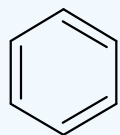


Reactions at the Benzylic Position and Reduction of Benzene

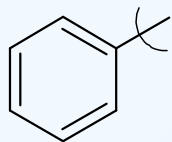
Dr. Sapna Gupta

Nomenclature Review



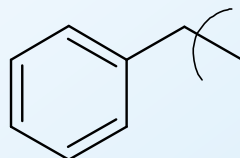
Benzene
Arene

ϕ H

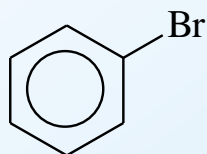


Phenyl (Ph)
Aryl

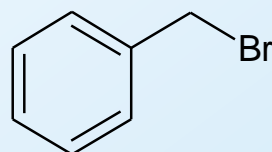
$\phi\sim$



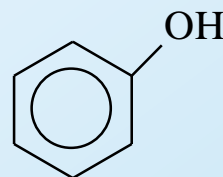
Benzyl
PhCH₂~



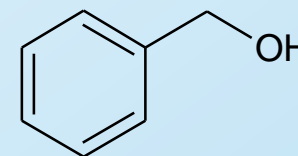
Bromobenzene
Phenylbromide



Benzylbromide



Phenol
Hydroxybenzene
Phenylalcohol



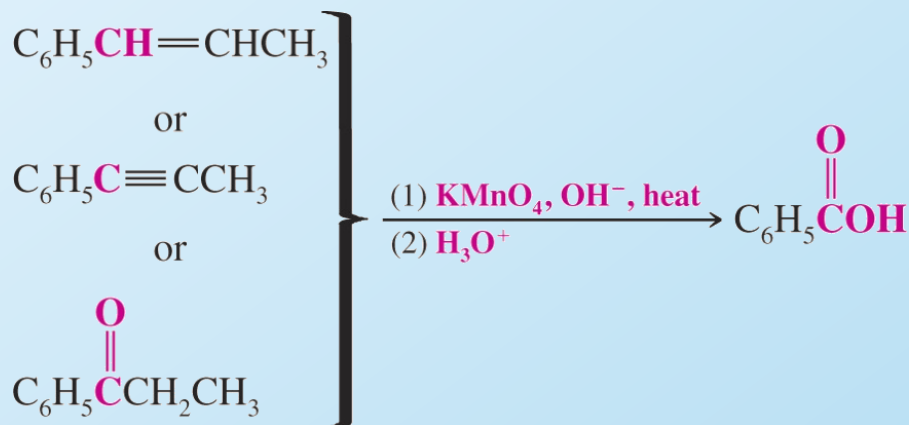
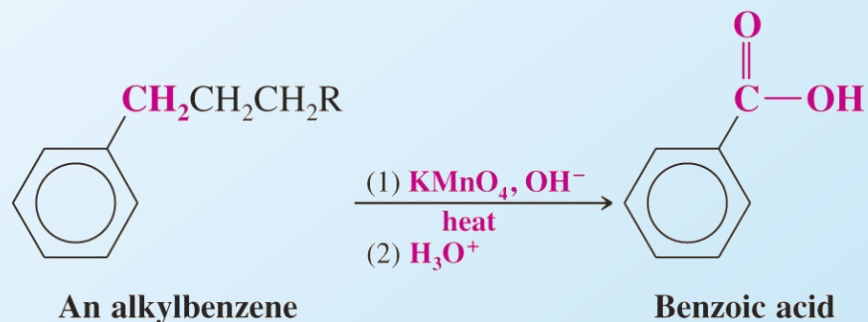
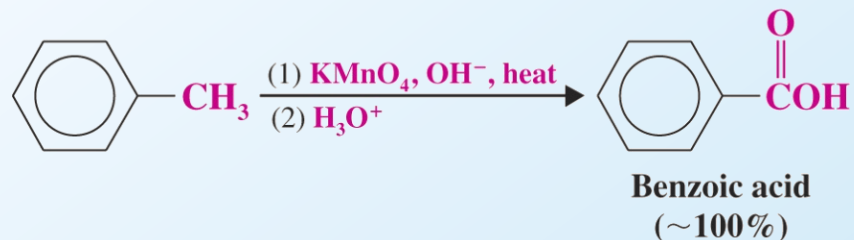
Benzylalcohol

Phenyl and Benzyl

Phenyl indicates the benzene ring attachment. The benzyl group has an additional carbon.

Oxidation of Benzene

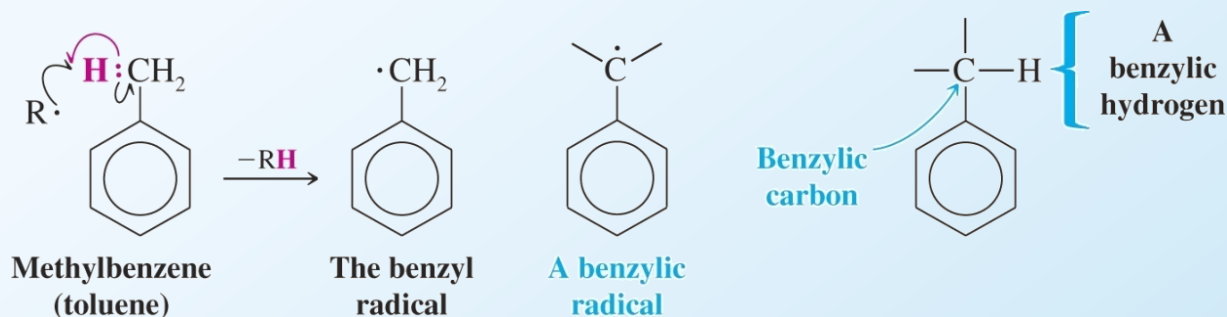
- Alkyl and unsaturated side chains of aromatic rings can be oxidized to the carboxylic acid using hot KMnO_4
- Can use H_2CrO_4 also.



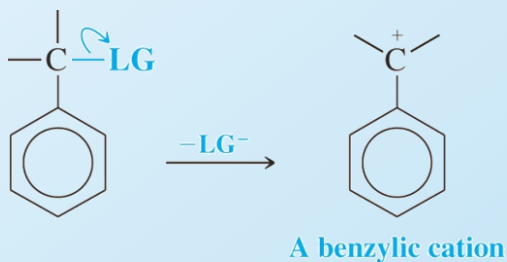
Side Chain Reactions on Benzene

Benzylic Radicals and Cations

- When toluene undergoes hydrogen abstraction from its methyl group it produces a benzyl radical. A benzylic radical is a radical in which the carbon bearing the unpaired electron is directly bonded to an aromatic ring

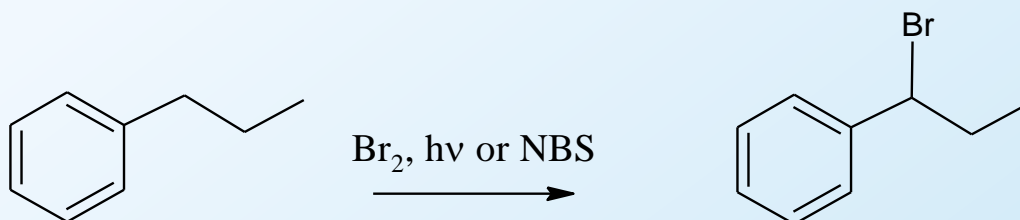


- Departure of a leaving group by an S_N1 process from a benzylic position leads to formation of a benzylic cation

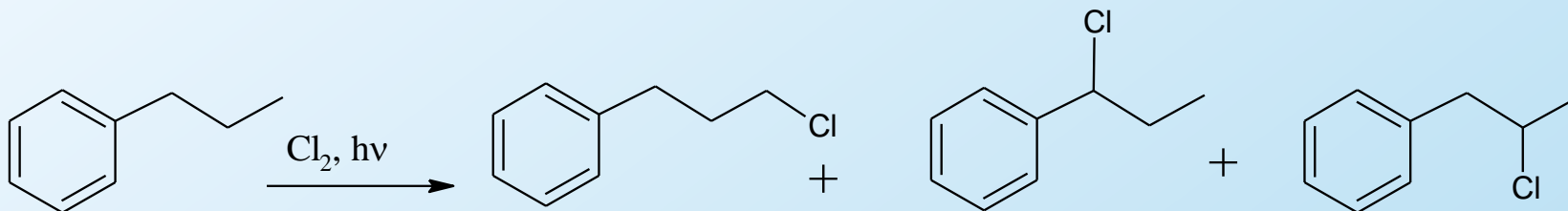


Benzylic Halogenation

- Benzylic halogenation takes place under conditions which favor radical reactions
- Reaction of *N*-bromosuccinamide with *n*-propylbenzene in the presence of light leads to allylic bromination. (*N*-bromosuccinamide favors radical reaction)

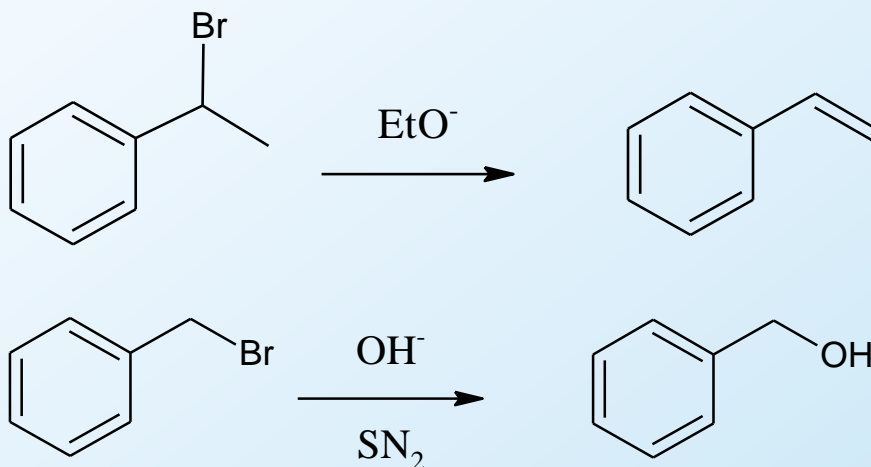


- Reaction of *n*-propylbenzene with excess chlorine can produce multiple chlorinations. Chlorination is not specific to the benzylic carbon.



Substitution on Benzylic Position

- Once there is a leaving group (Br) is on the benzylic position, any number of substitution or elimination reactions can be carried out on the side chain.

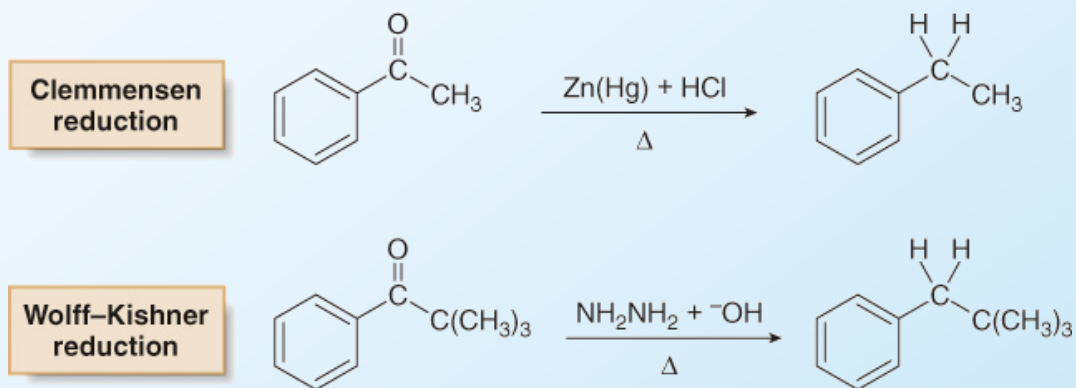


Side Chain Reduction on Benzene

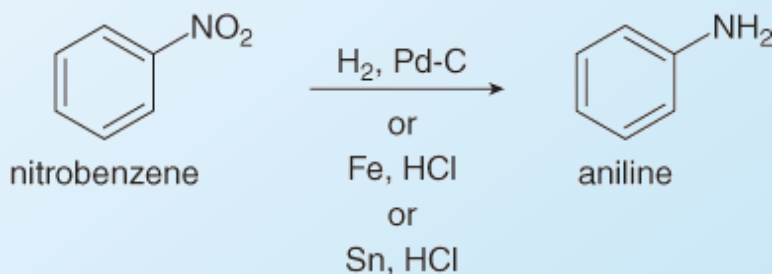
- Reduction of ketones

- The **Clemmensen reduction**—uses zinc and mercury in the presence of strong acid.

- The **Wolff-Kishner reduction**—uses hydrazine (NH_2NH_2) and strong base (KOH).

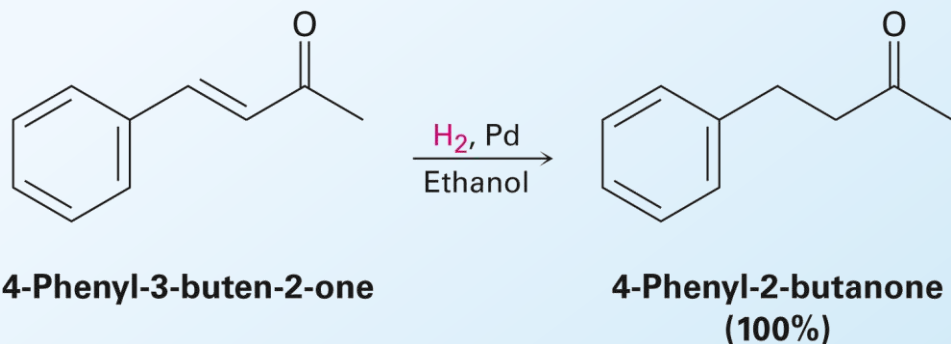
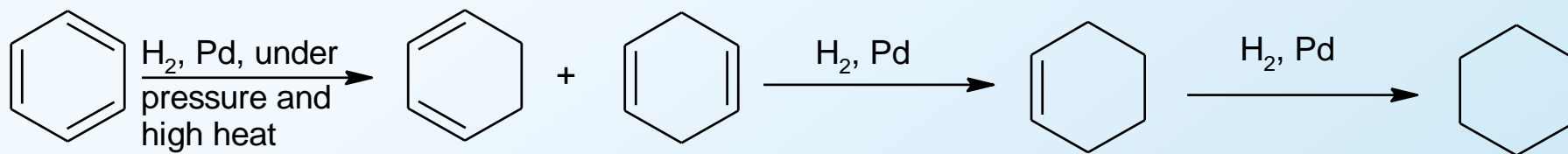


- Reduction of Nitro to give Amine group



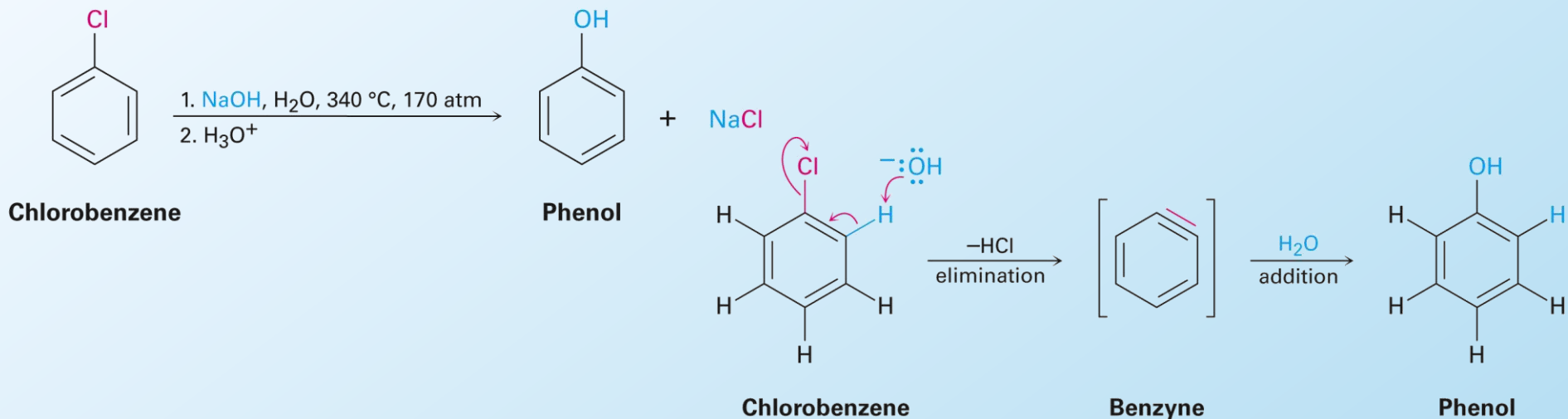
Reduction of Benzene

- Hydrogenation – reduces benzene ring all the way to cyclohexane.



Nucleophilic Substitution on Benzene Ring

- Aryl halides do not undergo nucleophilic substitution by either S_N1 or S_N2 pathways.
- They do undergo nucleophilic substitutions, but by mechanisms quite different from those of nucleophilic aliphatic substitution.
 - Nucleophilic aromatic substitutions are far less common than electrophilic aromatic substitutions.
- Phenol is prepared on an industrial scale by treatment of chlorobenzene with dilute aqueous NaOH at 340°C under high pressure
- The reaction involves an elimination reaction that gives a triple bond
- The intermediate is called benzyne



Key Concepts

- Oxidation of side chain
- Side chain reactions (benzylic position reactions)
- Reductions
- Nucleophilic reaction on benzene