


2-Methylphenol (*o*-Cresol) **3-Methylphenol (*m*-Cresol)**

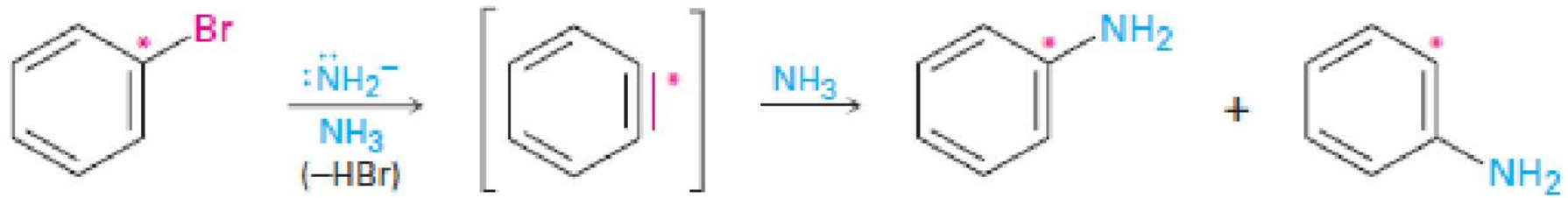


4-Methylaniline (*p*-Toluidine)

3-Methylaniline (*m*-Toluidine)

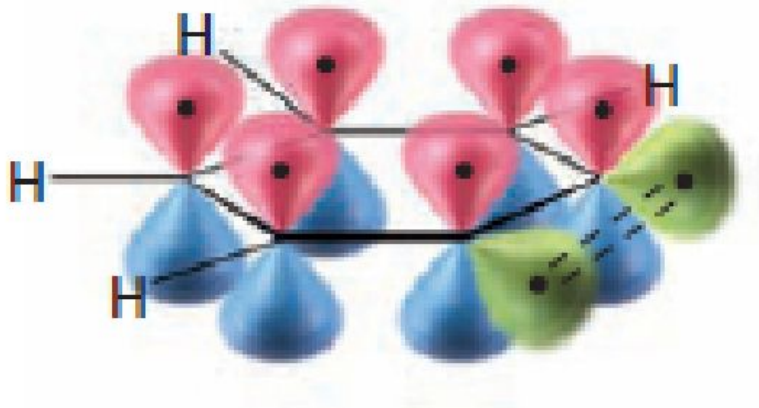


Chlorobenzene **Benzyne** **Phenol**

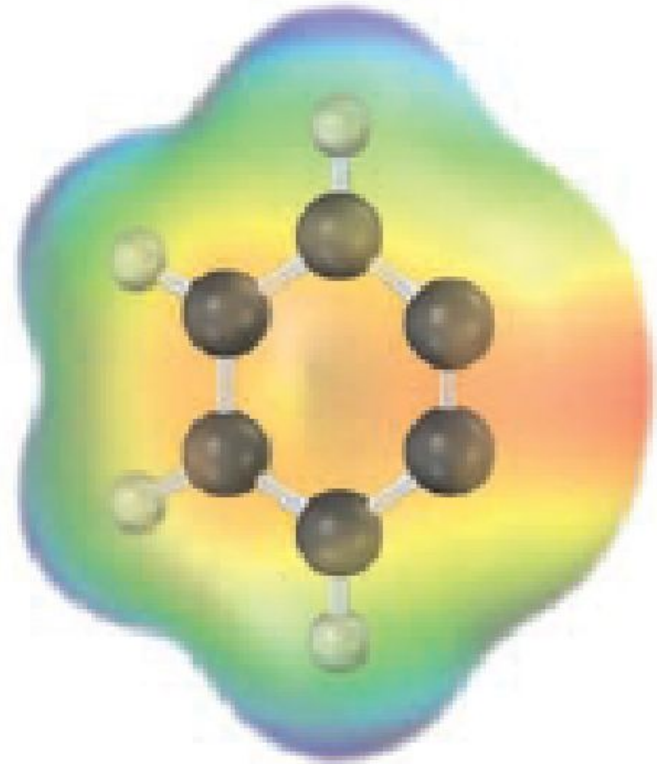


50% **50%**

Bromobenzene **Benzyne (symmetrical)** **Aniline**

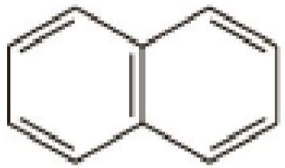
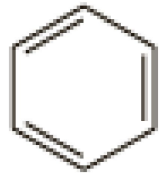


Side view

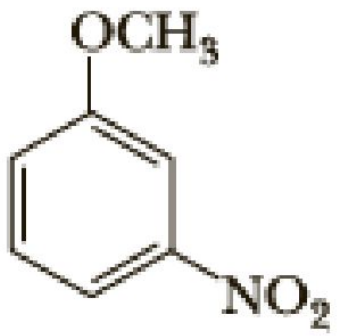


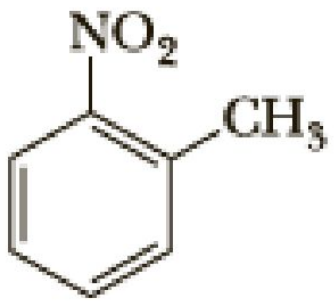
Benzyne

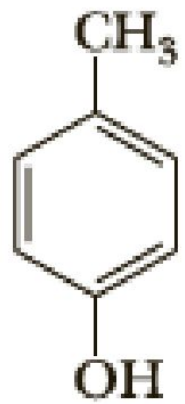
Problems

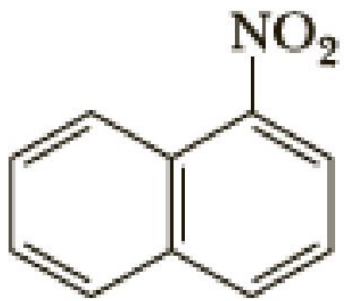
(a)  + Cl_2 $\xrightarrow{FeCl_3}$ (b)  +  $\xrightarrow{AlCl_3}$ (d)  + CH_2Cl_2 $\xrightarrow{AlCl_3}$

Predict the major product or products from treatment of each compound with HNO_3/H_2SO_4.

(a) 

(b) 

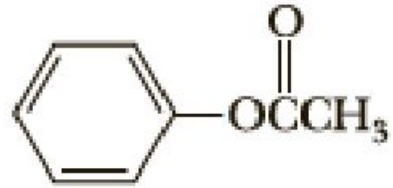
(c) 

(d) 

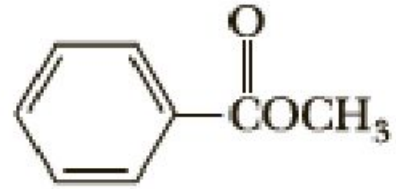
22.19 Arrange the compounds in each set in order of decreasing reactivity (fastest to slowest) toward electrophilic aromatic substitution.

(a)

(A)

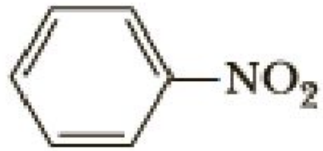


(B)

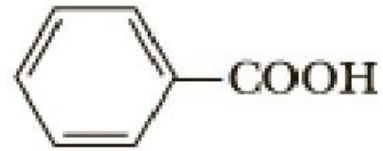


(C)

(b)



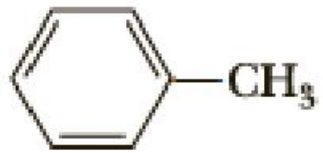
(A)



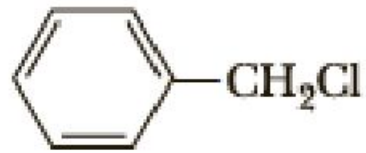
(B)

(C)

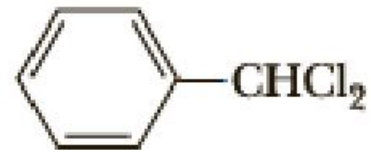
(c)



(A)

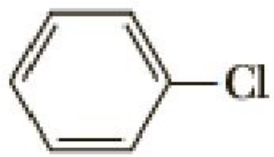


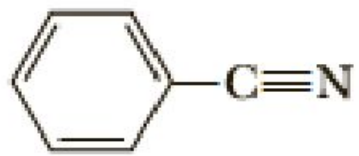
(B)

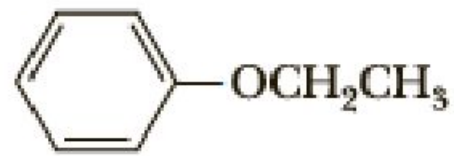


(C)

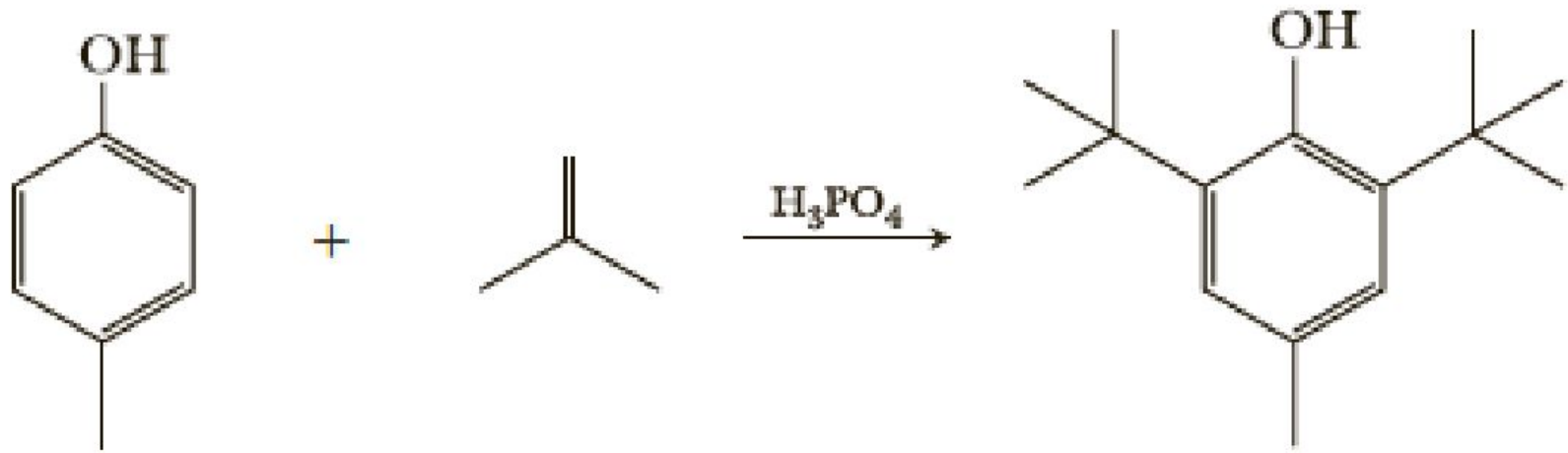
(d)





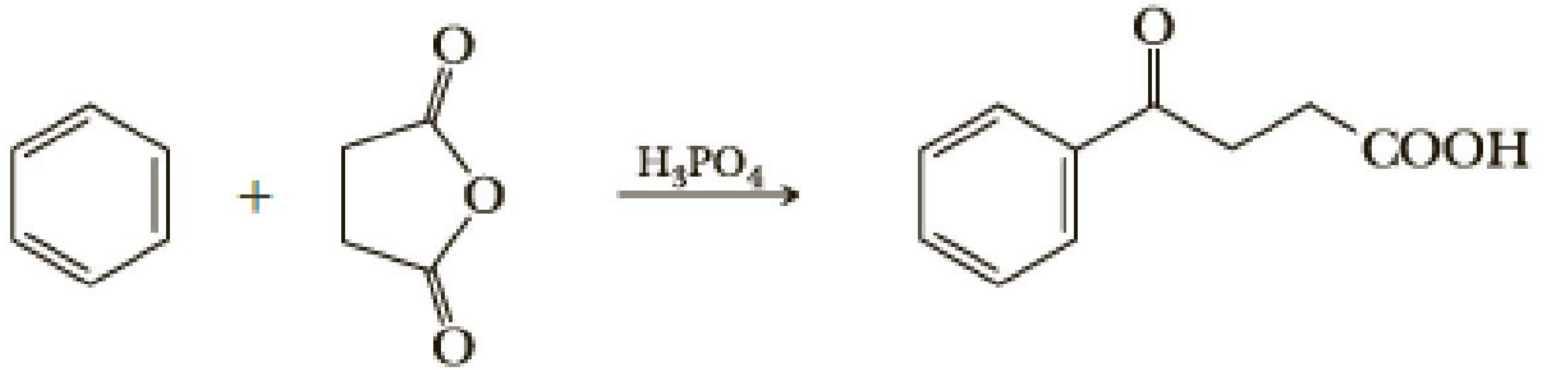


2,6-Di-*tert*-butyl-4-methylphenol, alternatively known as butylated hydroxytoluene (BHT), is used as an antioxidant in foods to "retard spoilage" (Section 8.7). BHT is synthesized industrially from 4-methylphenol by reaction with 2-methylpropene in the presence of phosphoric acid. Propose a mechanism for this reaction.

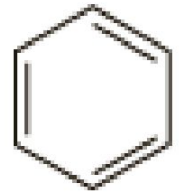


4-Methylphenol (*p*-Cresol) **2-Methylpropene** **2,6-Di-*tert*-butyl-4-methylphenol "Butylated hydroxytoluene" (BHT)**

22.27 Treatment of benzene with succinic anhydride in the presence of polyphosphoric acid gives the following γ-ketoacid. Propose a mechanism for this reaction.

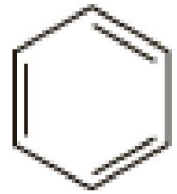


Succinic anhydride **4-Oxo-4-phenylbutanoic acid**

(a) 

An aryl ring

1. HNO_3, H_2SO_4
2. Cl_2, $FeCl_3$
3. H_2, Ni

(b) 

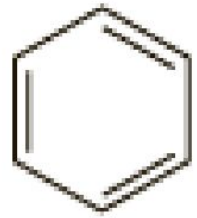
An aryl ring

1. Cl_2, $FeCl_3$
2. HNO_3, H_2SO_4
3. H_2, Ni

(c) 

An aryl ring

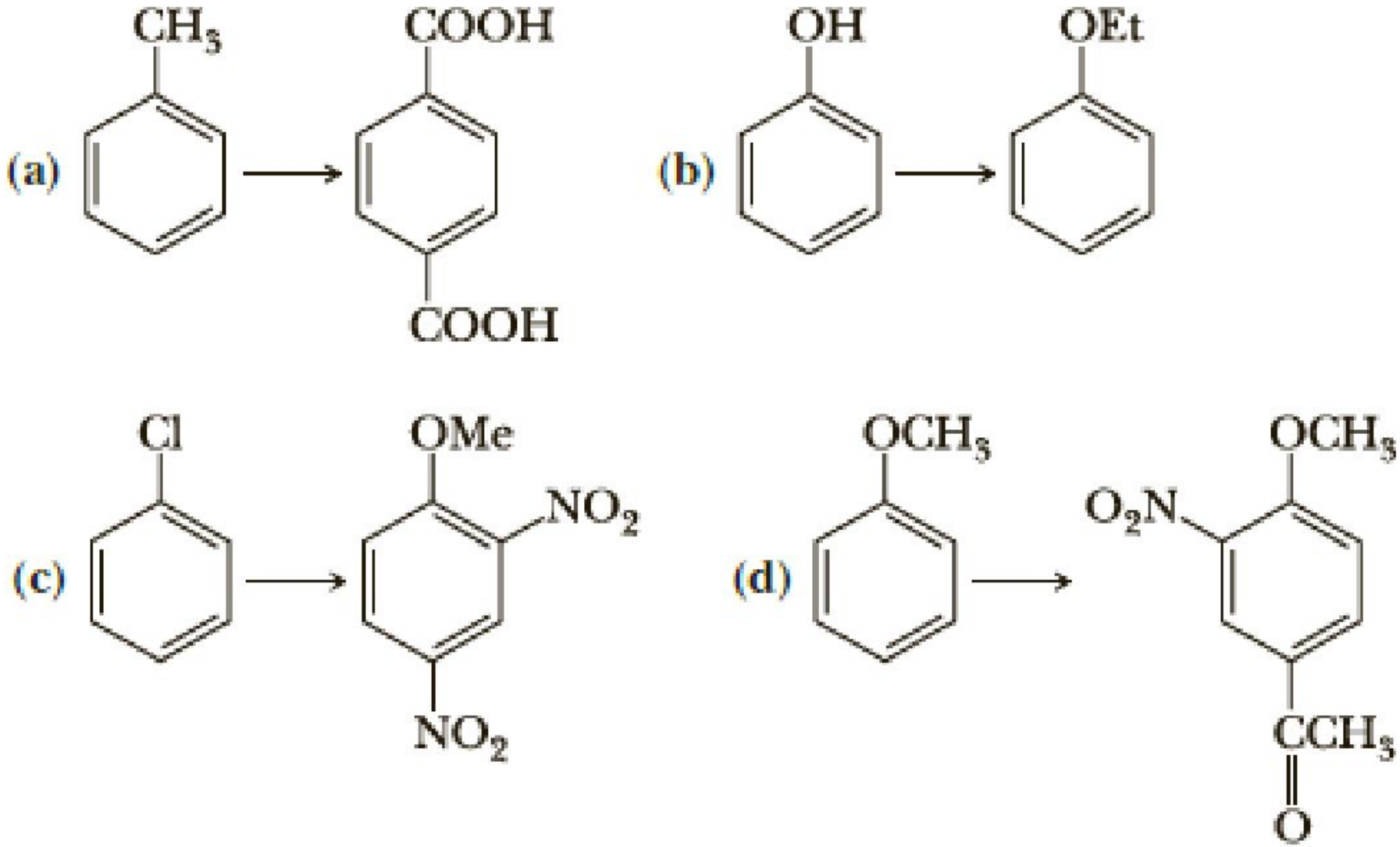
1. CH_3Cl, $AlCl_3$
2. H_2CrO_4
3. $SOCl_2$
4. EtOH
5. Excess 
6. Mild H_3O^+

(d) 

An aryl ring

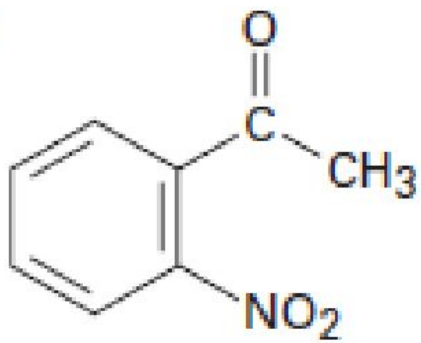
1.  Cl, $AlCl_3$
2. HNO_3, H_2SO_4
3. $H_2C^-—P^+Ph_3$
4. BH_3
5. H_2O_2
6. H_2CrO_4

22.35 Show reagents and conditions to bring about the following conversions.



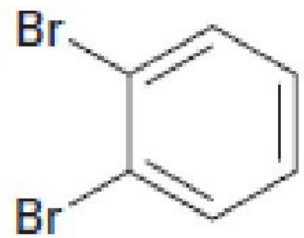
16.35 What product(s) would you expect to obtain from the following reactions?

(a)



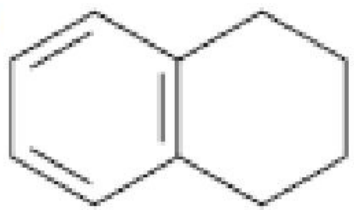
$\xrightarrow{H_2/Pd}$?

(b)



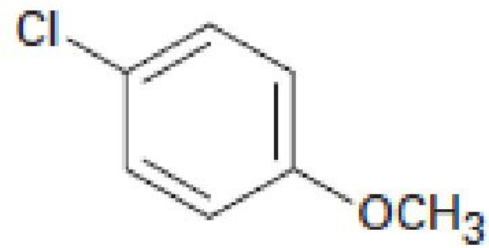
$\xrightarrow[2.\ Fe,\ H_3O^+]{1.\ HNO_3,\ H_2SO_4}$?

(c)



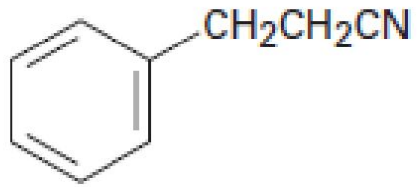
$\xrightarrow[H_2O]{KMnO_4}$?

(d)

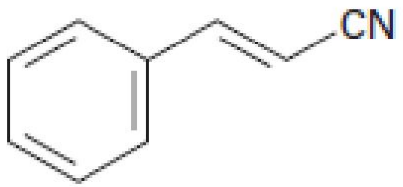


$\xrightarrow[AlCl_3]{CH_3CH_2CH_2Cl}$?

16.50 ▲ Electrophilic substitution on 3-phenylpropanenitrile occurs at the ortho and para positions, but reaction with 3-phenylpropenenitrile occurs at the meta position. Explain, using resonance structures of the intermediates.

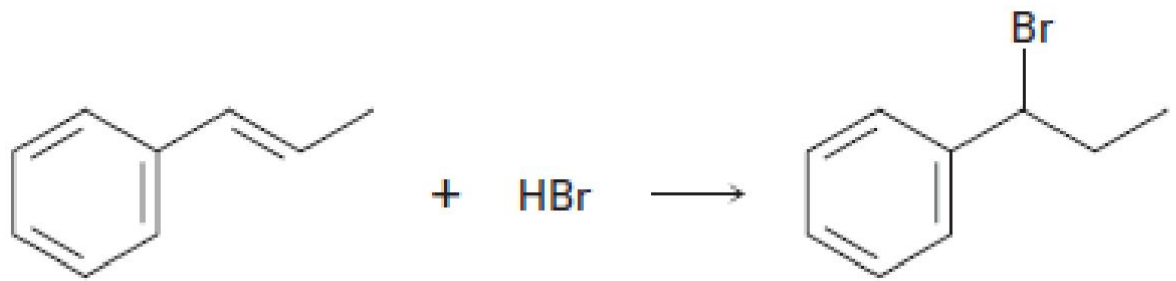


3-Phenylpropanenitrile

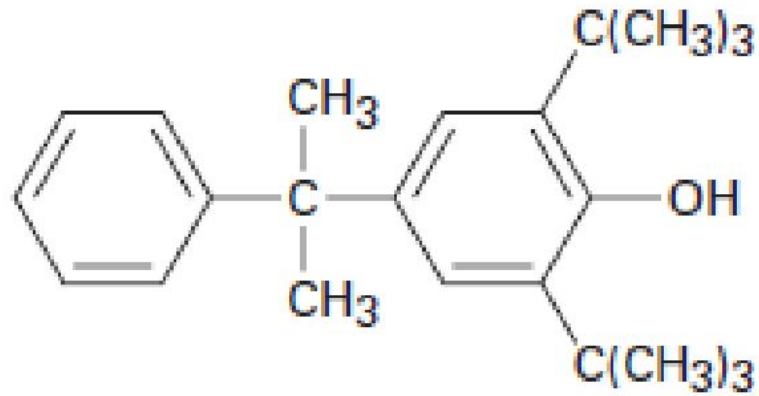


3-Phenylpropenenitrile

16.51 Addition of HBr to 1-phenylpropene yields only (1-bromopropyl)benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced.



16.56 The compound MON-0585 is a nontoxic, biodegradable larvicide that is highly selective against mosquito larvae. Synthesize MON-0585 using either benzene or phenol as a source of the aromatic rings.



MON-0585