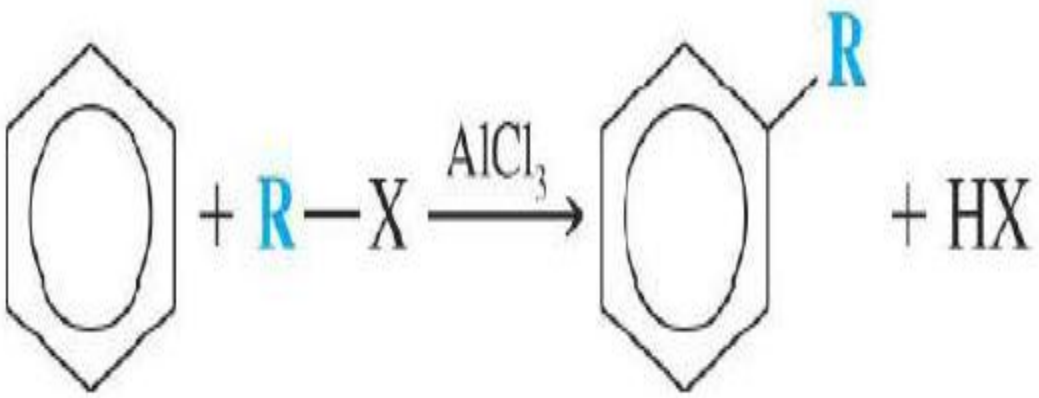
Chemical Reactions of Benzene:

Electrophilic Aromatic Substitution:

4- Friedel–Crafts Alkylation of Benzene:

An aromatic ring can be **alkylated** by an **alkyl halide** in the presence of a **Lewis acid**

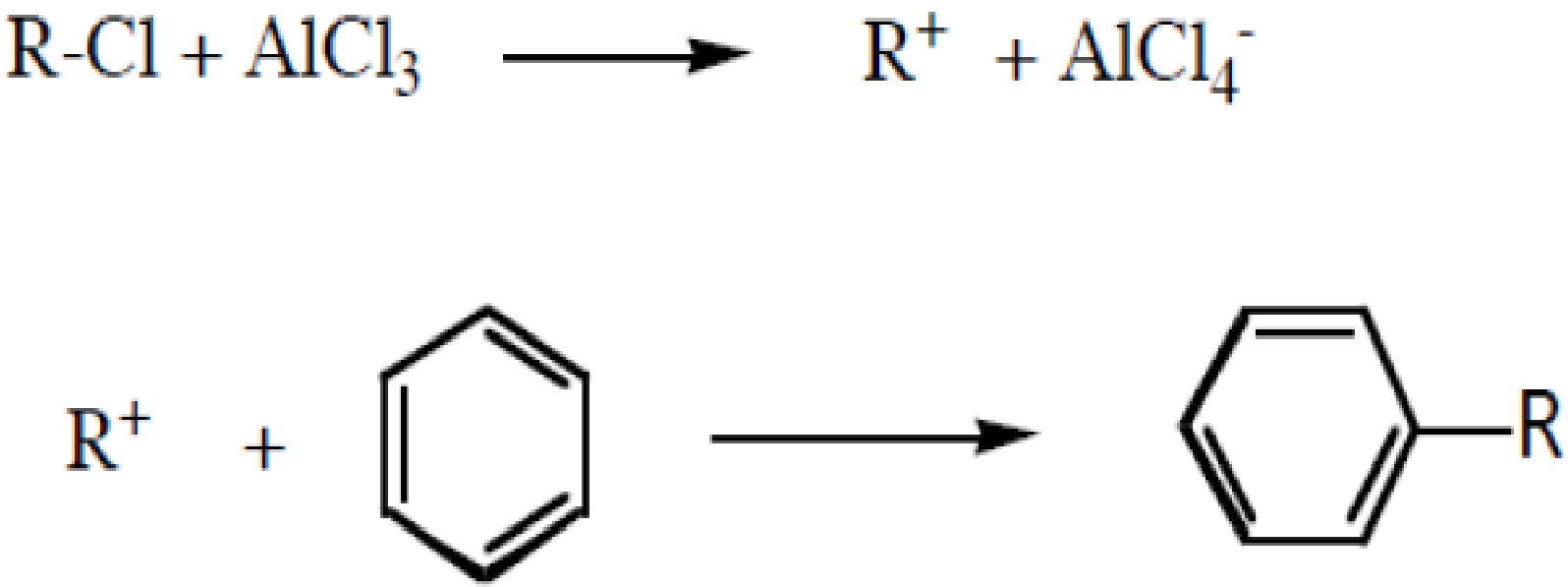
(The **Lewis acid** serves to generate a **carbocation electrophile**)



Chemical Reactions of Benzene:

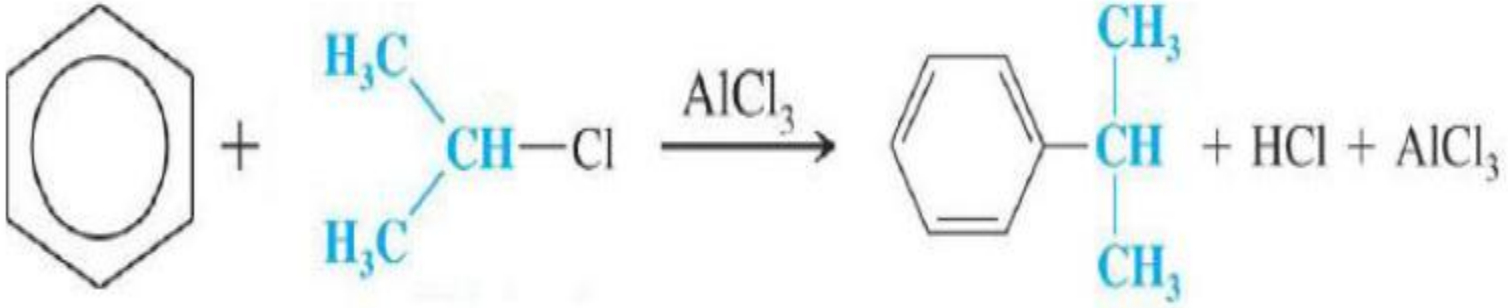
Electrophilic Aromatic Substitution:

4- Friedel–Crafts Alkylation of Benzene:

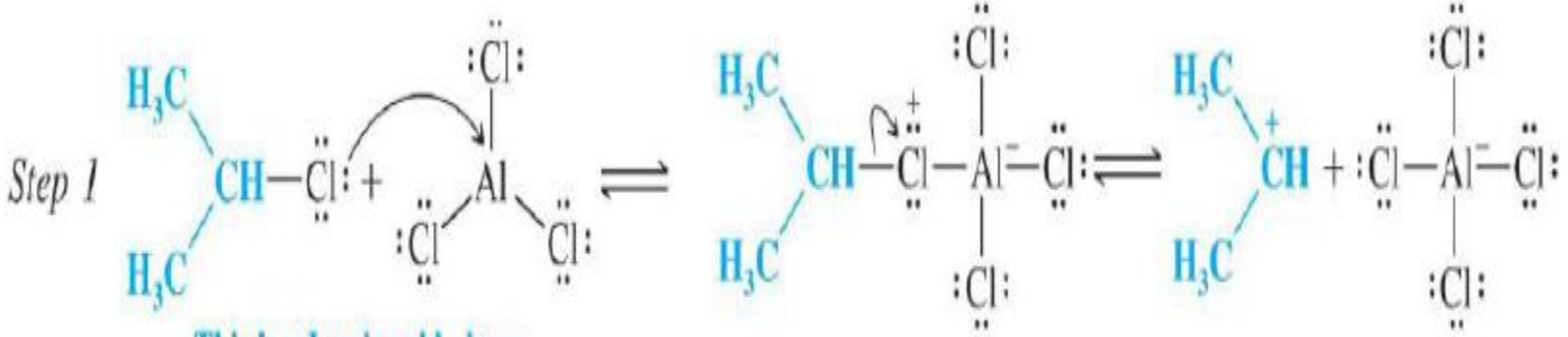


(R = alkyl)

4- Friedel–Crafts Alkylation of Benzene:



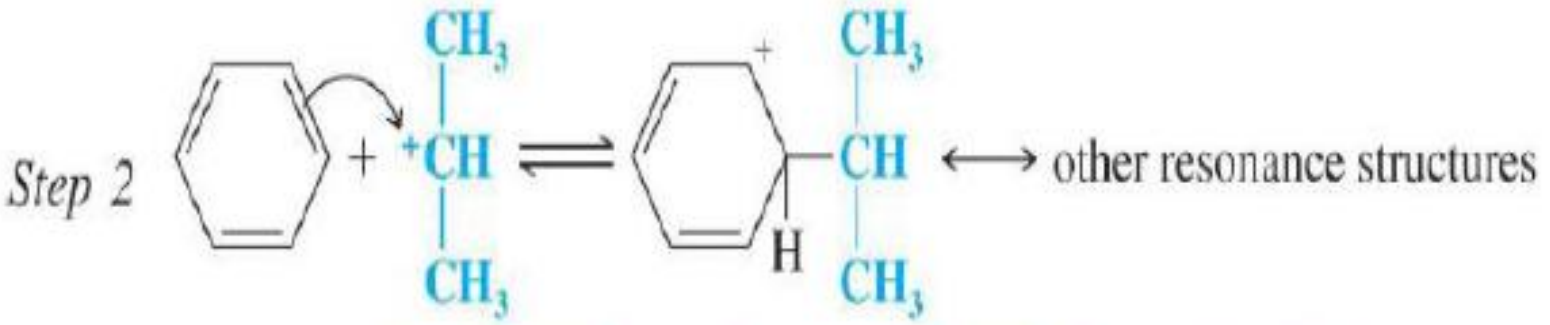
Mechanism



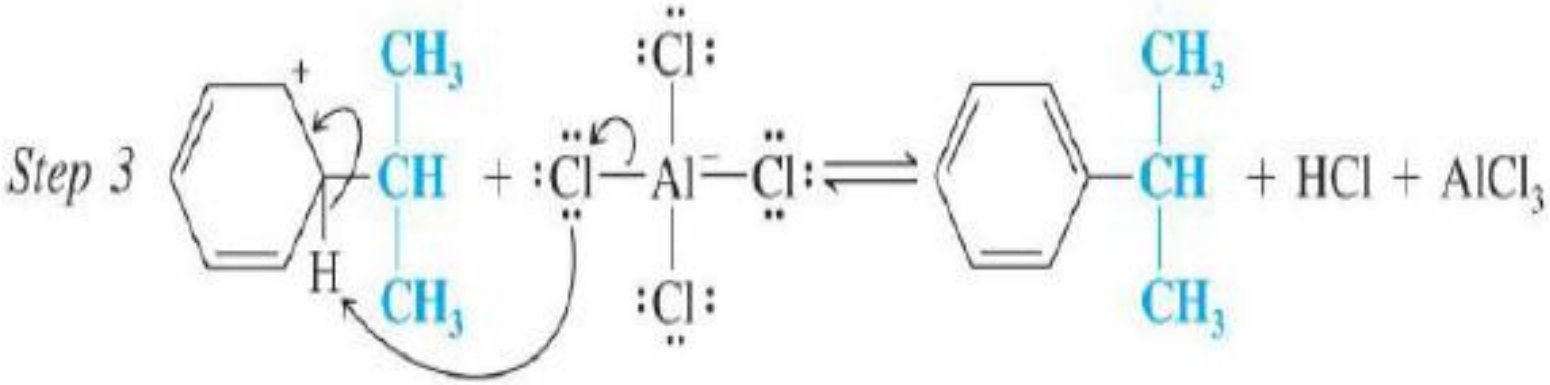
This is a Lewis acid–base reaction (see Section 3.2B).

The complex dissociates to form a carbocation and $AlCl_4^-$.

4- Friedel–Crafts Alkylation of Benzene:



The carbocation, acting as an electrophile, reacts with benzene to produce an arenium ion.

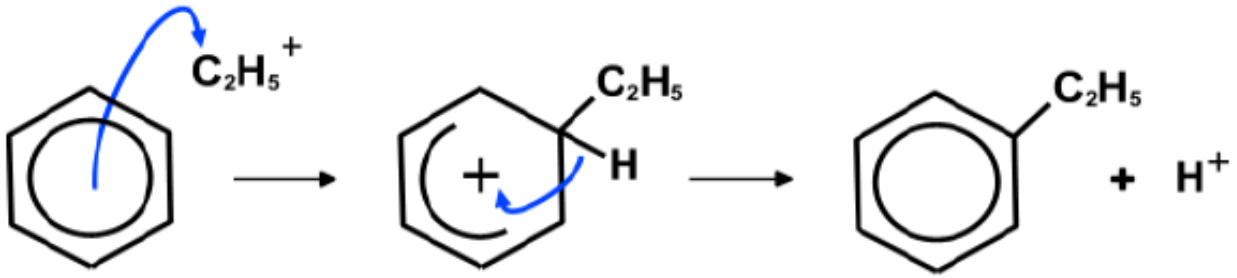


A proton is removed from the arenium ion to form isopropylbenzene. This step also regenerates the $AlCl_3$ and liberates HCl.

4- Friedel–Crafts Alkylation of Benzene:

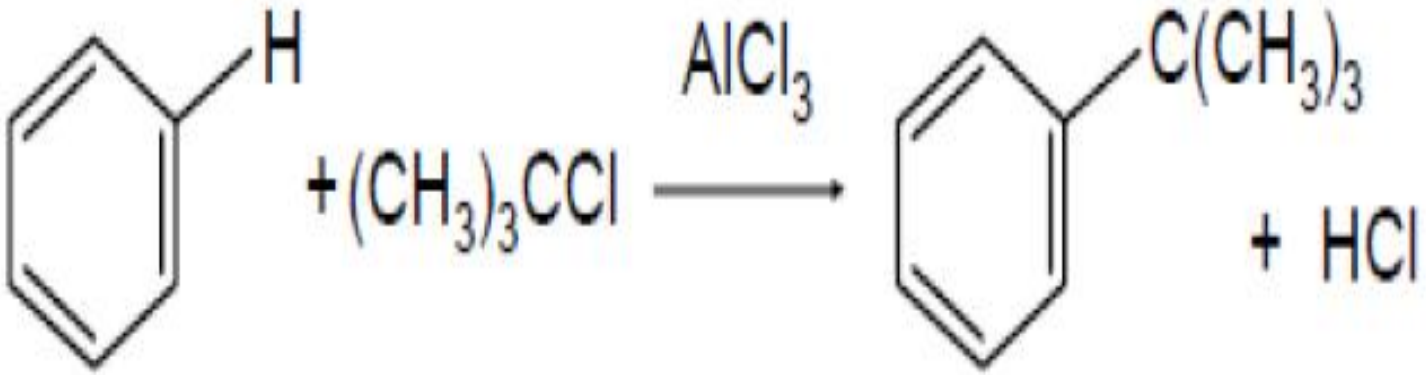
Another example:

$$C_6H_6 + C_2H_5Cl \longrightarrow C_6H_5C_2H_5 + HCl$$

Overview	Alkylation involves substituting an alkyl (methyl, ethyl) group
Reagents	a halogenoalkane (RX) and anhydrous aluminium chloride $AlCl_3$
Conditions	room temperature; dry inert solvent (ether)
Electrophile	a carbocation ion R^+ (e.g. CH_3^+)
Equation	$C_6H_6 + C_2H_5Cl \longrightarrow C_6H_5C_2H_5 + HCl$
Mechanism	

4- Friedel–Crafts Alkylation of Benzene:

Another example:

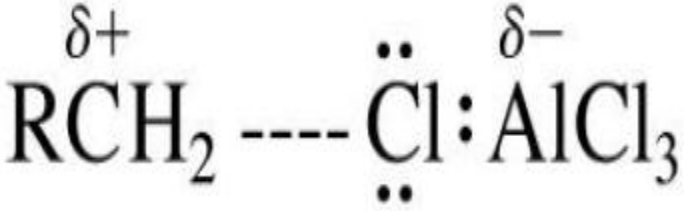


tert-Butylbenzene
(60%)

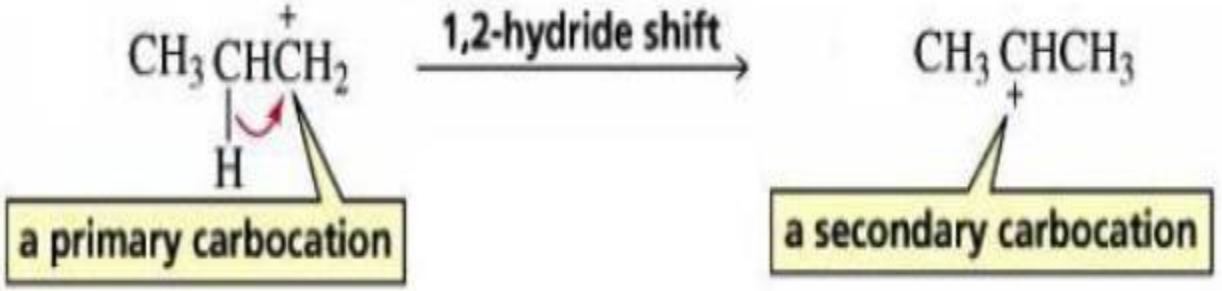
4- Friedel–Crafts Alkylation of Benzene:

Rearrangements in Friedel-Crafts Alkylation

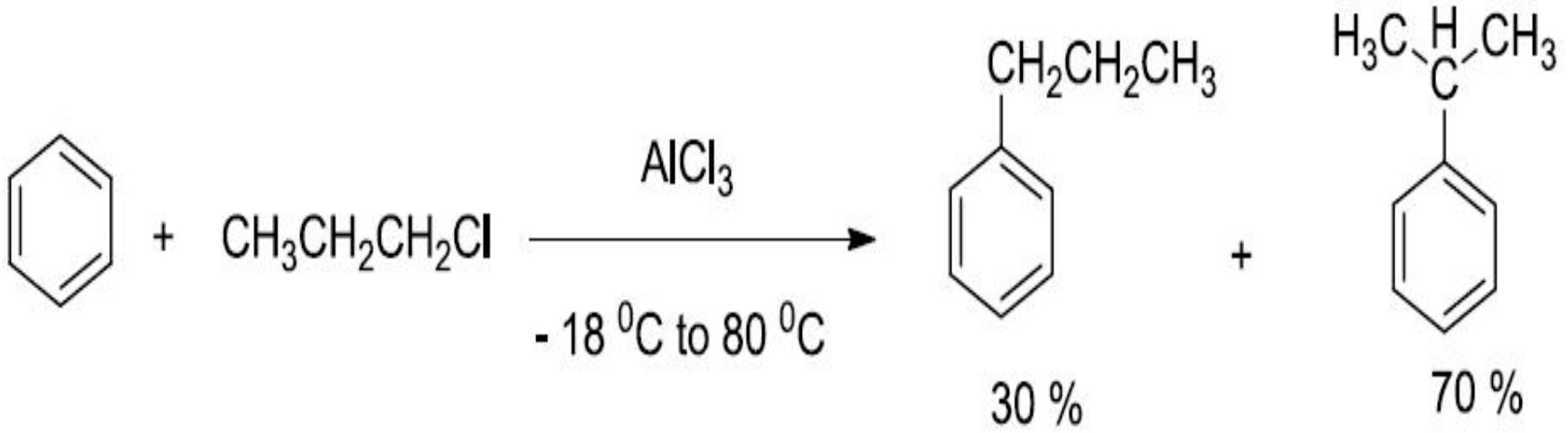
Primary alkyl halides probably do not form discreet carbocations but the primary carbon in the complex develops considerable positive charge.



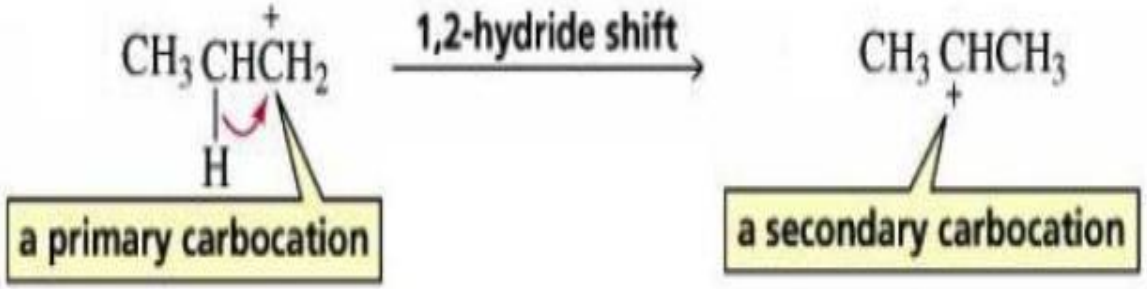
The carbocation will rearrange to a more stable species:



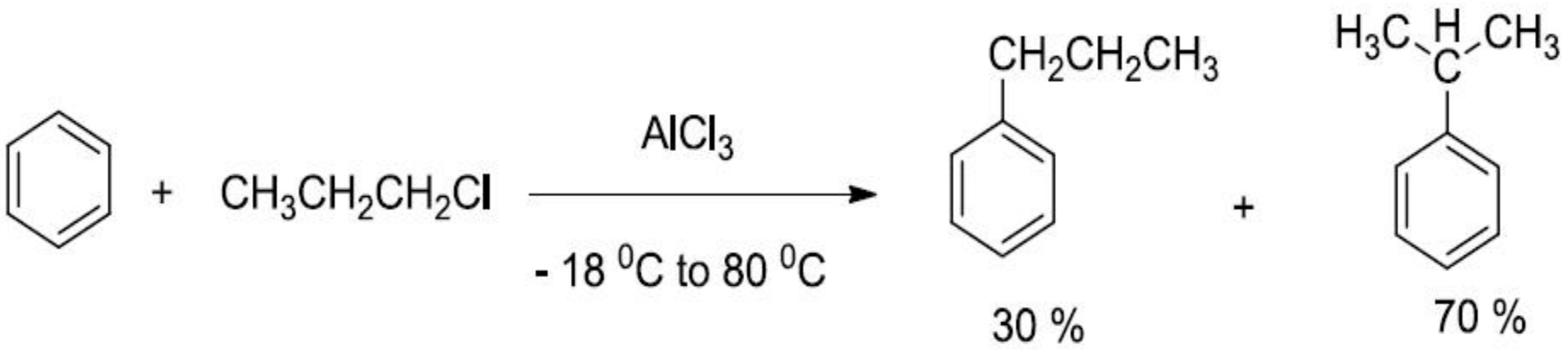
Rearrangements in Friedel-Crafts Alkylation

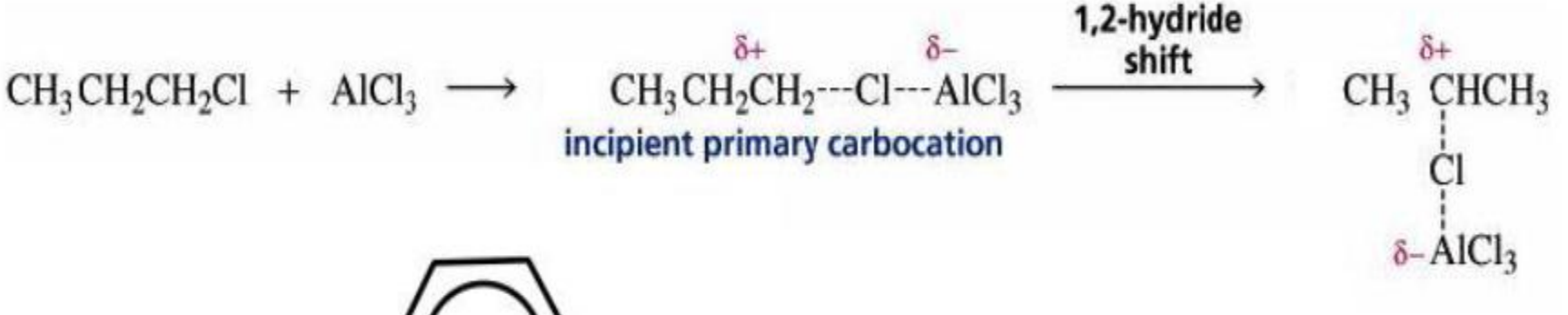


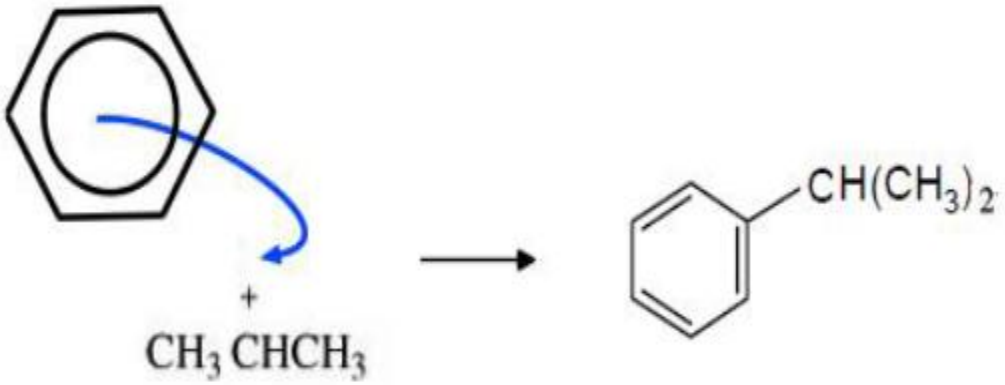
Mechanism



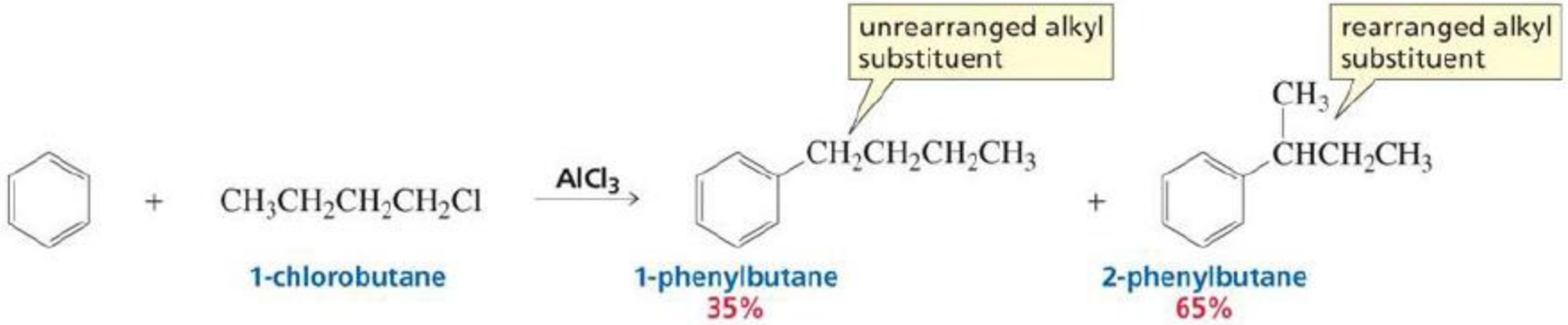
Rearrangements in Friedel-Crafts Alkylation



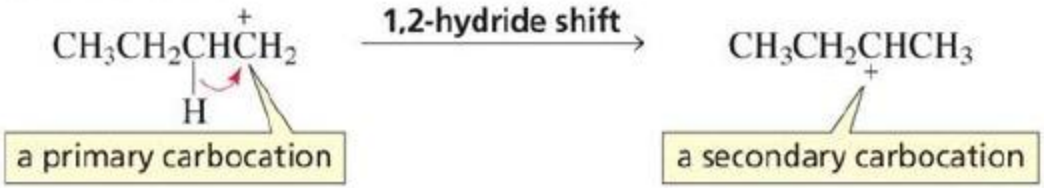


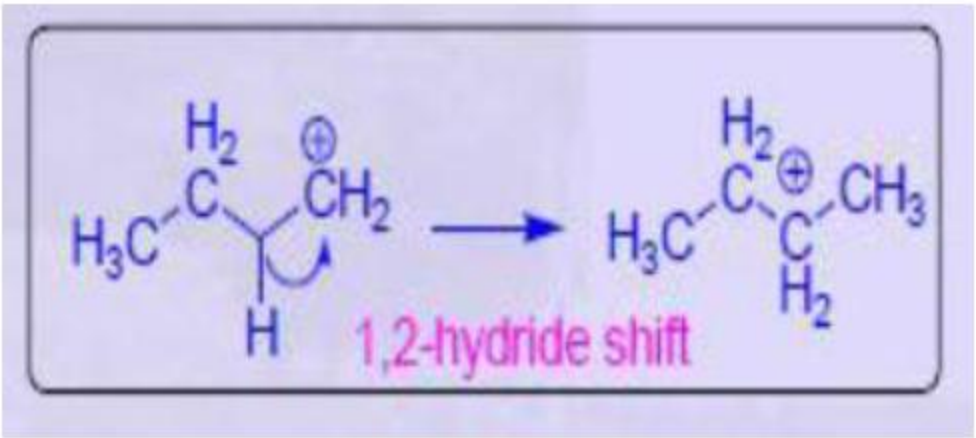


Rearrangements in Friedel-Crafts Alkylation

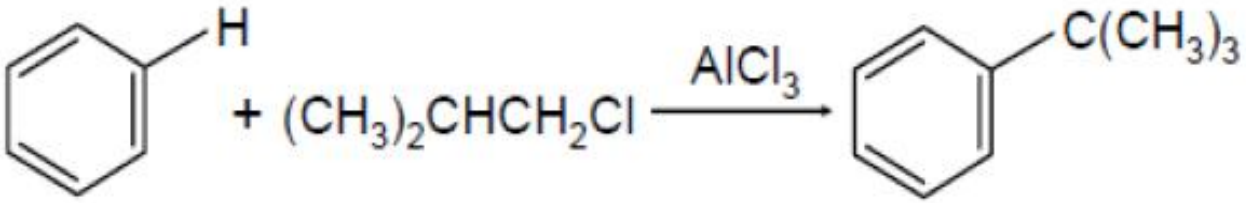


rearrangement of the carbocation





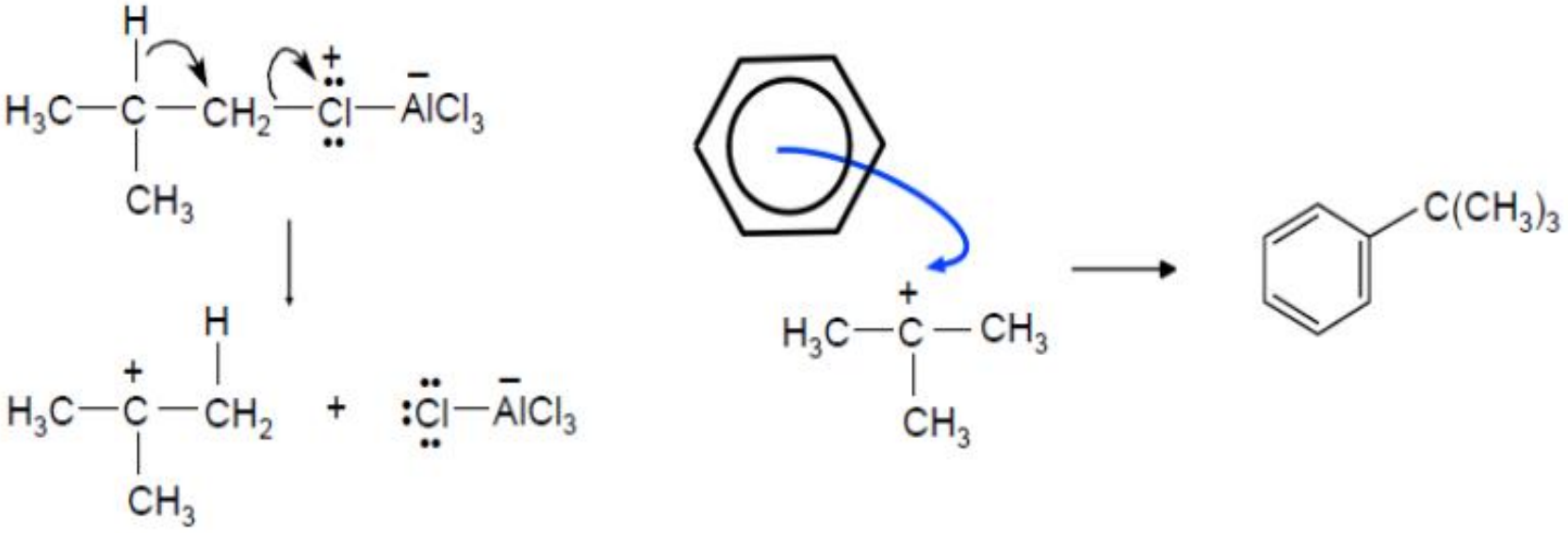
Rearrangements in Friedel-Crafts Alkylation



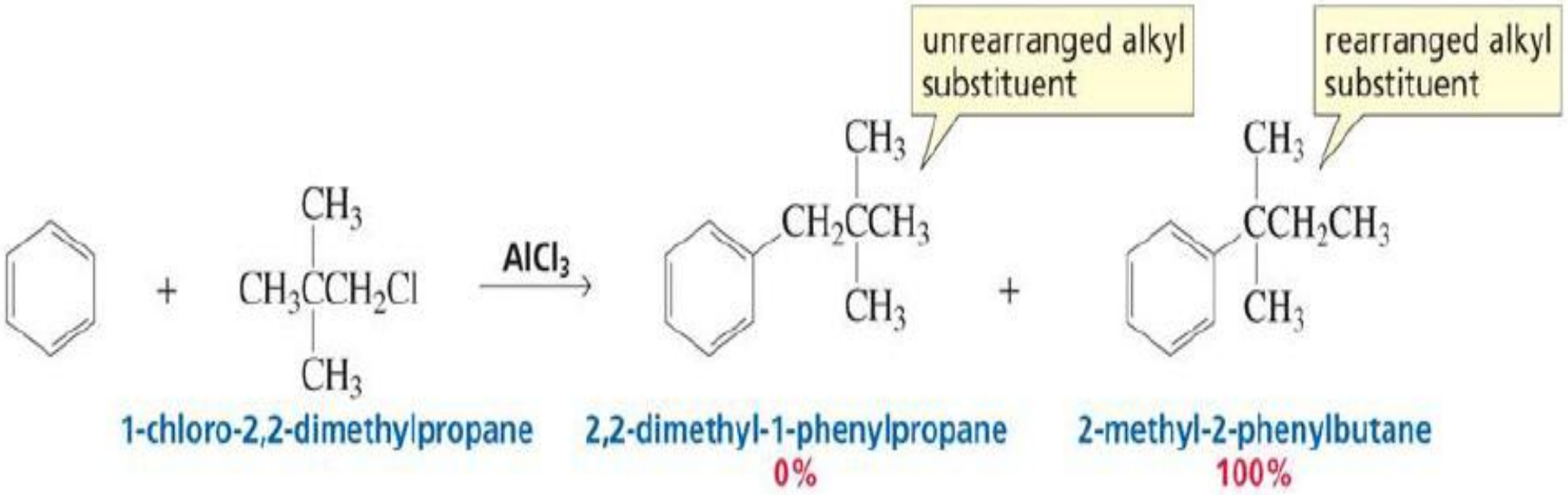
Isobutyl chloride

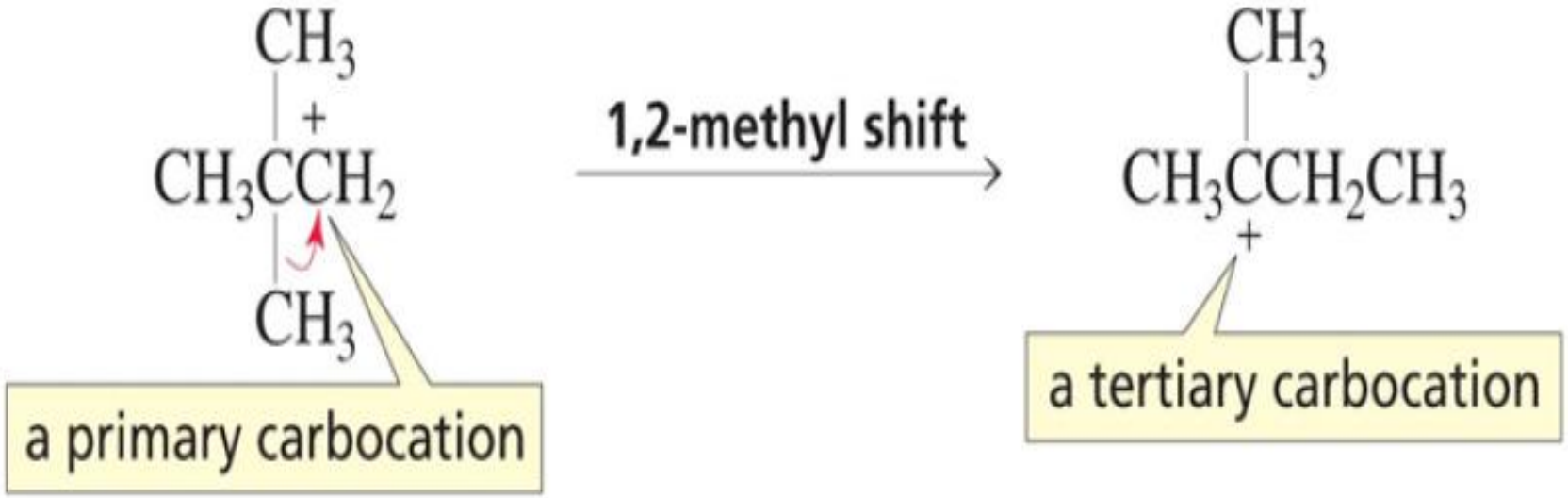
tert-Butylbenzene
(66%)

Mechanism



Rearrangements in Friedel-Crafts Alkylation





Chemical Reactions of Benzene:

Electrophilic Aromatic Substitution:

5- Friedel–Crafts Acylation of Benzene:

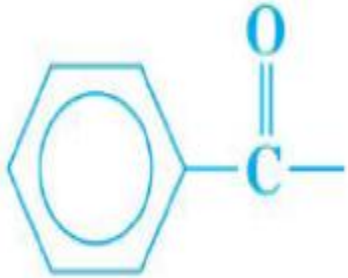
Friedel–Crafts acylation, an acyl group, typically derived from an acid chloride, is introduced into an aromatic ring in the presence of a Lewis acid.

An acyl group has a carbonyl attached to some R group

an acid chloride

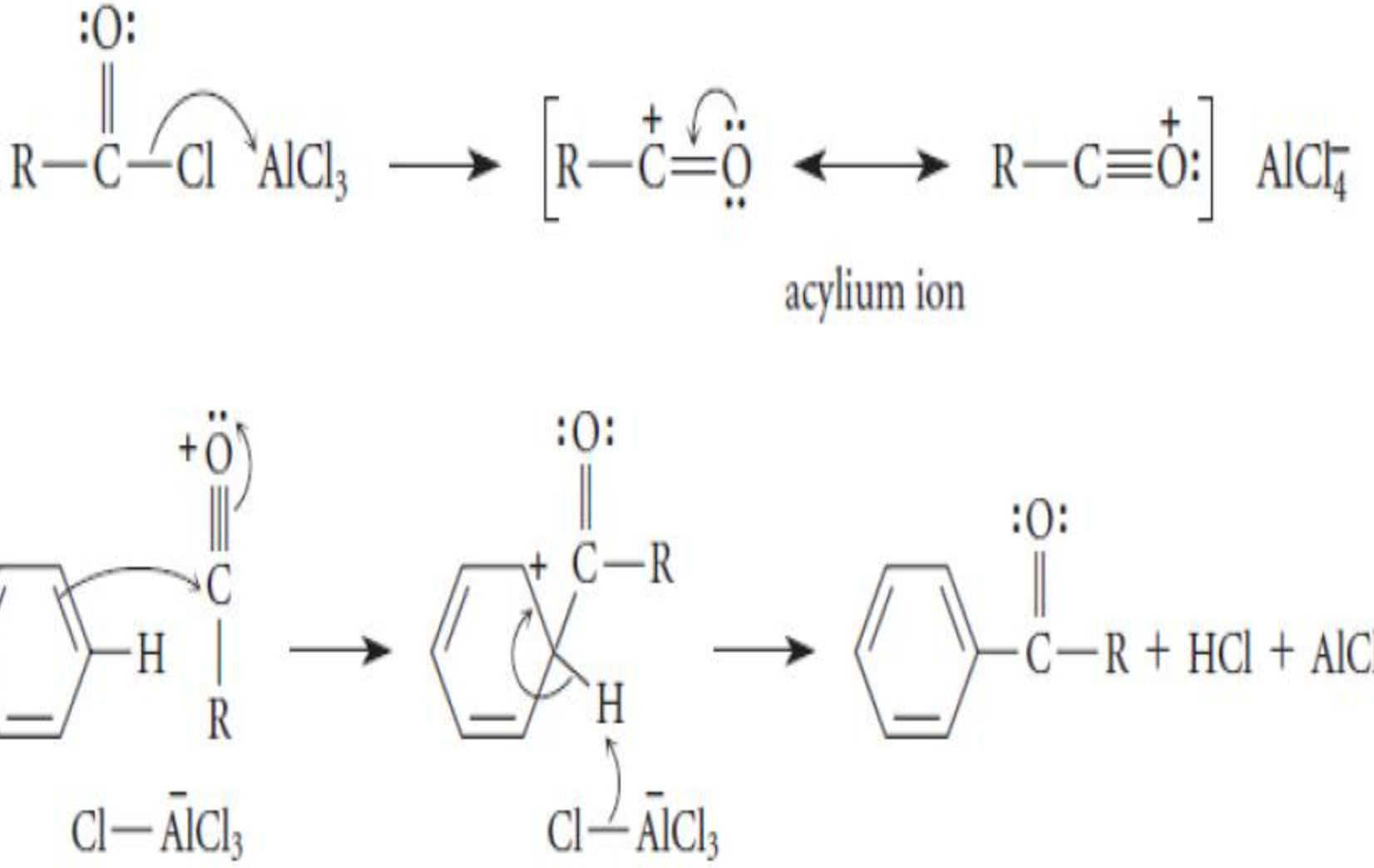
an acyl group

Acetyl group (ethanoyl group)

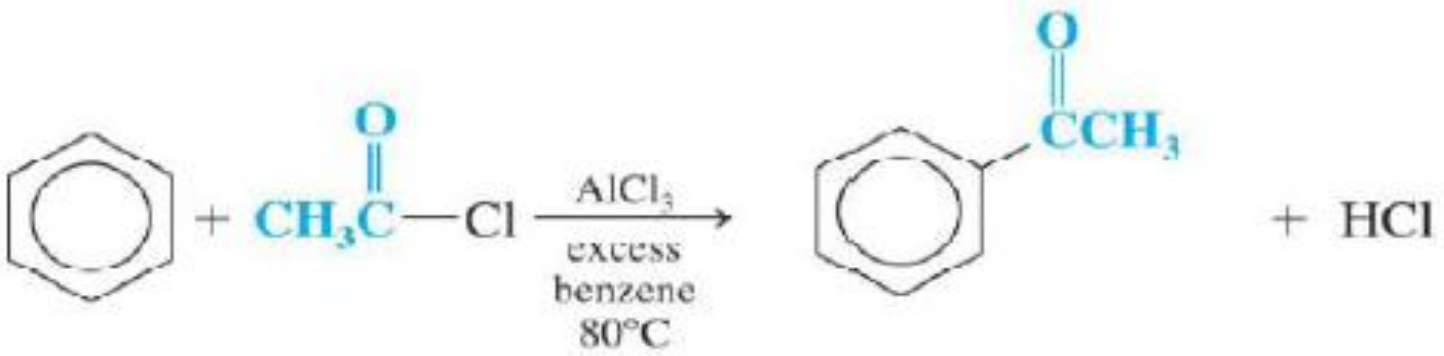


Benzoyl group

5- Friedel–Crafts Acylation of Benzene:



5- Friedel–Crafts Acylation of Benzene:



Acetyl chloride

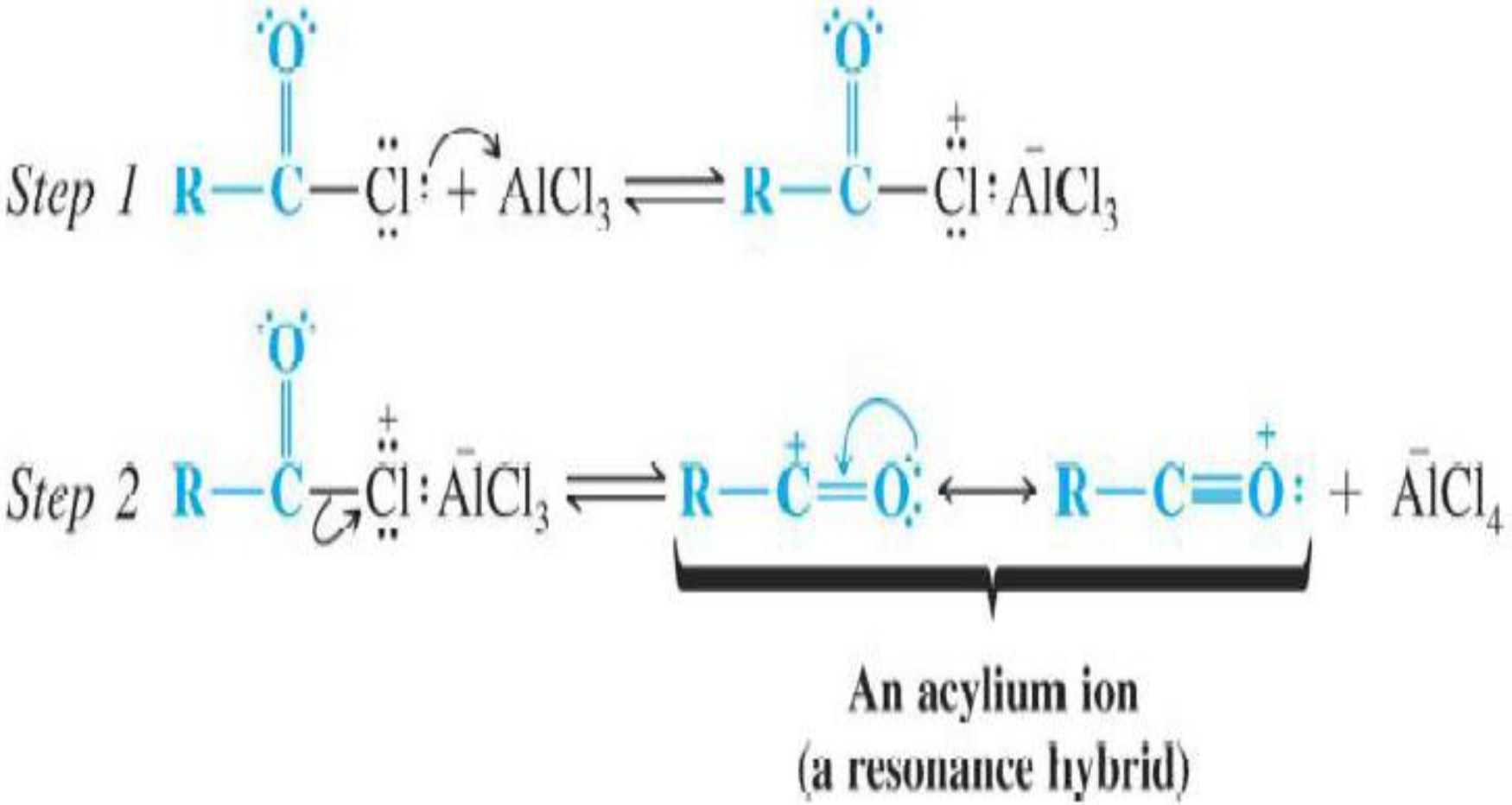
Acetophenone (methyl phenyl ketone) (97%)

Acetic anhydride (a carboxylic acid anhydride)

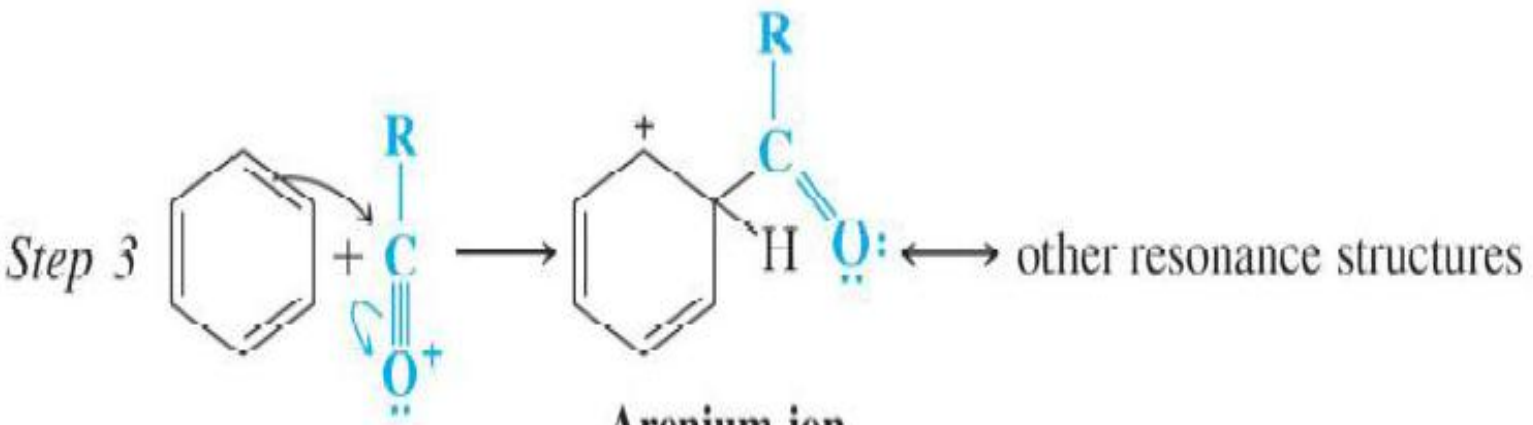
Acetophenone (82–85%)

5- Friedel–Crafts Acylation of Benzene:

Mechanism

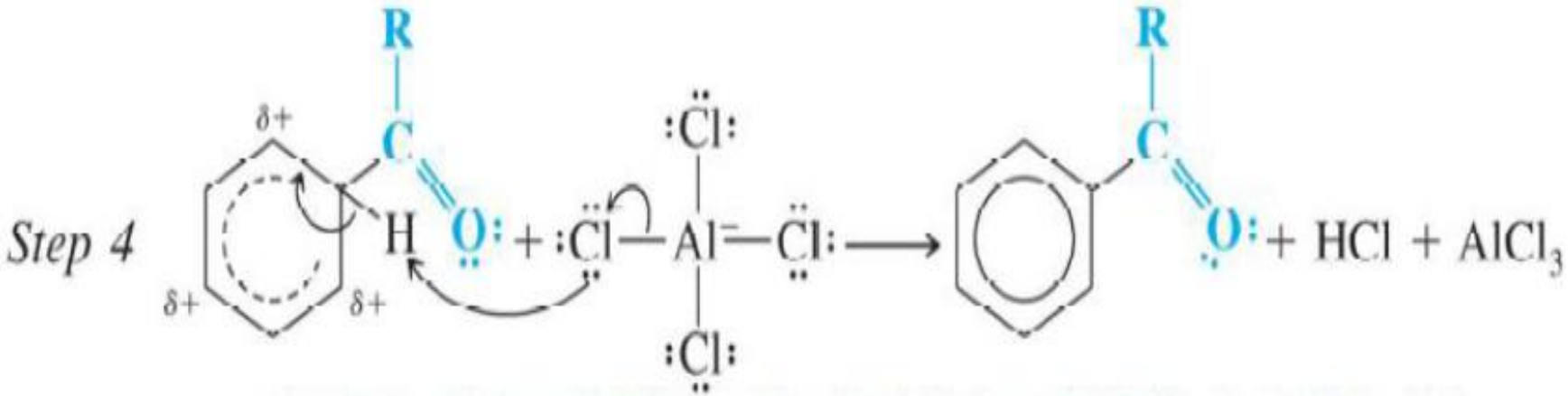


5- Friedel–Crafts Acylation of Benzene:



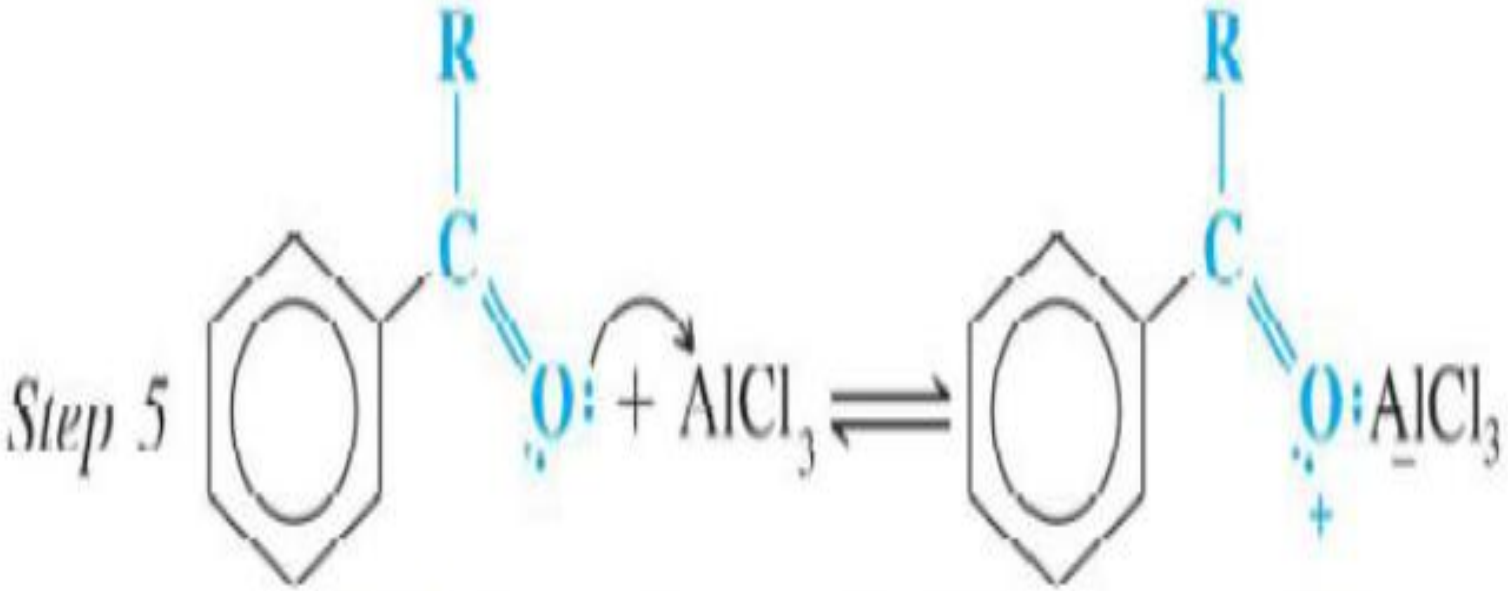
Arenium ion

The acylium ion, acting as an electrophile, reacts with benzene to form the arenium ion.



A proton is removed from the arenium ion, forming the aryl ketone.

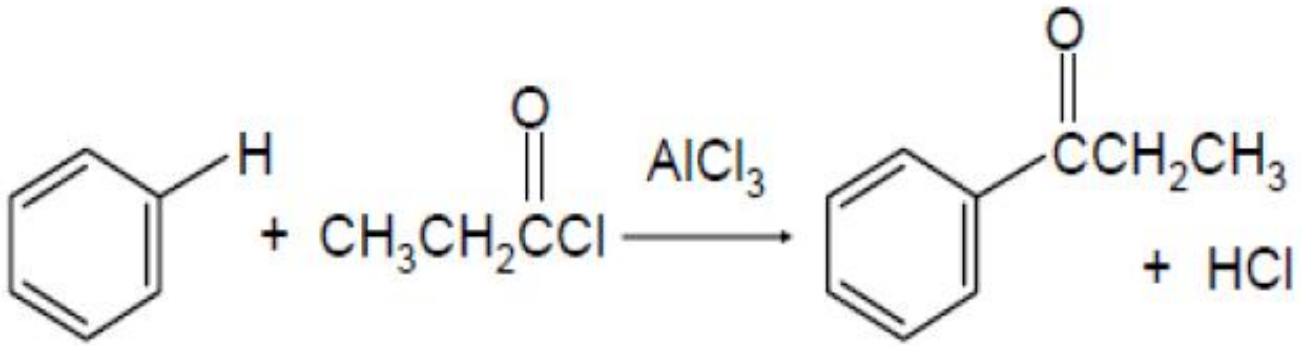
5- Friedel–Crafts Acylation of Benzene:



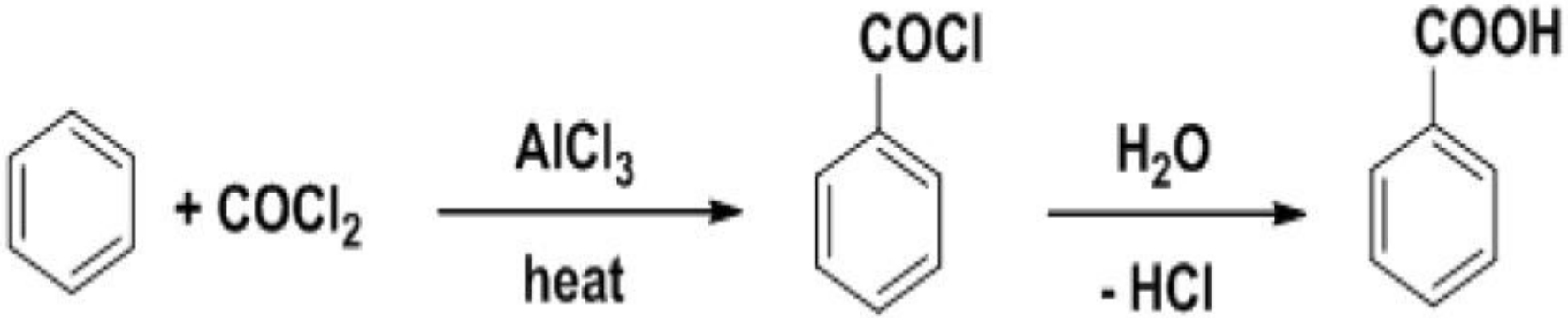
The ketone, acting as a Lewis base, reacts with aluminum chloride (a Lewis acid) to form a complex.

5- Friedel–Crafts Acylation of Benzene:

Another examples:

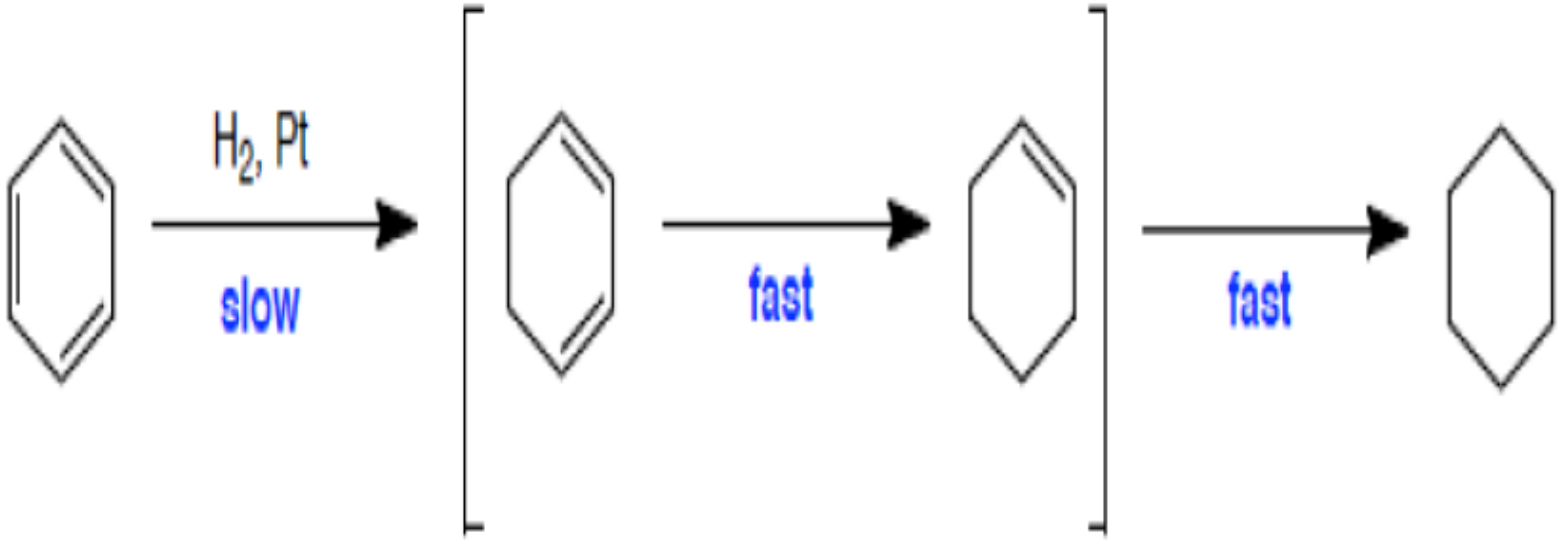


1-Phenyl-1-propanone
(88%)

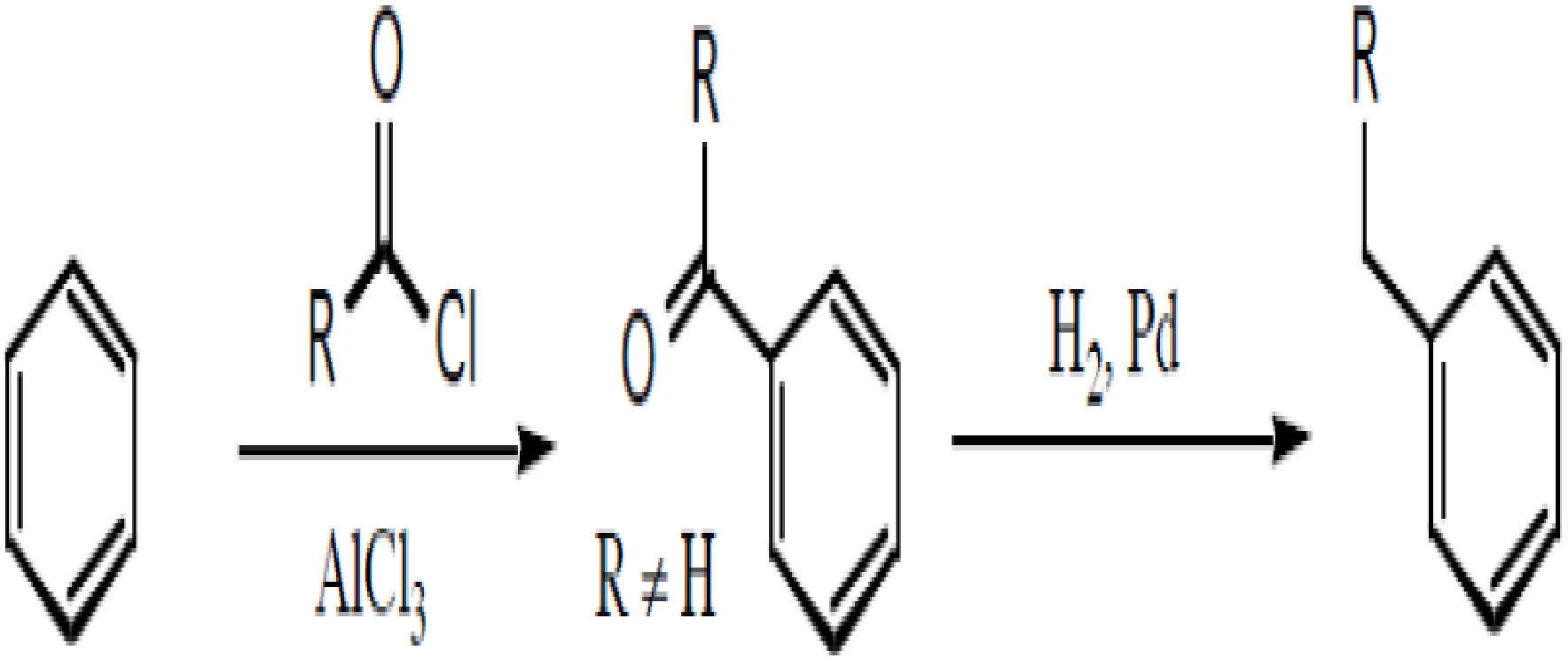


Reduction of Aromatic Compounds:

Reduction of an aromatic ring requires forcing reducing conditions (high pressure and/or highly active catalysts)

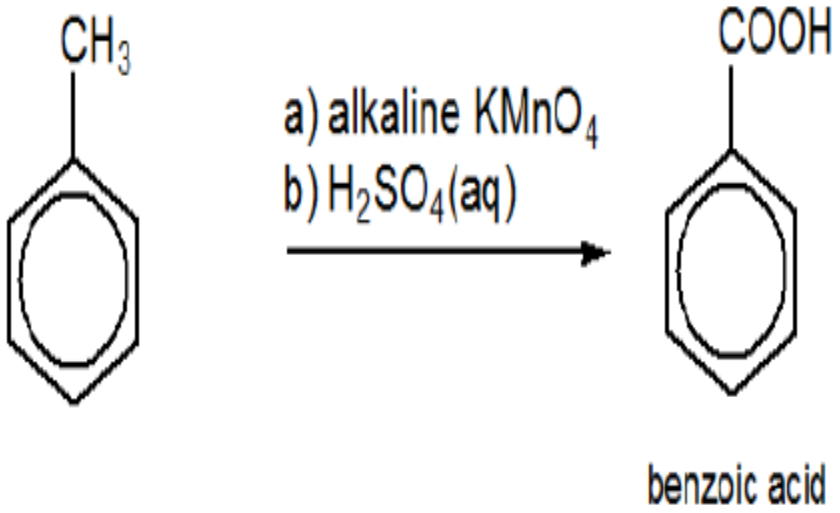


Reduction of Aromatic Compounds:



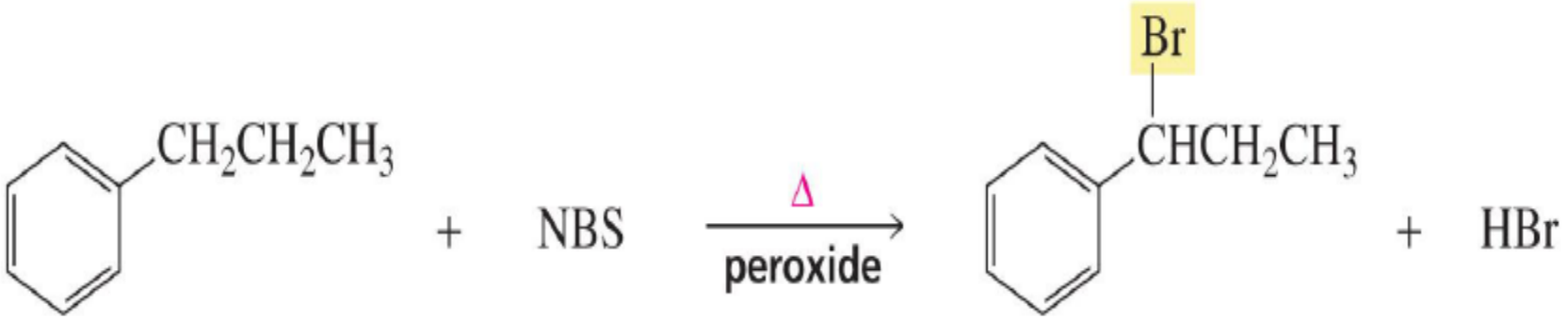
Chemical Modification of Substituents of Benzene

Oxidation of the side chain:



benzoic acid

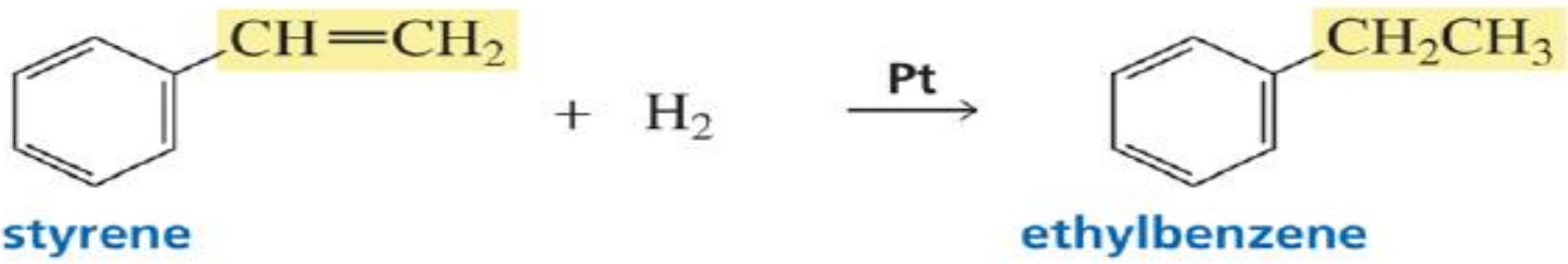
Reactions of alkyl substituent's:



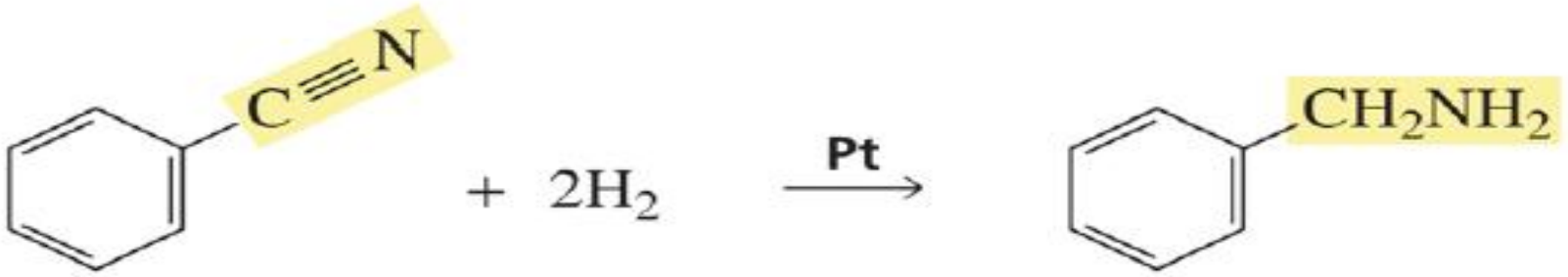
propylbenzene

1-bromo-1-phenylpropane

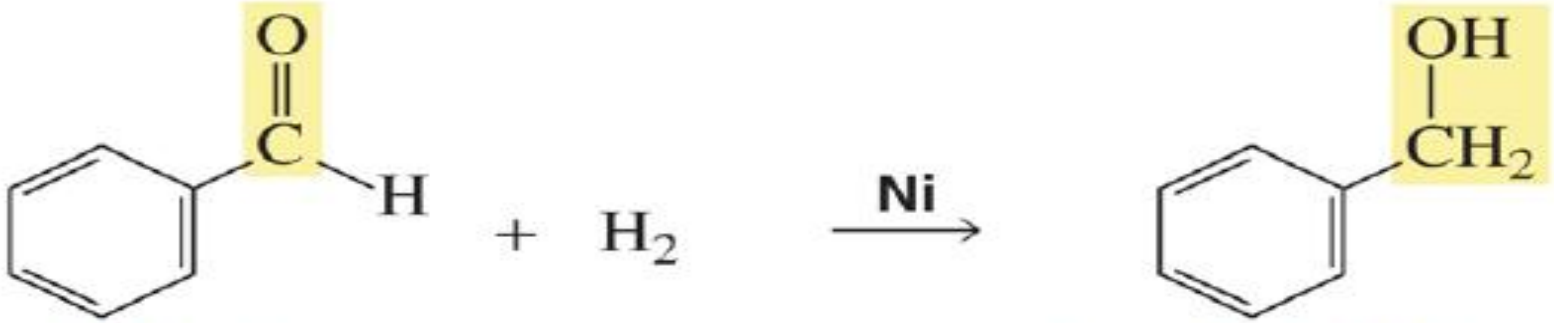
Chemical Modification of Substituents of Benzene



styrene ethylbenzene



benzonitrile benzylamine

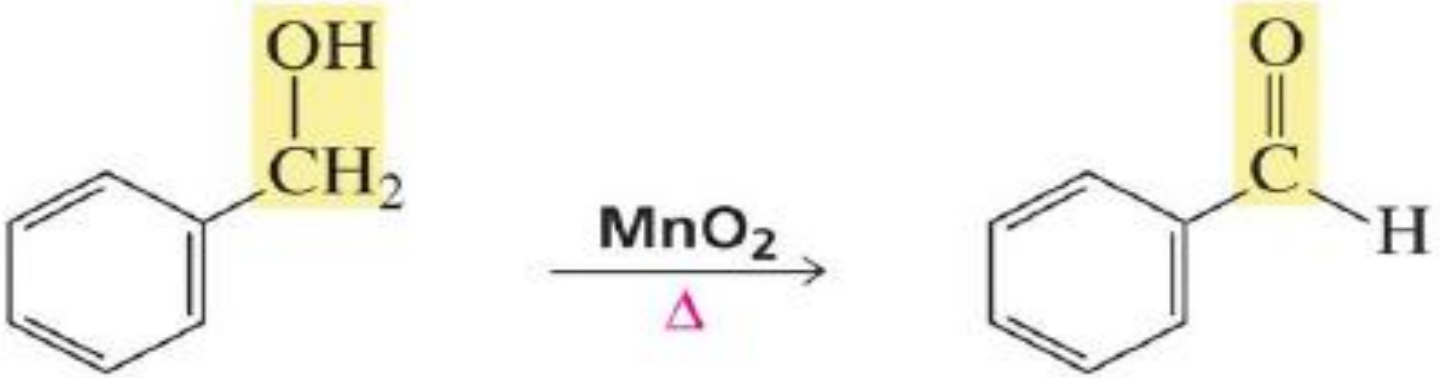


benzaldehyde benzyl alcohol

Chemical Modification of Substituents of Benzene

1-phenylethanol

acetophenone



phenylmethanol
benzyl alcohol

benzaldehyde

Chemical Modification of Substituents of Benzene