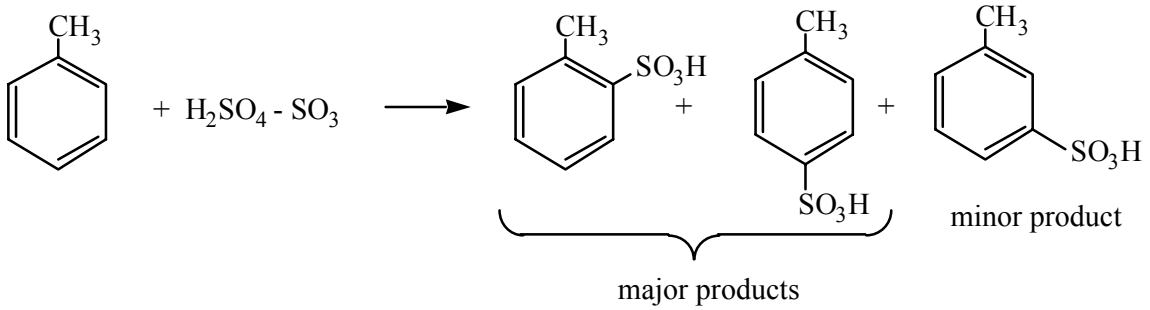
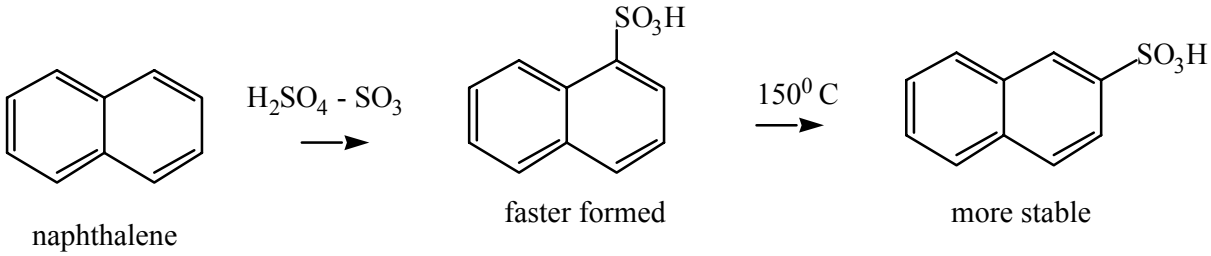
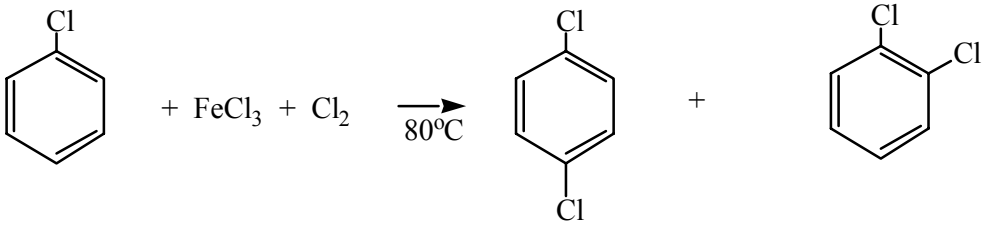
Examples of electrophilic aromatic substitution when there is already a substituent in the ring



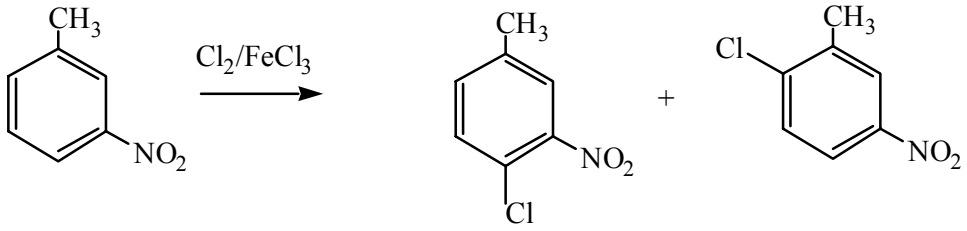
However, sulfonation is reversible:





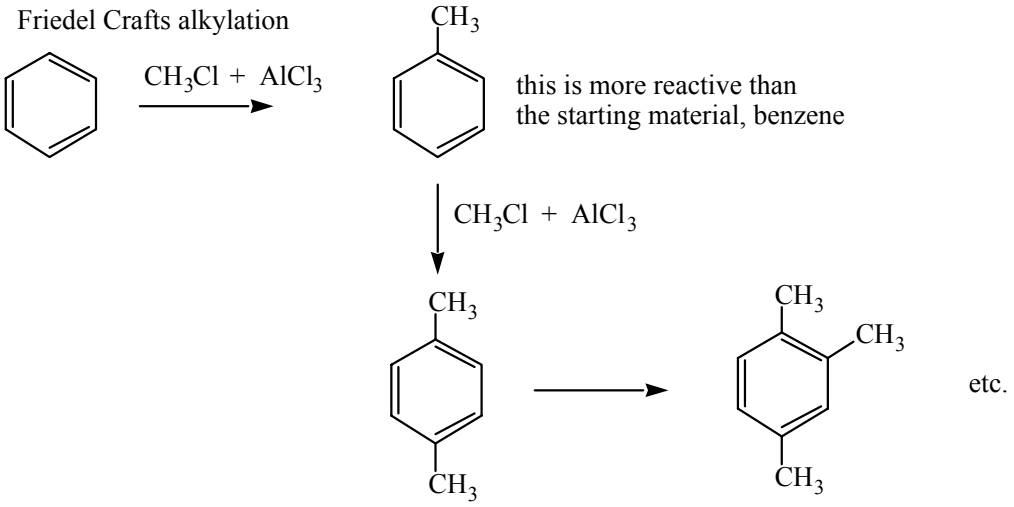
easily separated

If there are two substituents in the ring being further substituted, and one is an m-director and one an o,p-director, the o,p-director dominates. e.g.:

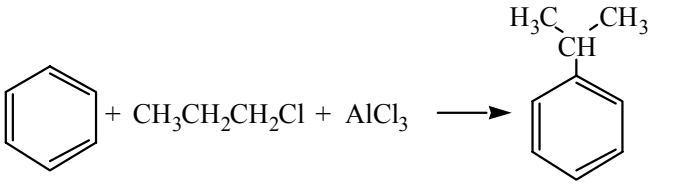


Knowing the mechanism of electrophilic aromatic subsitution and the effect on this reaction of substitutents in the ring, we can explain some of the reactions we have already seen.

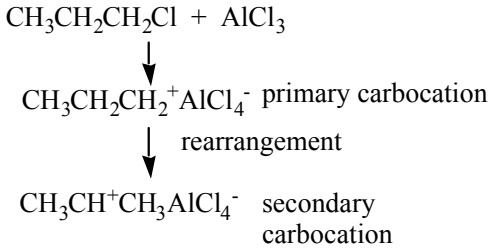
Friedel Crafts alkylation



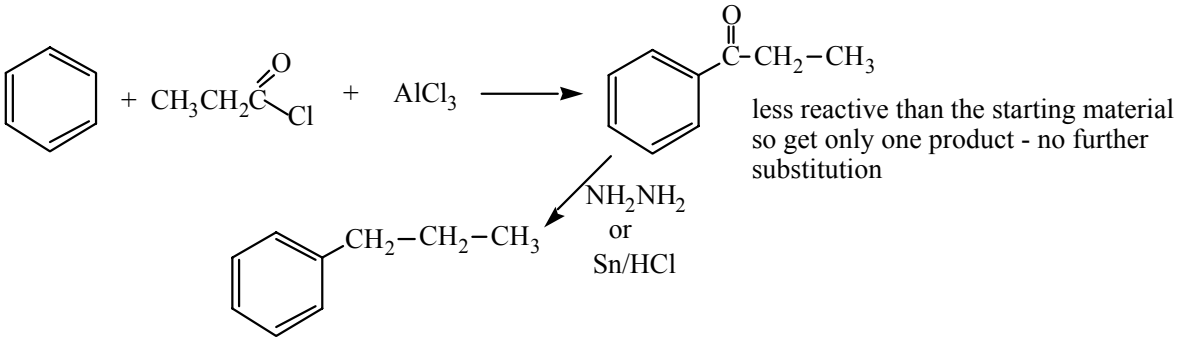
There can also be a problem with carbocation rearrangement

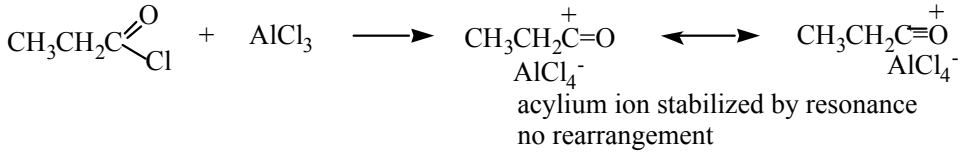


Reason:



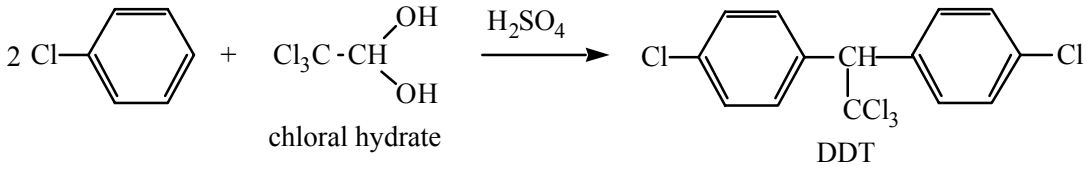
In Friedel Crafts acylation, neither of these problems occurs

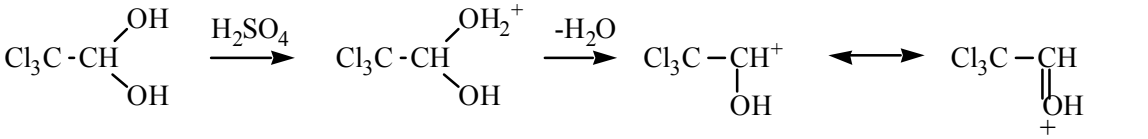




The Friedel Crafts reaction does not occur with deactivated benzene rings, i.e. rings substituted with NO_2, COR, COOH, NR_3^+ groups.

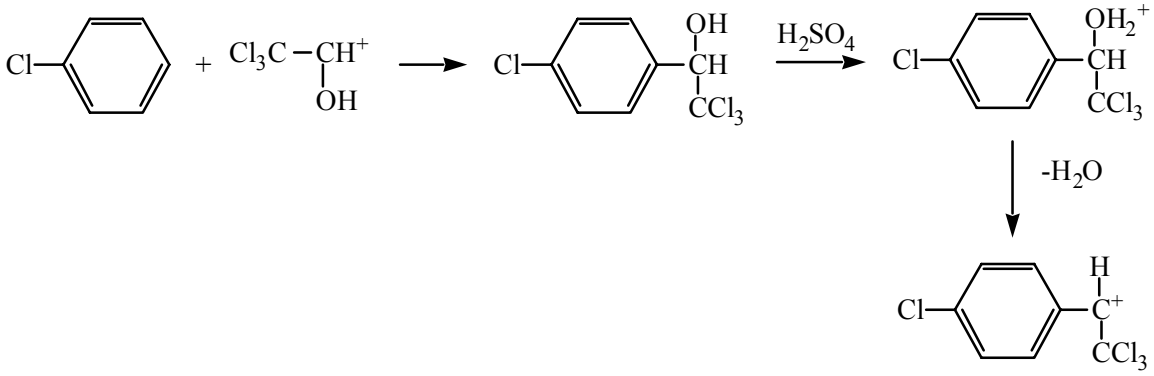
Preparation of DDT



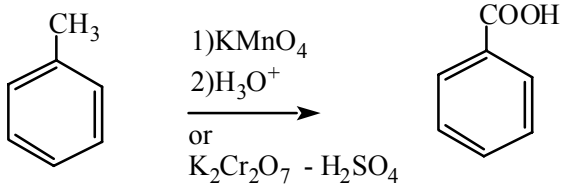


stabilized acylium ion is the electrophilic reagent

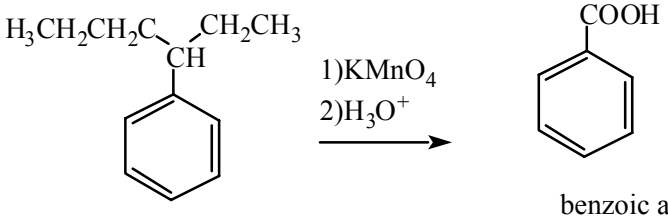
Mechanism



Oxidation of Alkyl Benzenes

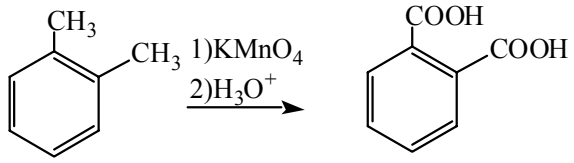


benzoic acid



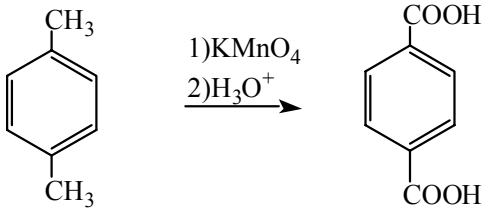
benzoic acid

No matter how long the alkyl chain, the product is benzoic acid



o-xylene
1,2-dimethoxybenzene

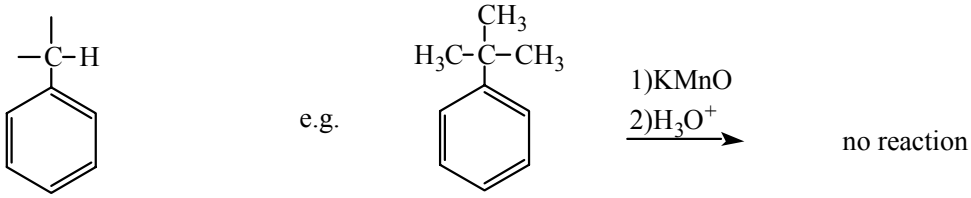
o-phthalic acid



p-xylene
1,4-dimethylbenzene

phthalic acid

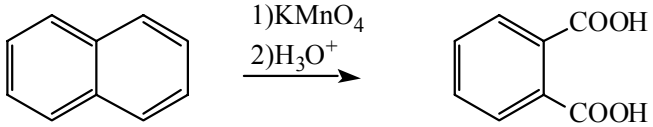
For the oxidation to proceed, there must be at least one hydrogen on the carbon adjacent to the benzene ring. This hydrogen is called a benzylic hydrogen



no reaction

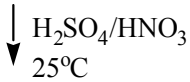
Other groups on the benzene ring are also stable to oxidation - Br, Cl, NO_2, COOH, SO_3H

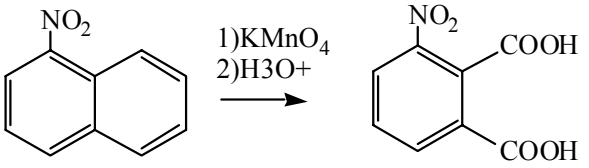
Oxidation of naphthalene



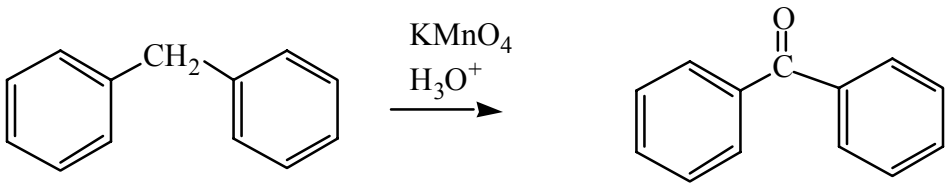
naphthalene

o-phthalic acid



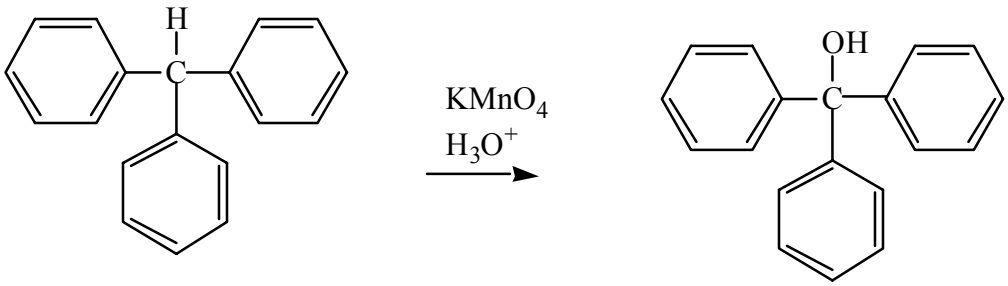


the NO_2 group deactivates the ring to oxidation



diphenylmethane

benzophenone



triphenylmethane

triphenylmethanol