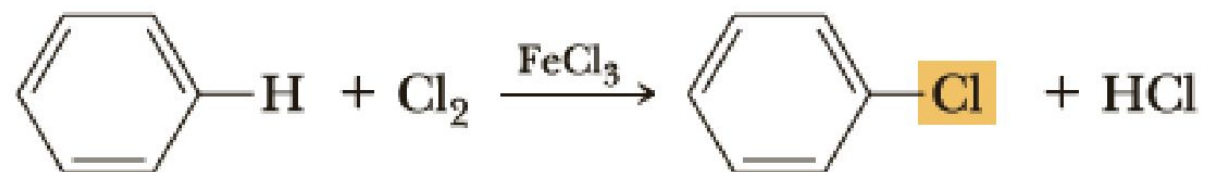


Свойства аренов

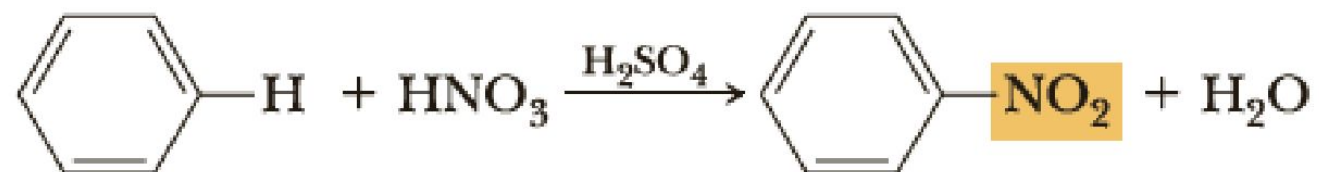
Реакции электрофильного замещения S_E

Halogenation:



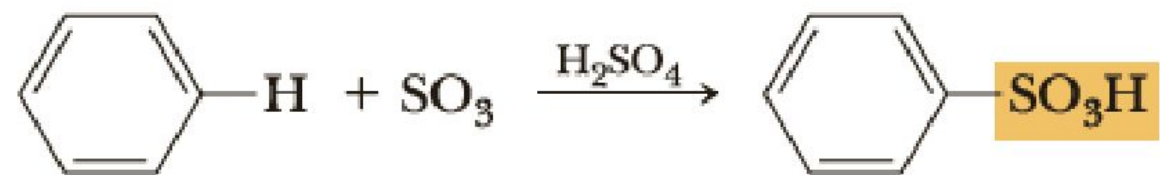
Chlorobenzene

Nitration:



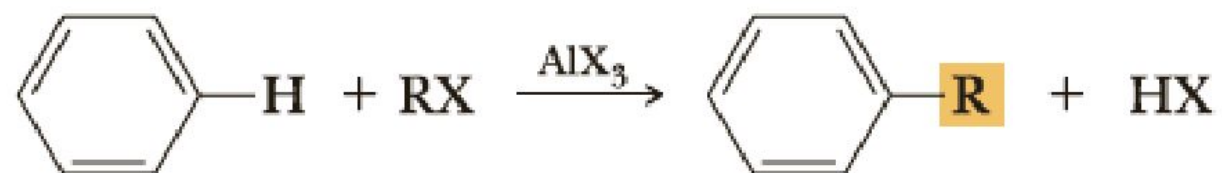
Nitrobenzene

Sulfonation:



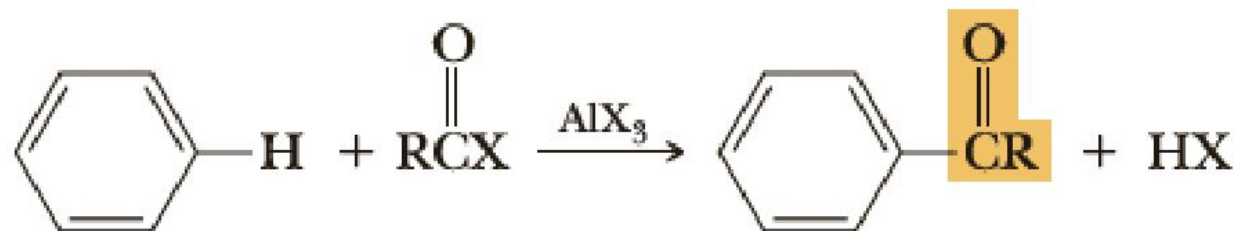
Benzenesulfonic acid

Alkylation:

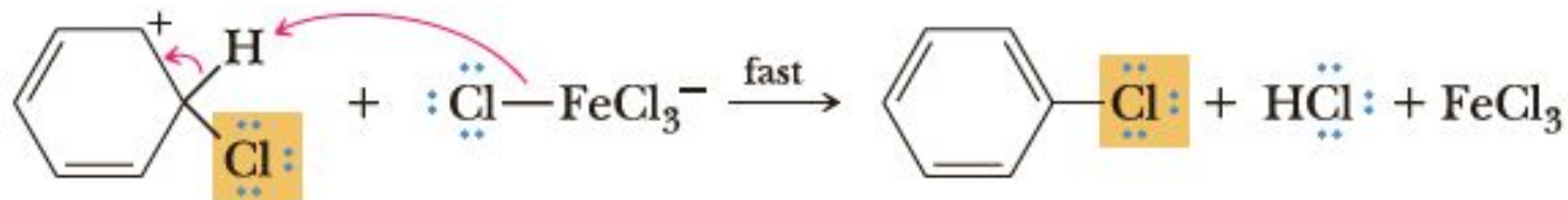
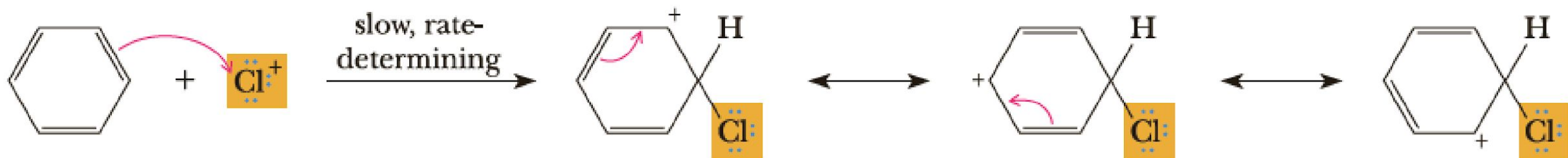
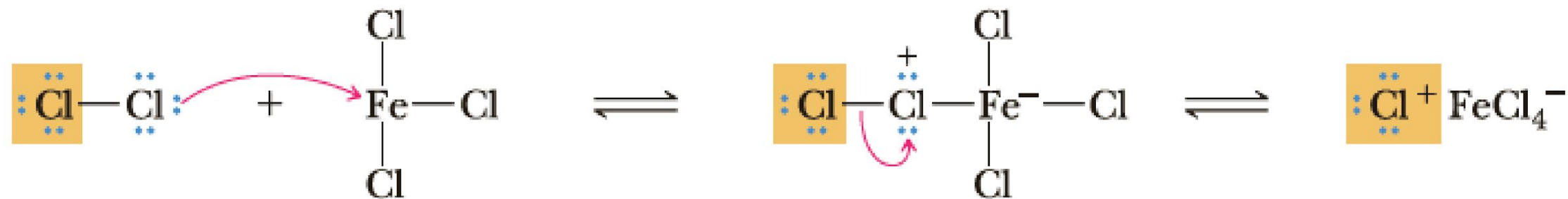
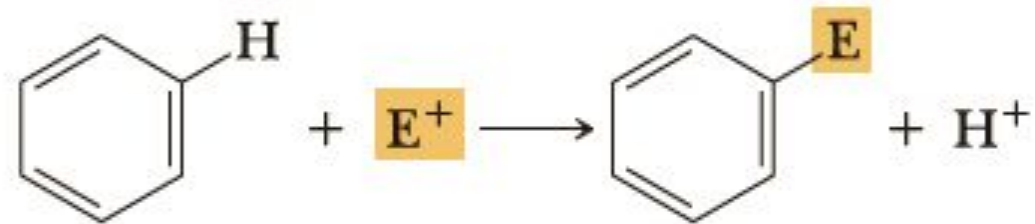


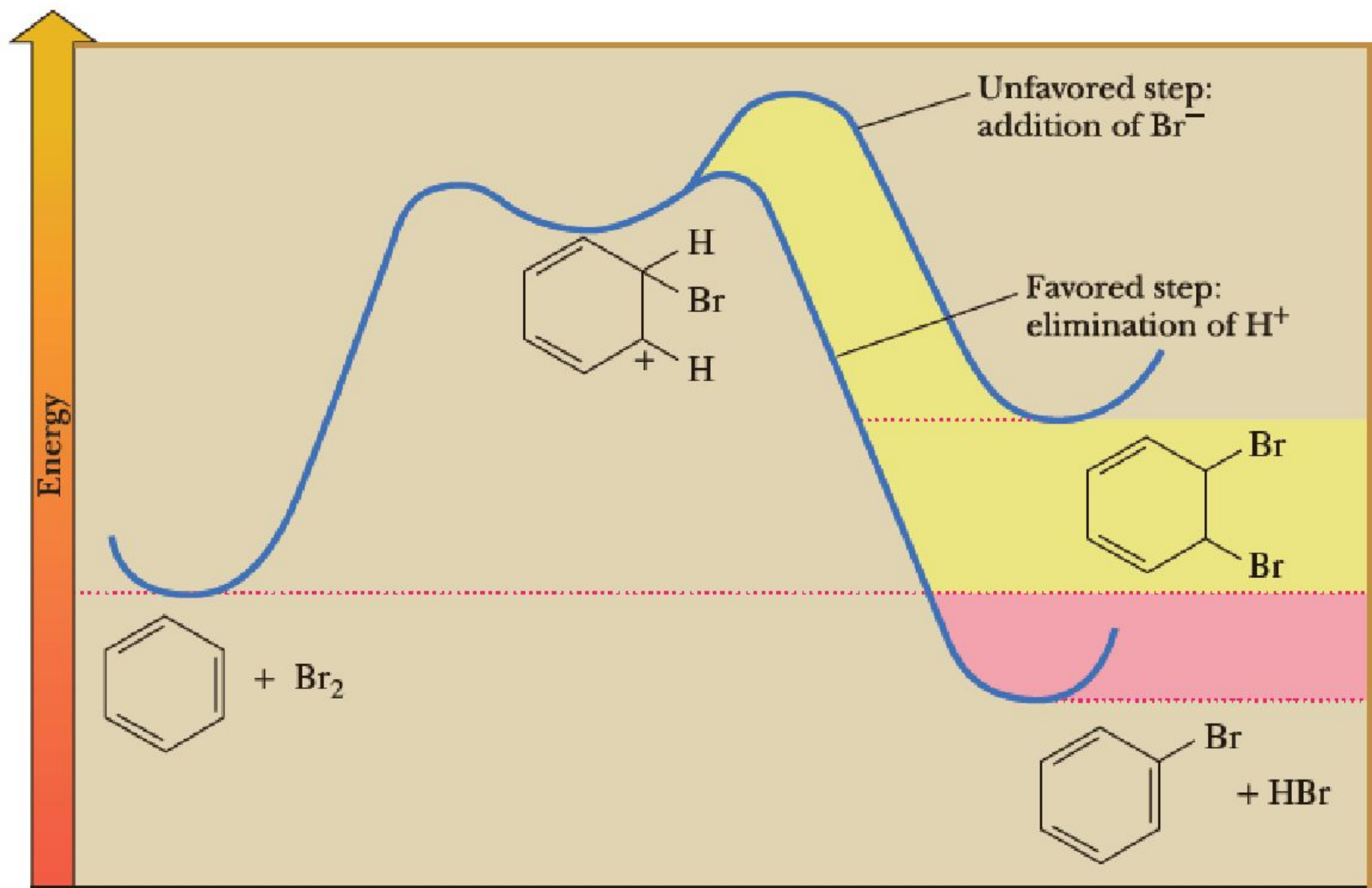
An alkylbenzene

Acylation:



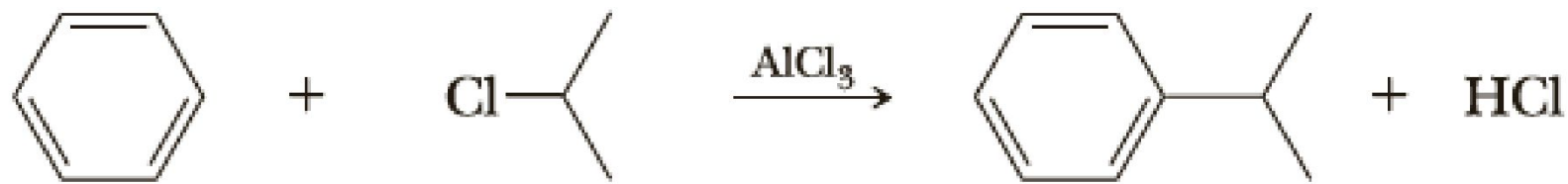
An acylbenzene





Reaction coordinate

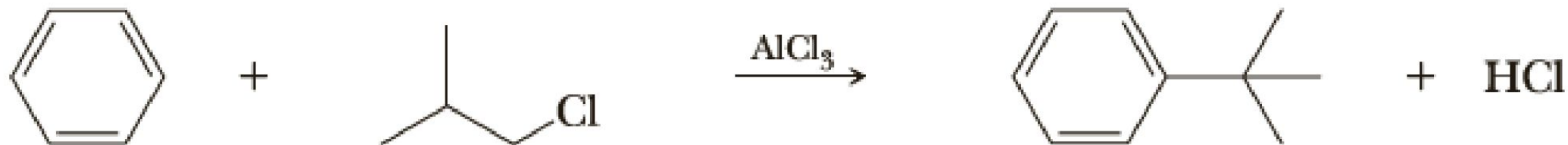
Алкилирование по Фриделю-Крафтсу



Benzene

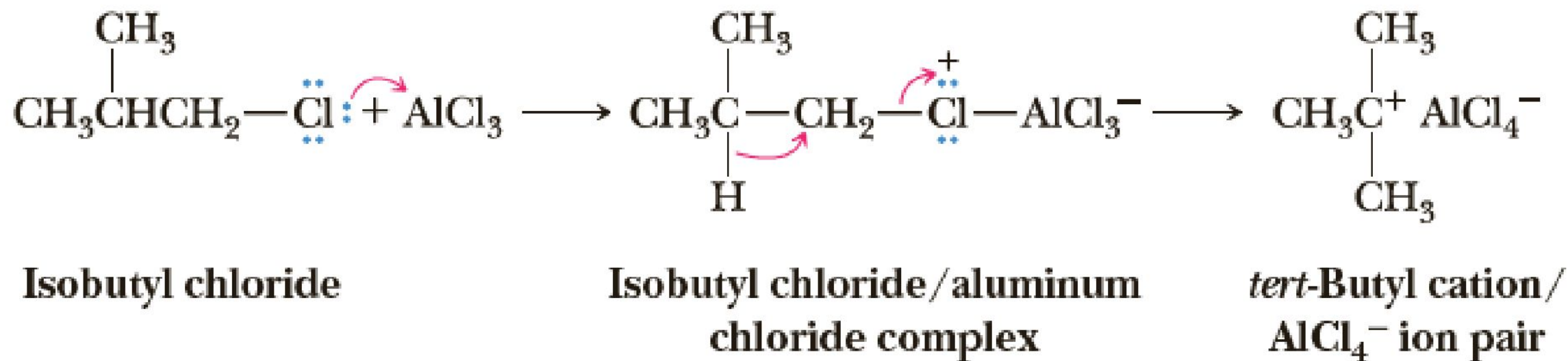
2-Chloropropane
(Isopropyl chloride)

Cumene
(Isopropylbenzene)

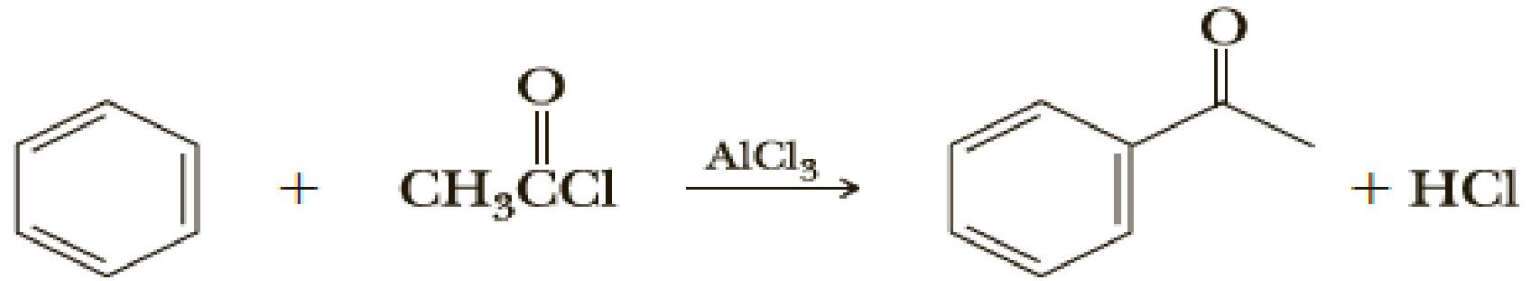


1-Chloro-2-methylpropane
(Isobutyl chloride)

2-Methyl-2-phenylpropane
(*tert*-Butylbenzene)



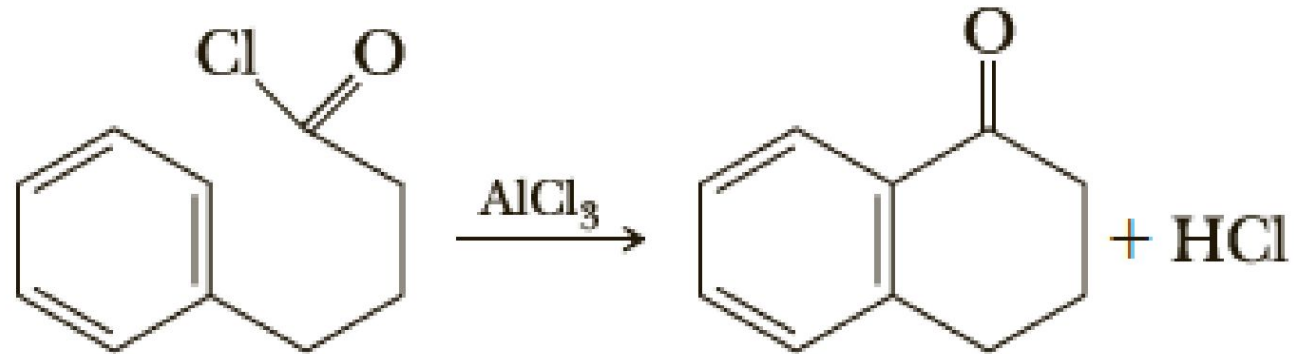
Ацилирование по Фриделю-Крафтсу



Benzene

Acetyl chloride
(an acyl halide)

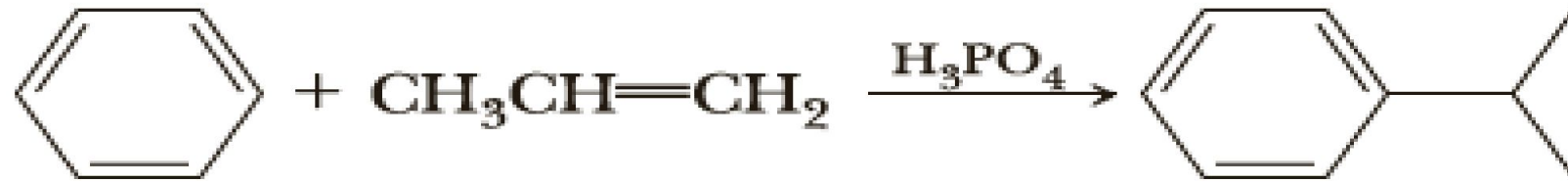
Acetophenone
(a ketone)



**4-Phenylbutanoyl
chloride**

α -Tetralone

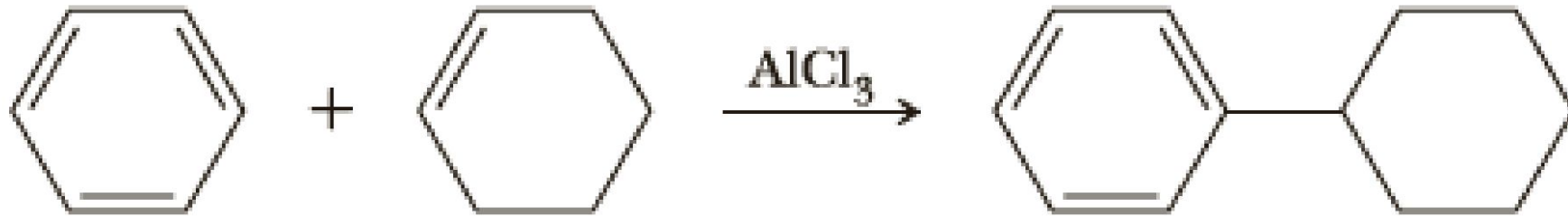
Присоединение алкенов



Benzene

Propene

Cumene



Benzene

Cyclohexene

Phenylcyclohexane

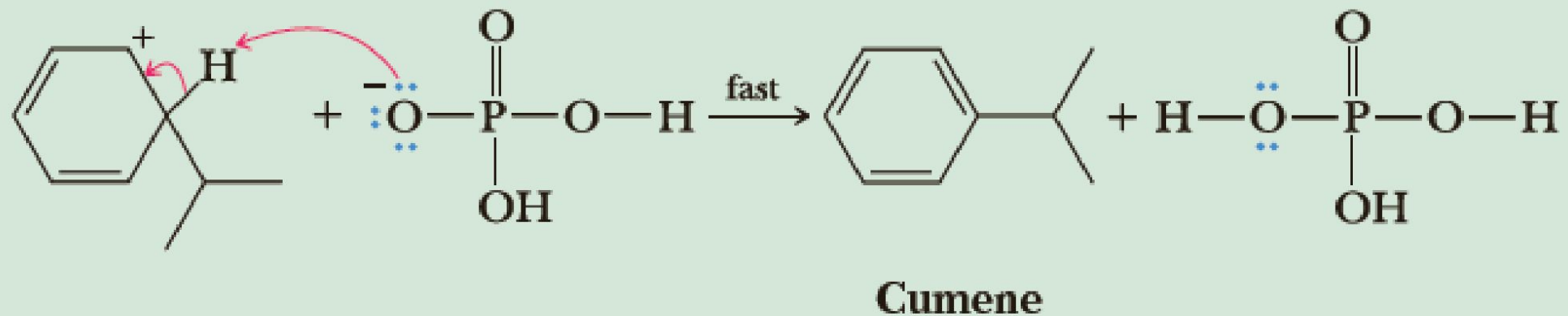
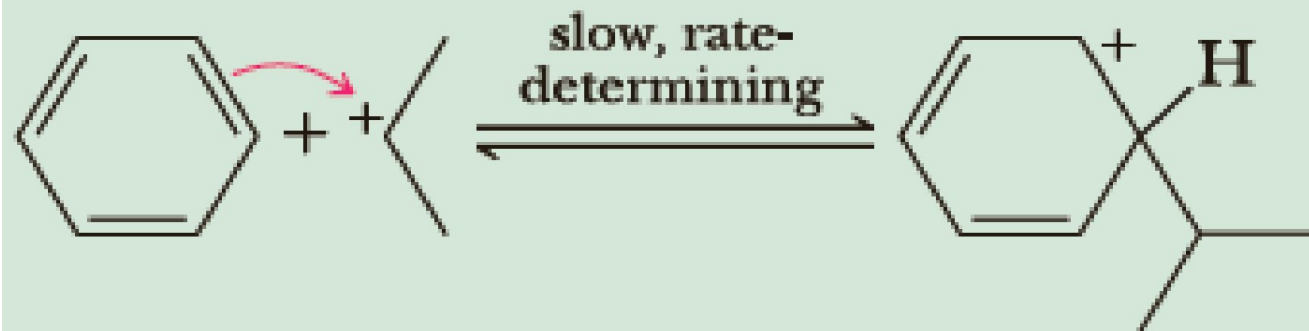
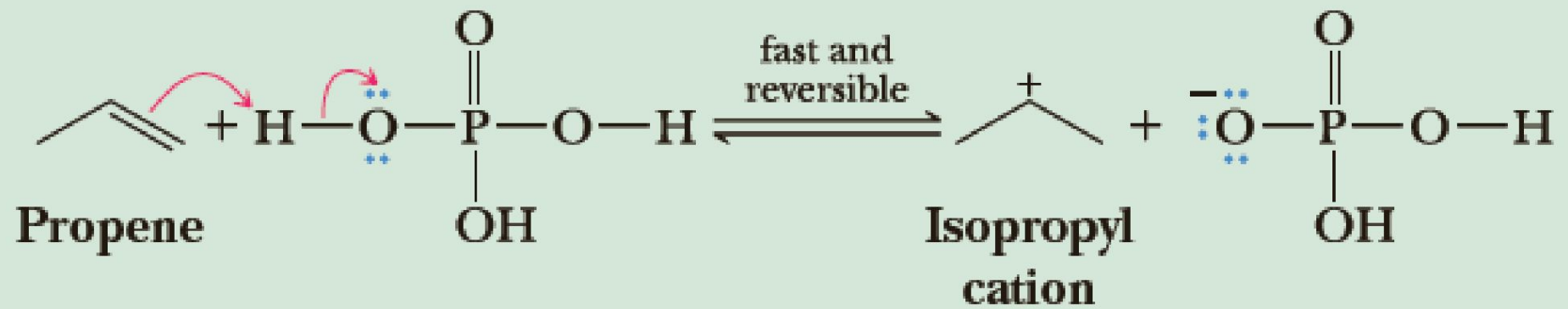
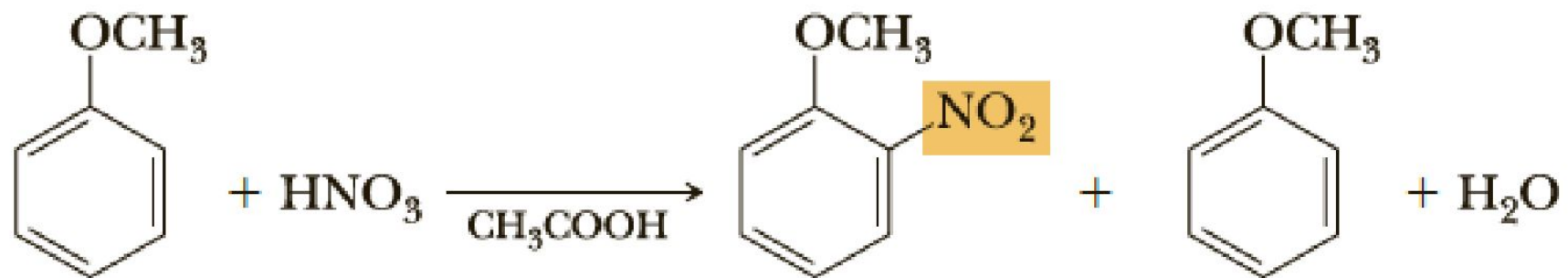


Table 22.1 Orientation on Nitration of Monosubstituted Benzenes

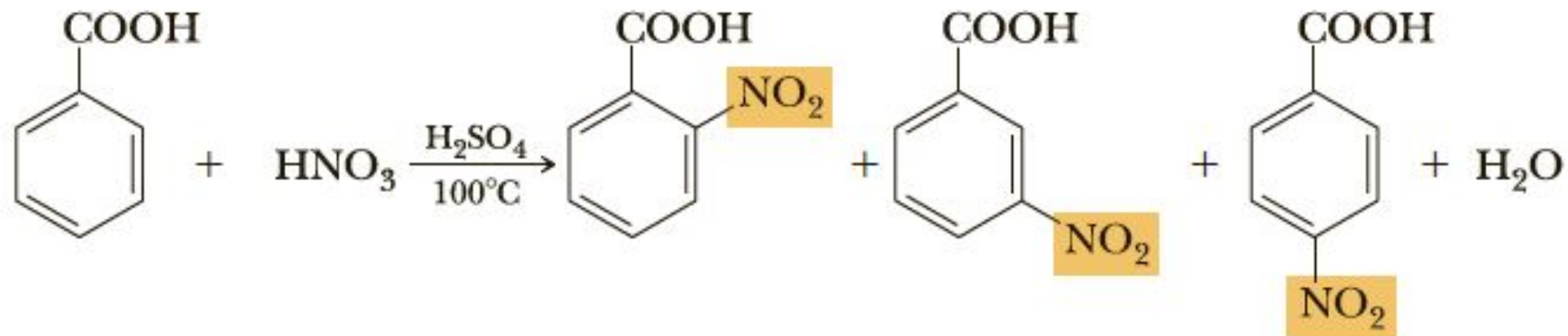
Substituent	ortho	meta	para	ortho + para	meta
—OCH ₃	44	—	55	99	trace
—CH ₃	58	4	38	96	4
—Cl	70	—	30	100	trace
—Br	37	1	62	99	1
—COOH	18	80	2	20	80
—CN	19	80	1	20	80
—NO ₂	6.4	93.2	0.3	6.7	93.2



Anisole

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

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

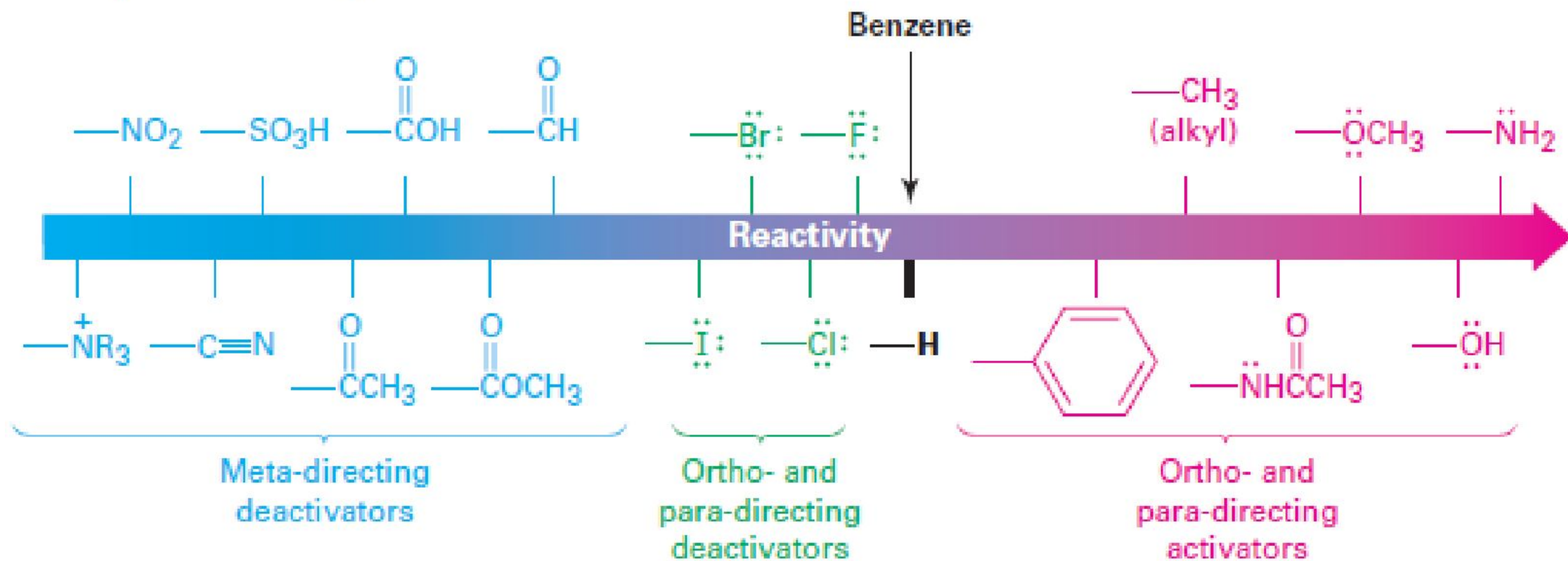


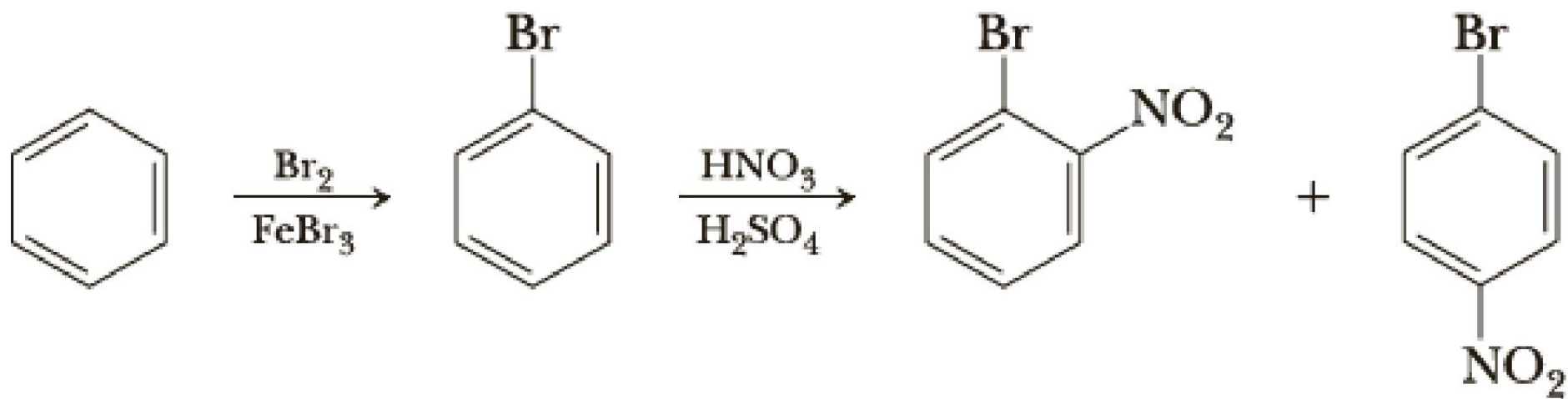
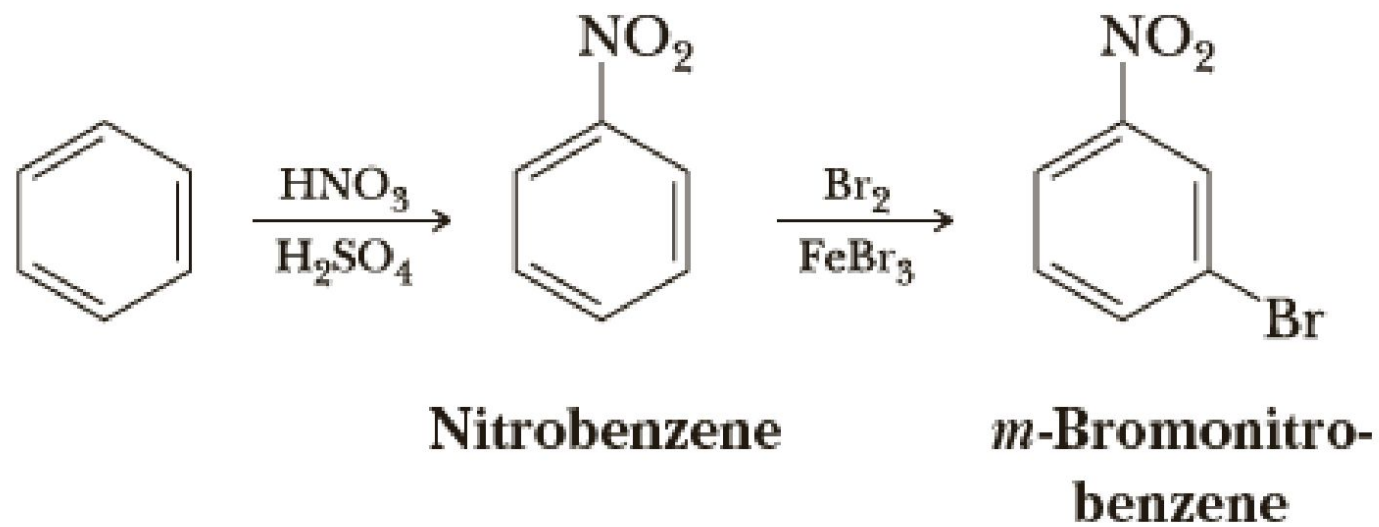
Benzoic acid

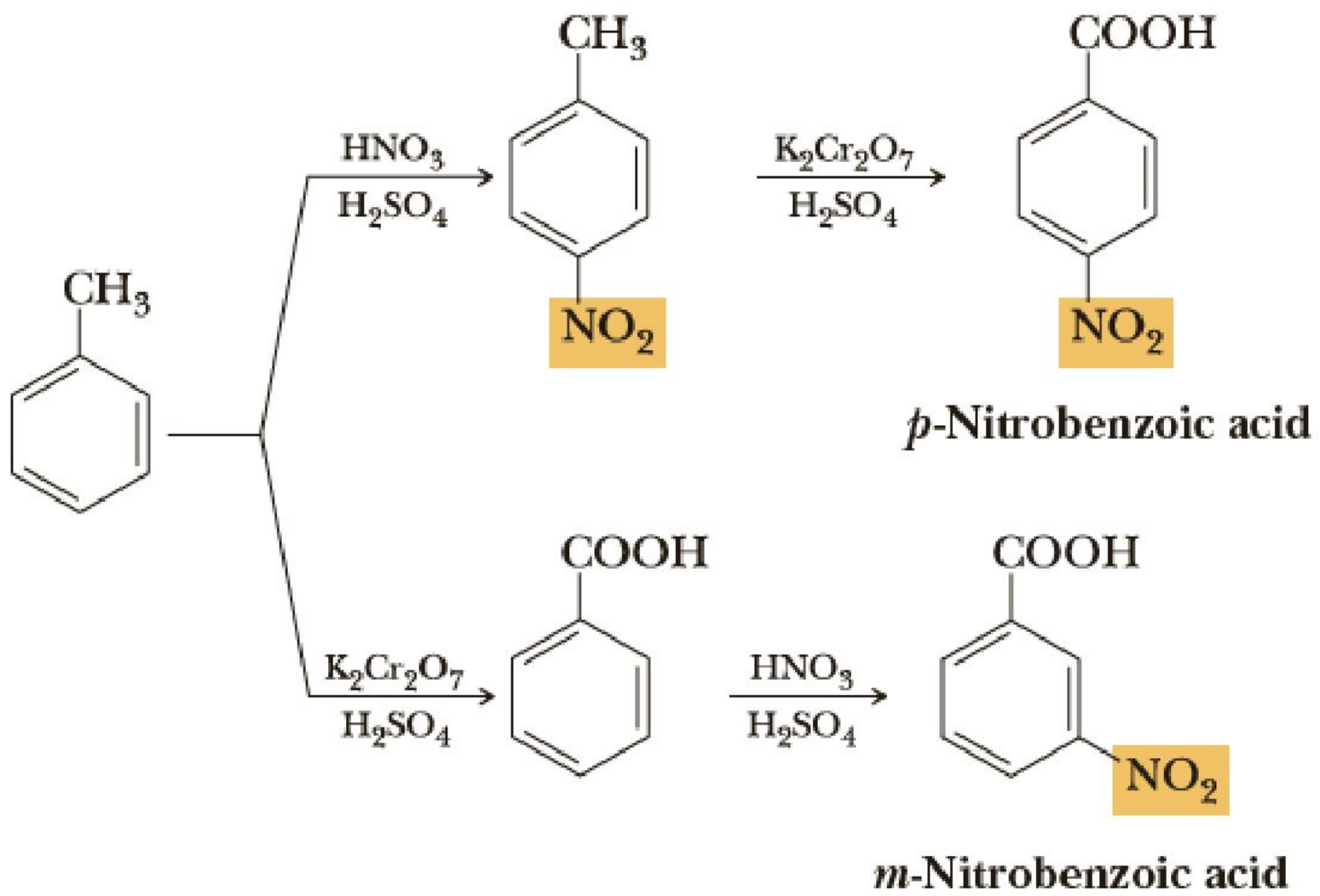
***o*-Nitro-
benzoic acid
(18%)**

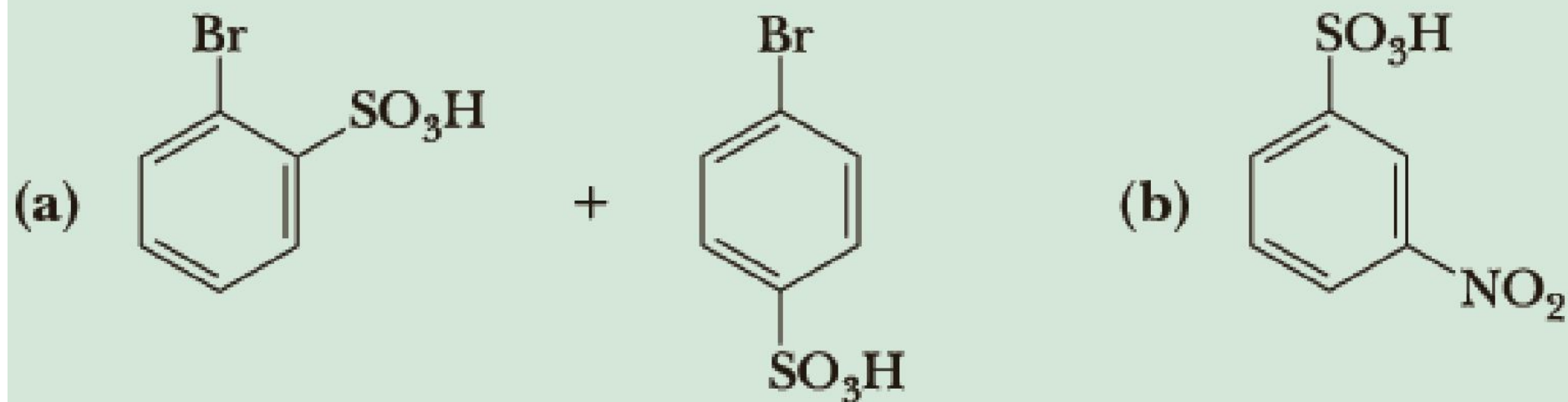
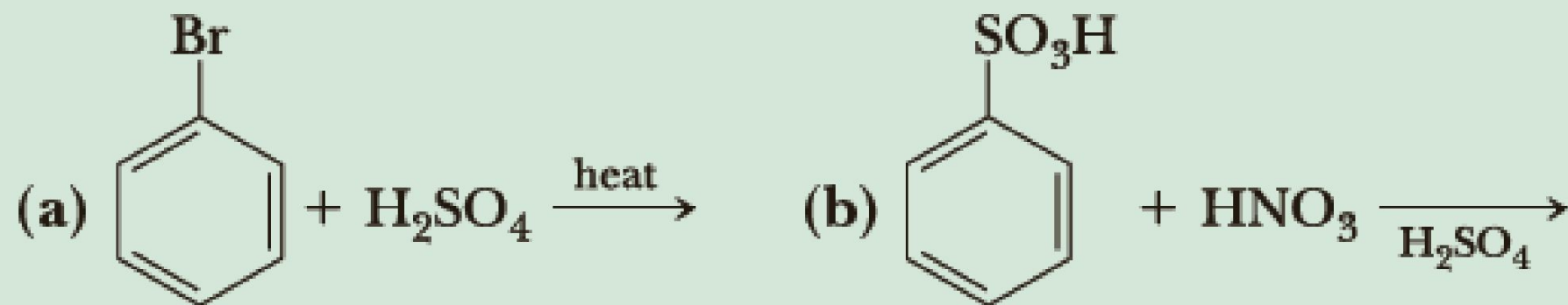
***m*-Nitro-
benzoic acid
(80%)**

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





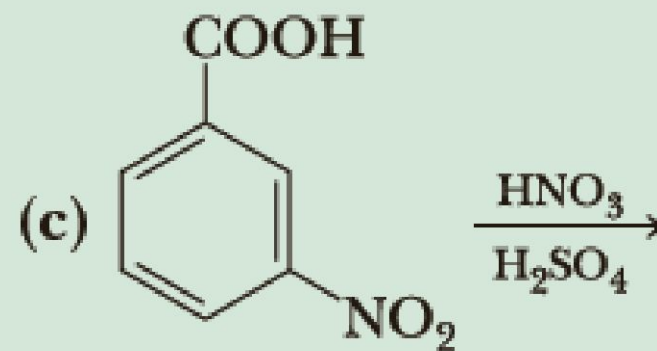
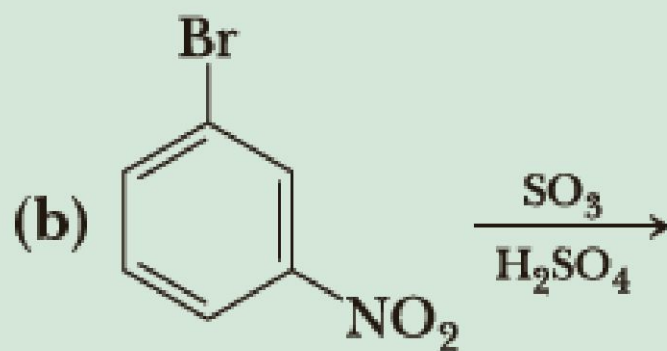
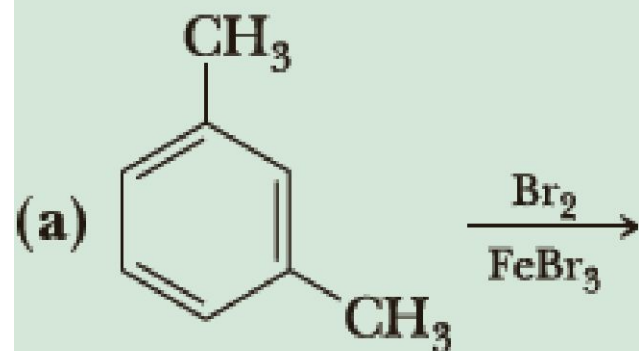
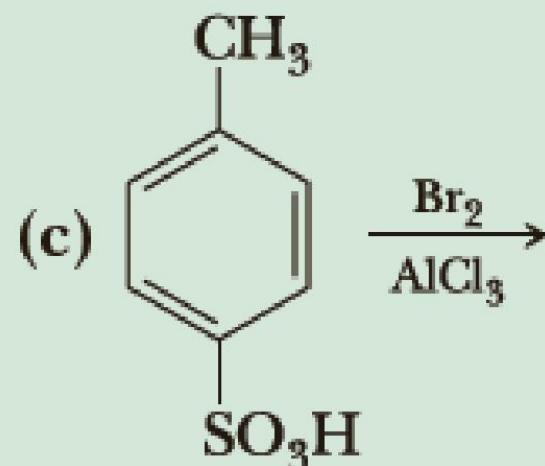
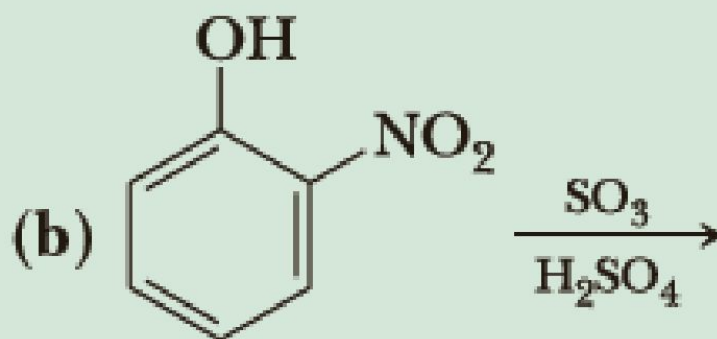
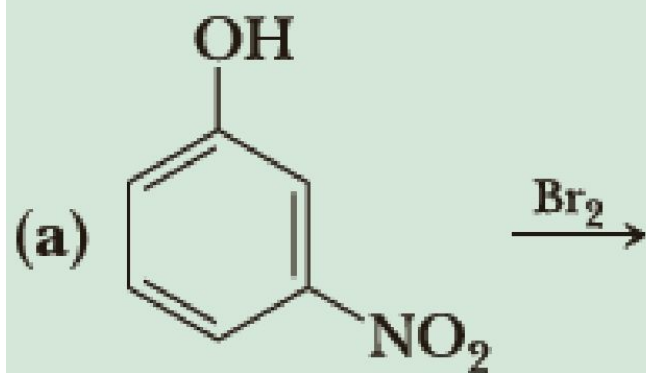




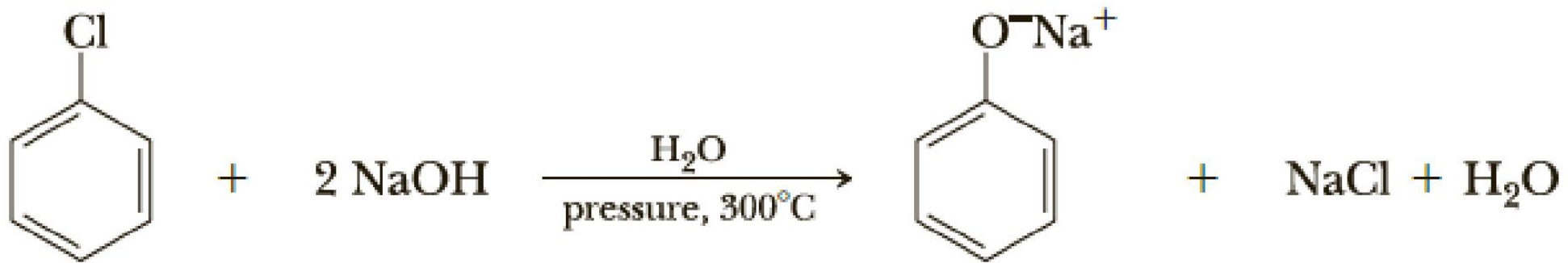
o-Bromobenzene-sulfonic acid

p-Bromobenzene-sulfonic acid

m-Nitrobenzene-sulfonic acid

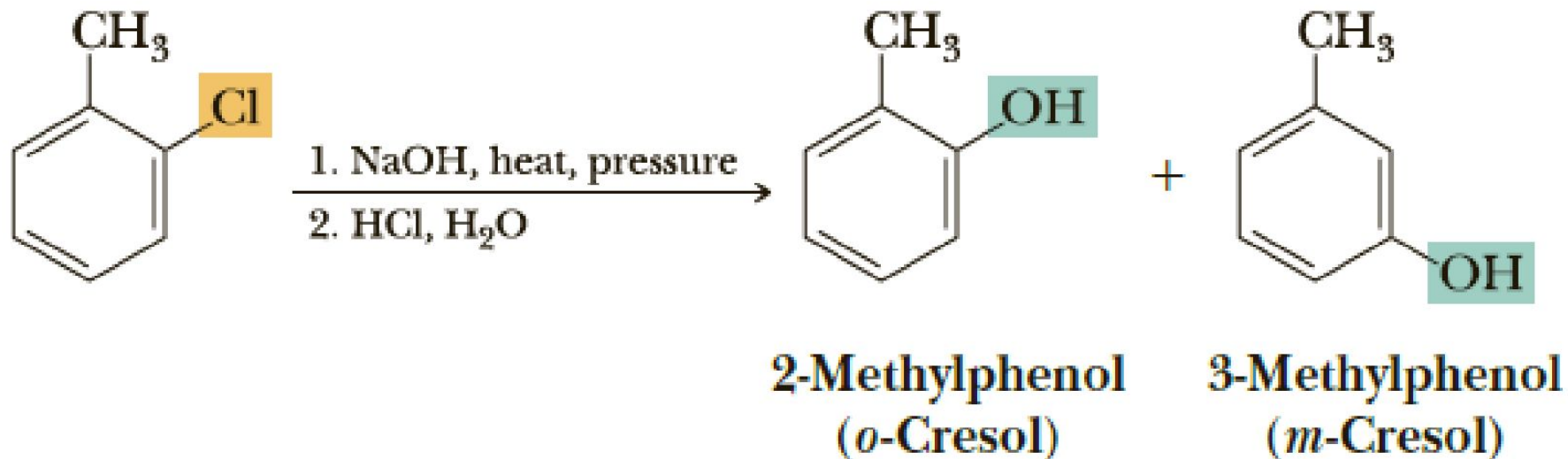


Нуклеофильное замещение S_N



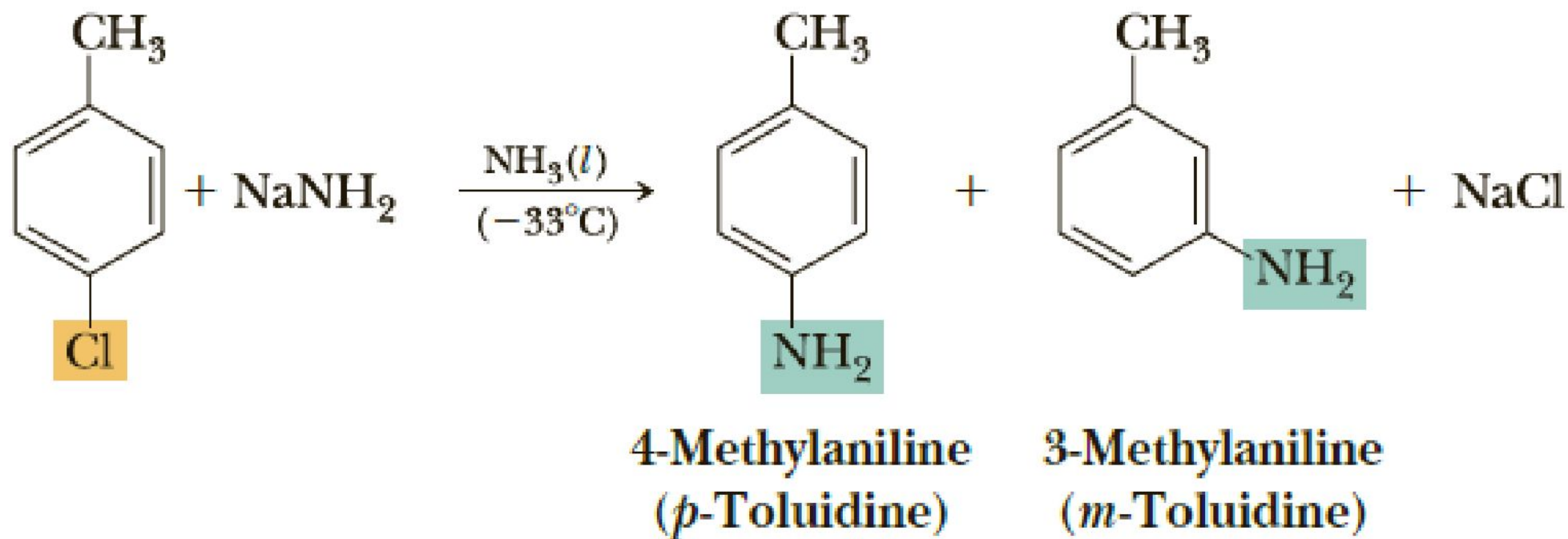
Chlorobenzene

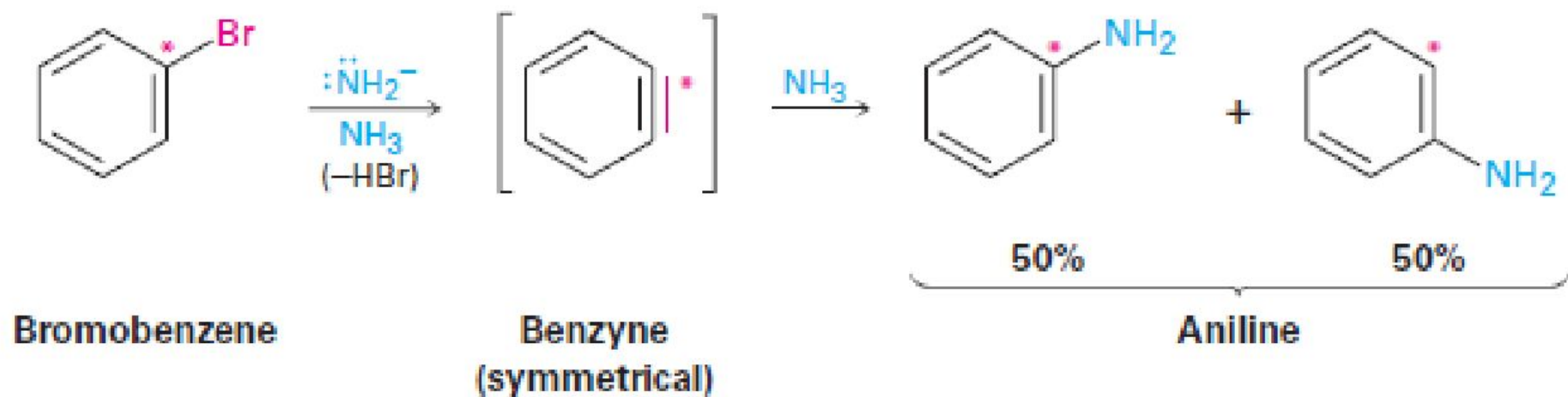
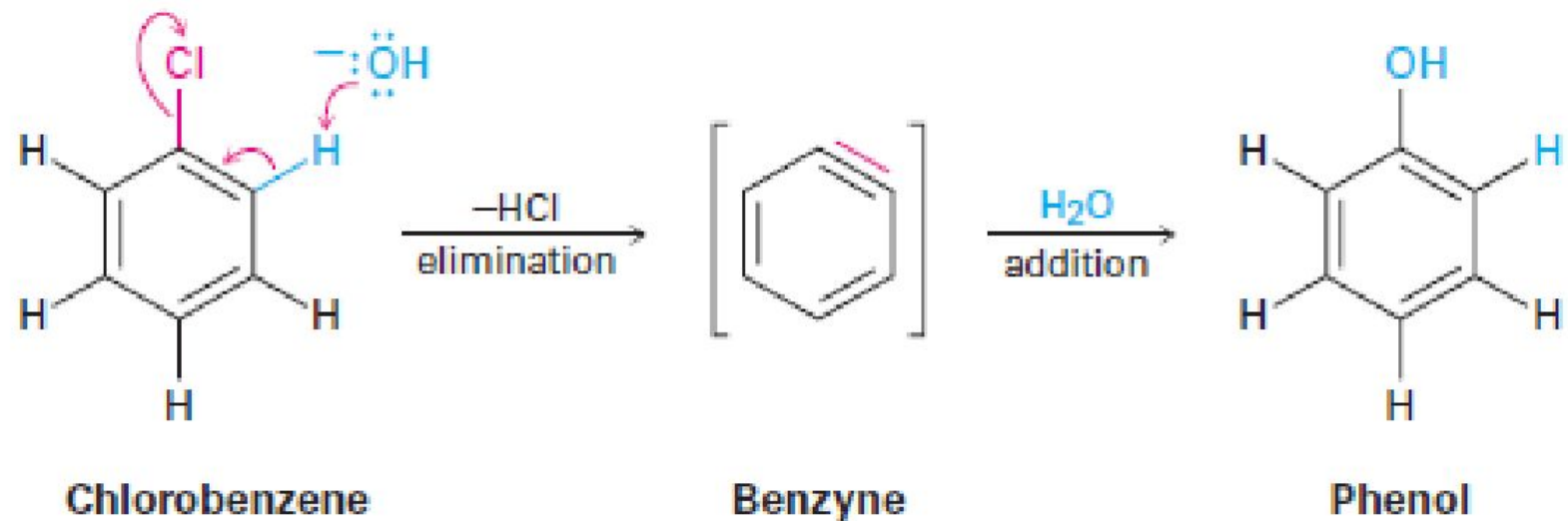
Sodium phenoxide



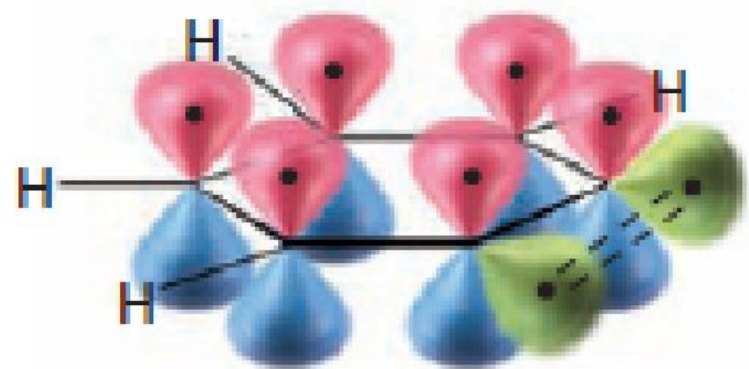
2-Methylphenol
(*o*-Cresol)

3-Methylphenol
(*m*-Cresol)

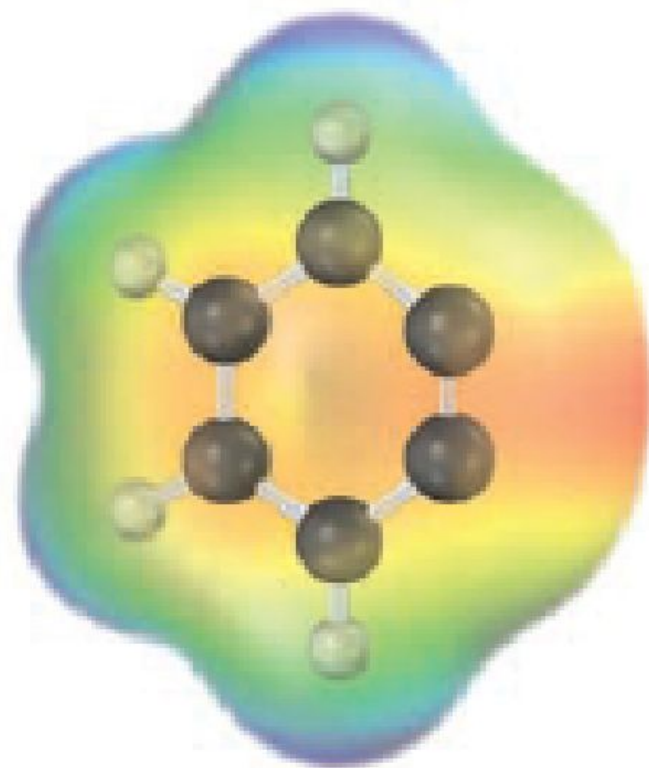




0 1

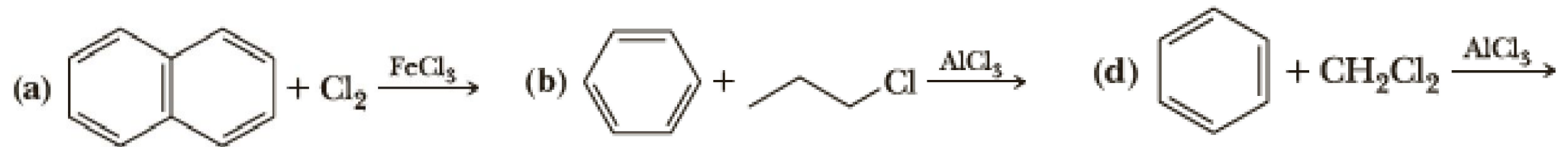


Side view

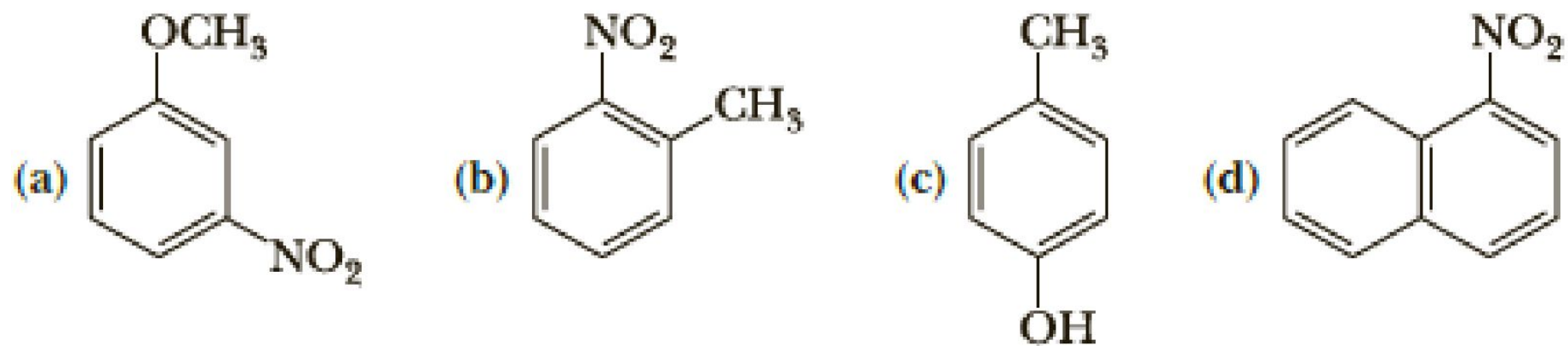


Benzyne

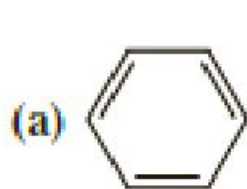
Problems



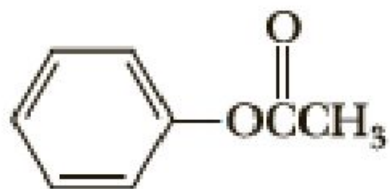
Predict the major product or products from treatment of each compound with HNO₃/H₂SO₄.



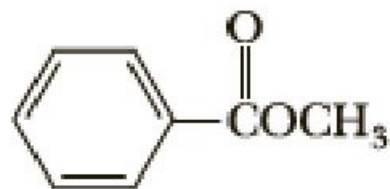
22.19 Arrange the compounds in each set in order of decreasing reactivity (fastest to slowest) toward electrophilic aromatic substitution.



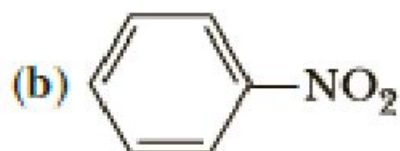
(A)



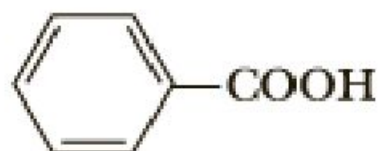
(B)



(C)



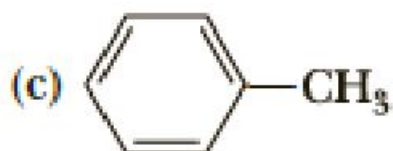
(A)



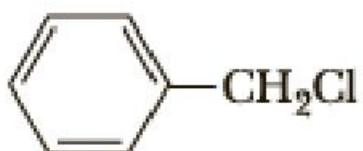
(B)



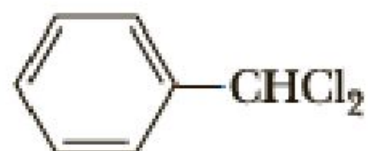
(C)



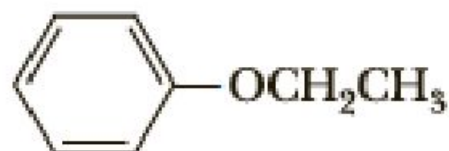
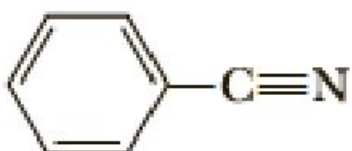
(A)



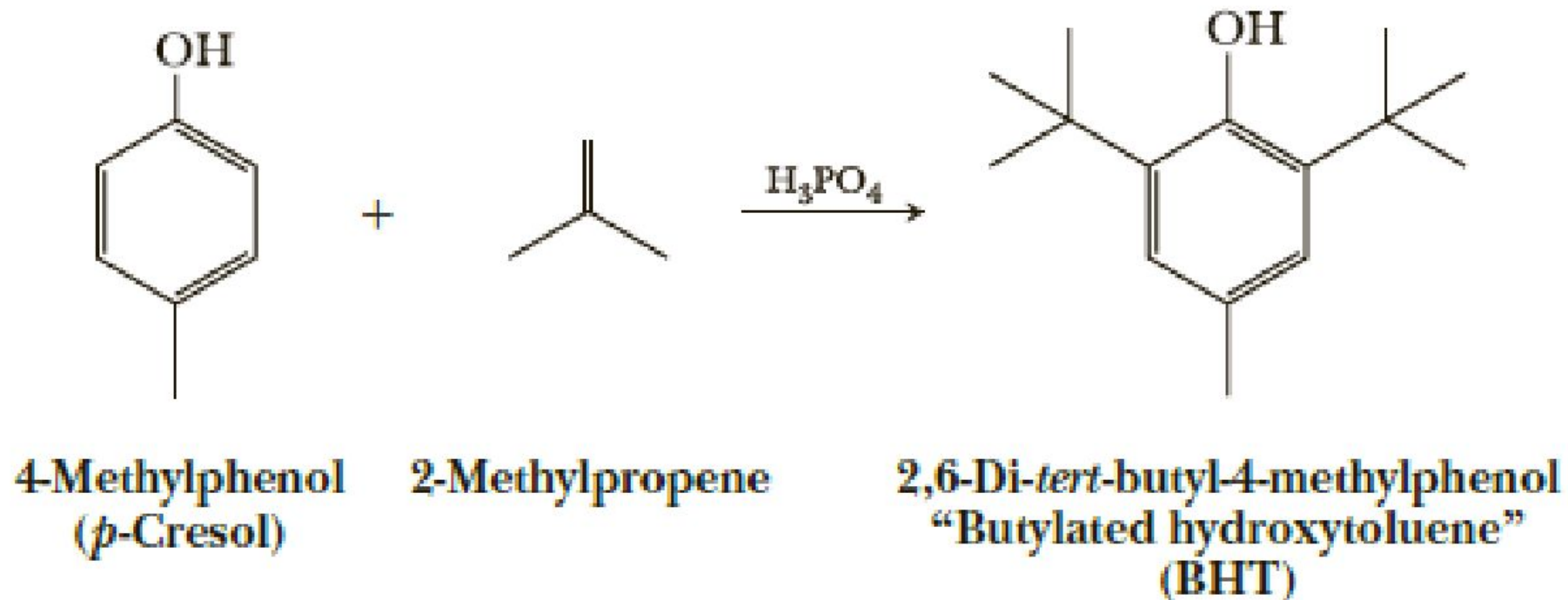
(B)



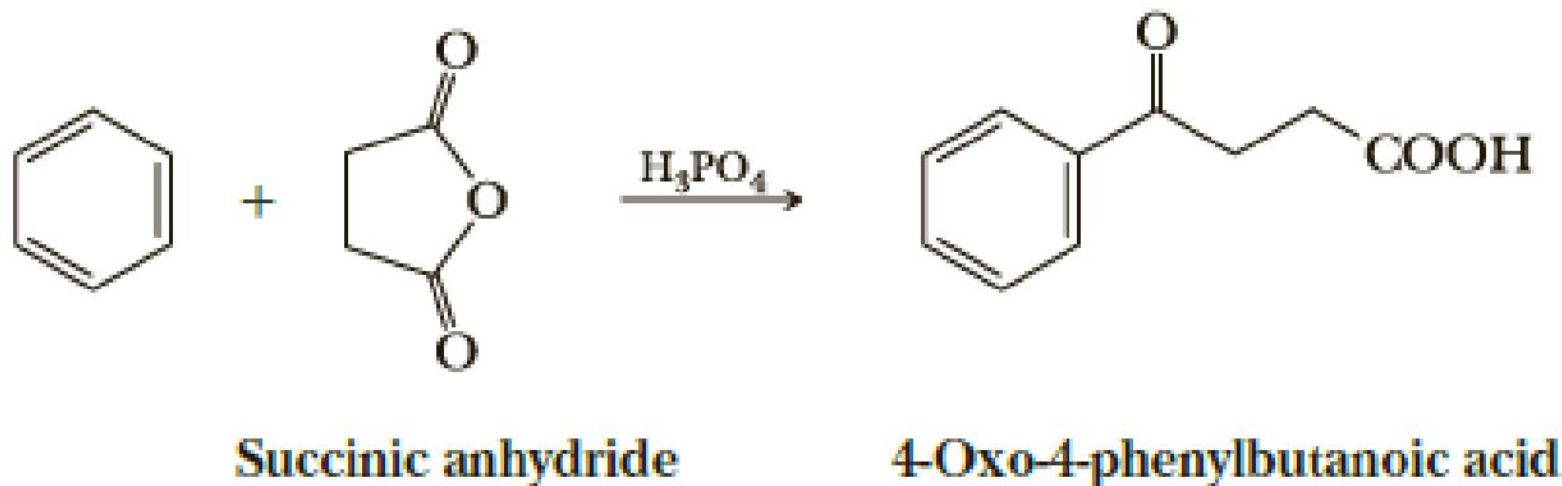
(C)

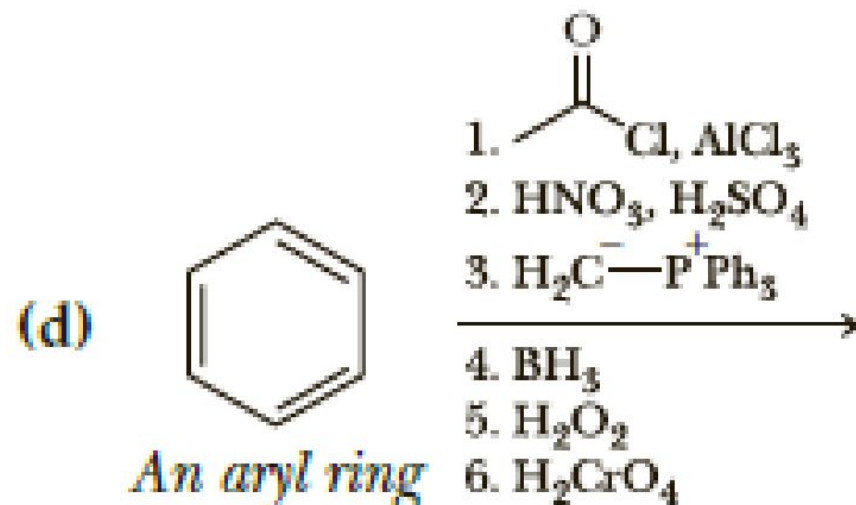
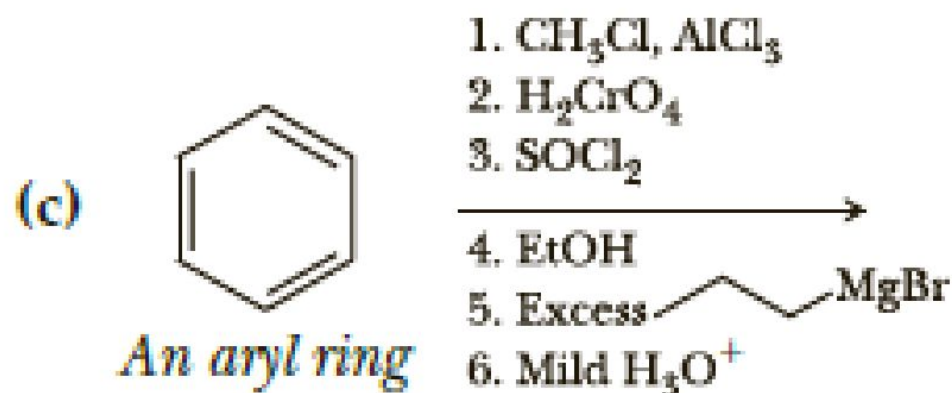
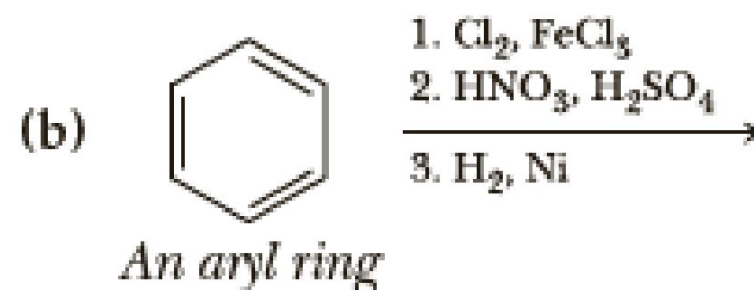
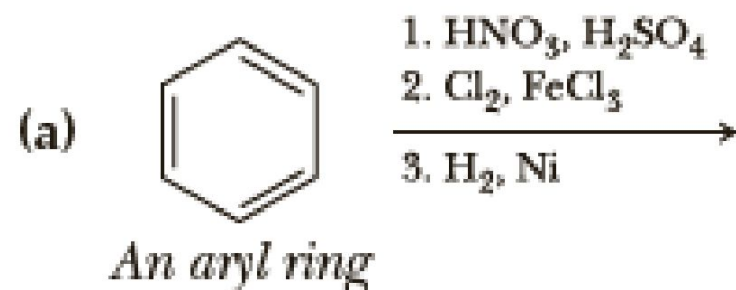


2,6-Di-*tert*-butyl-4-methylphenol, alternatively known as butylated hydroxytoluene (BHT), is used as an antioxidant in foods to “retard spoilage” (Section 8.7). BHT is synthesized industrially from 4-methylphenol by reaction with 2-methylpropene in the presence of phosphoric acid. Propose a mechanism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

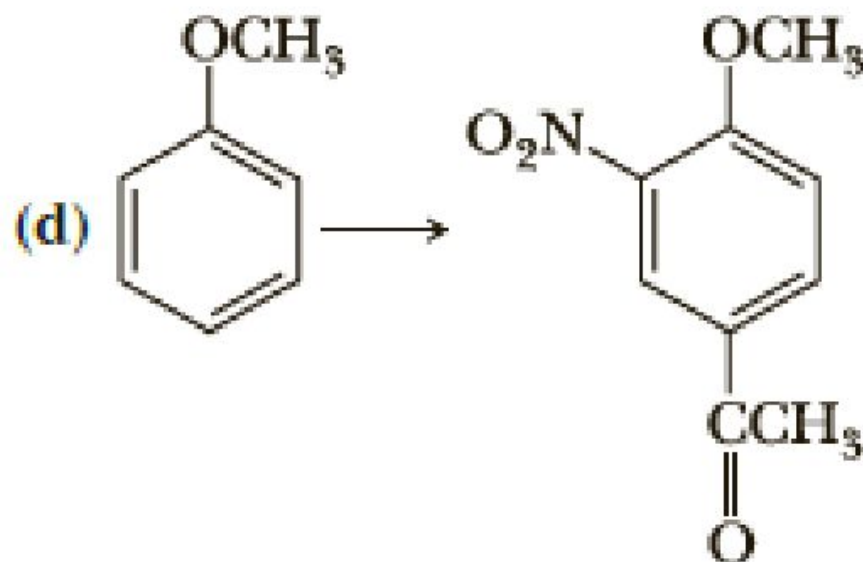
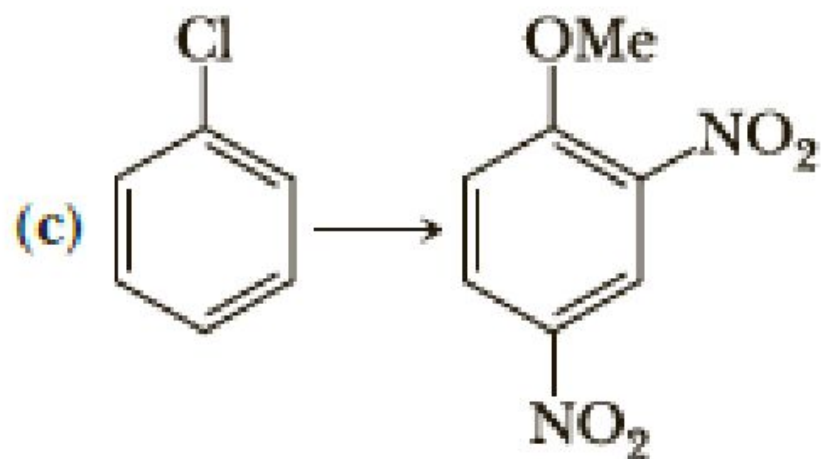
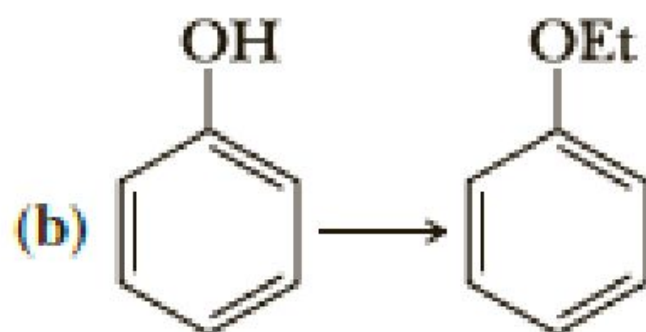
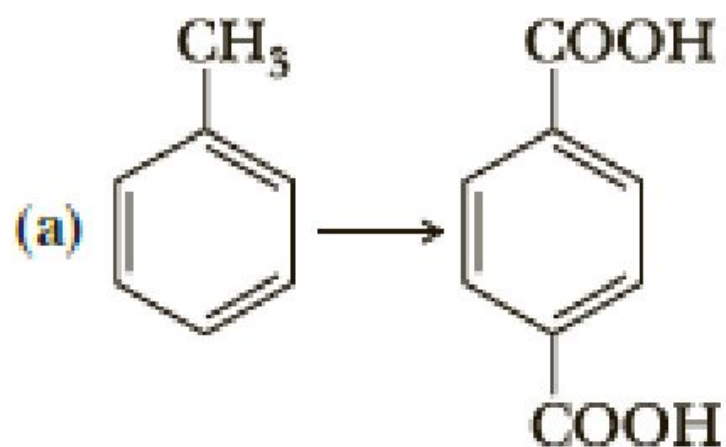


22.27 Treatment of benzene with succinic anhydride in the presence of polyphosphoric acid gives the following γ -ketoacid. Propose a mechanism for this reaction.

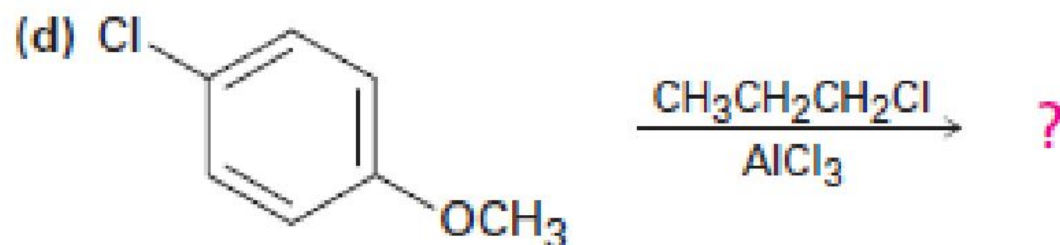
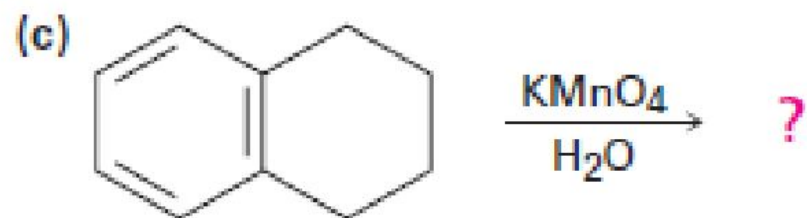
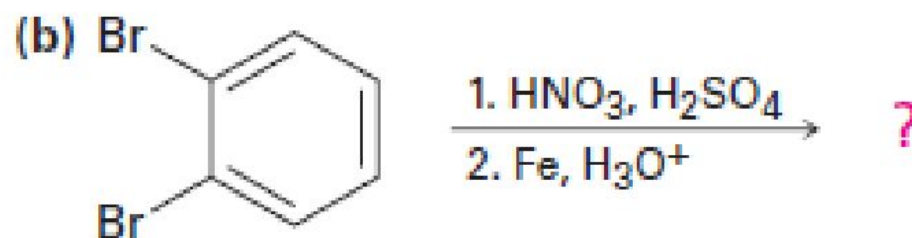
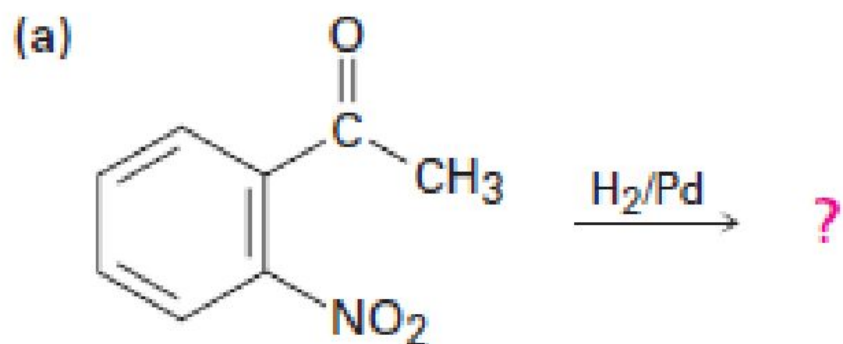




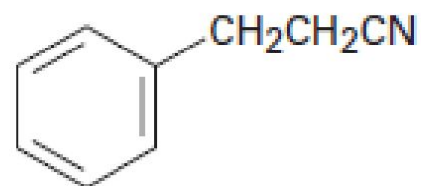
22.35 Show reagents and conditions to bring about the following conversions.



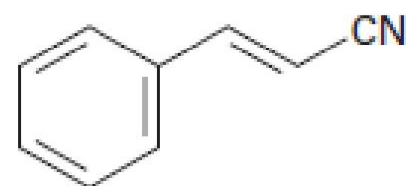
16.35 What product(s) would you expect to obtain from the following reactions?



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.

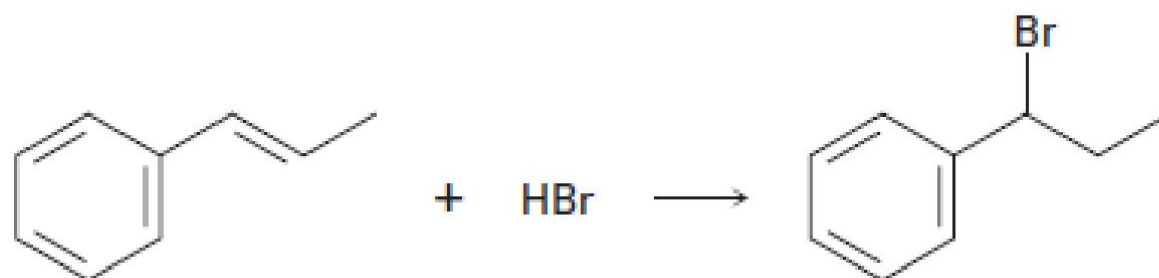


3-Phenylpropanenitrile



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.

