1. Reactions involving the ring

   a) Reduction

      Catalytic hydrogenation (Section 11.4)

      Birch reduction (Section 11.11)

   b) Electrophilic aromatic substitution (Chapter 12)

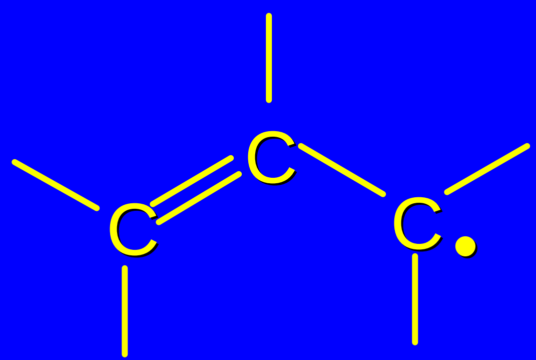
   c) Nucleophilic aromatic substitution (Chapter 23)

2. The ring as a substituent (Sections 11.12-11.17)

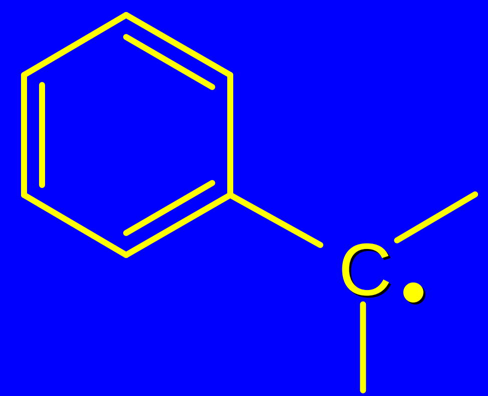
# 11.12

# Free-Radical Halogenation of Alkylbenzenes

# *The Benzene Ring as a Substituent*




*allylic radical*




*benzylic radical*

benzylic carbon is analogous to allylic carbon

*Recall:*

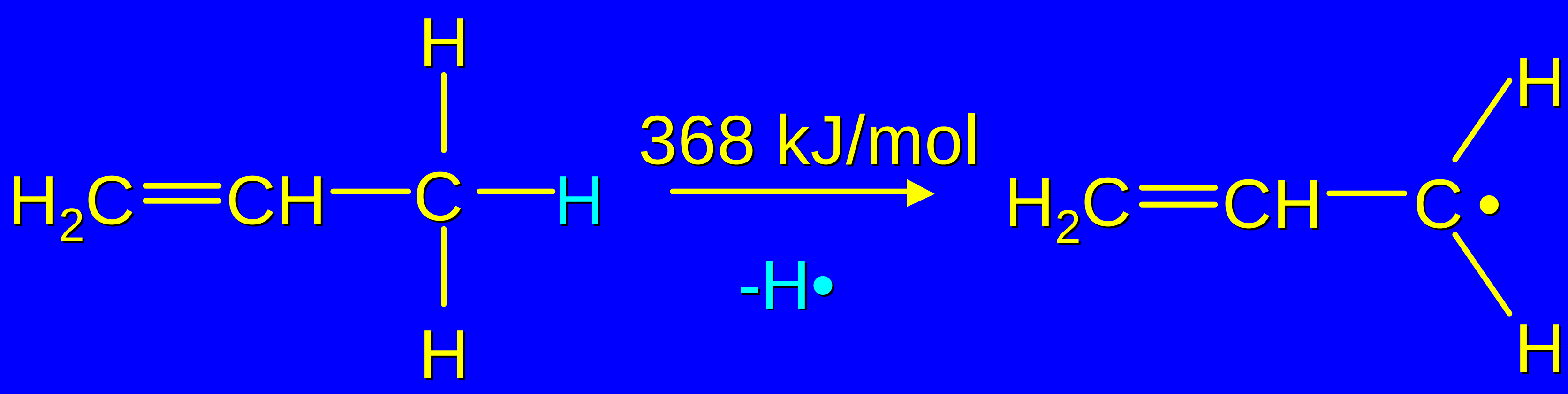
Bond-dissociation energy for C—H bond
is equal to $\Delta H°$ for:

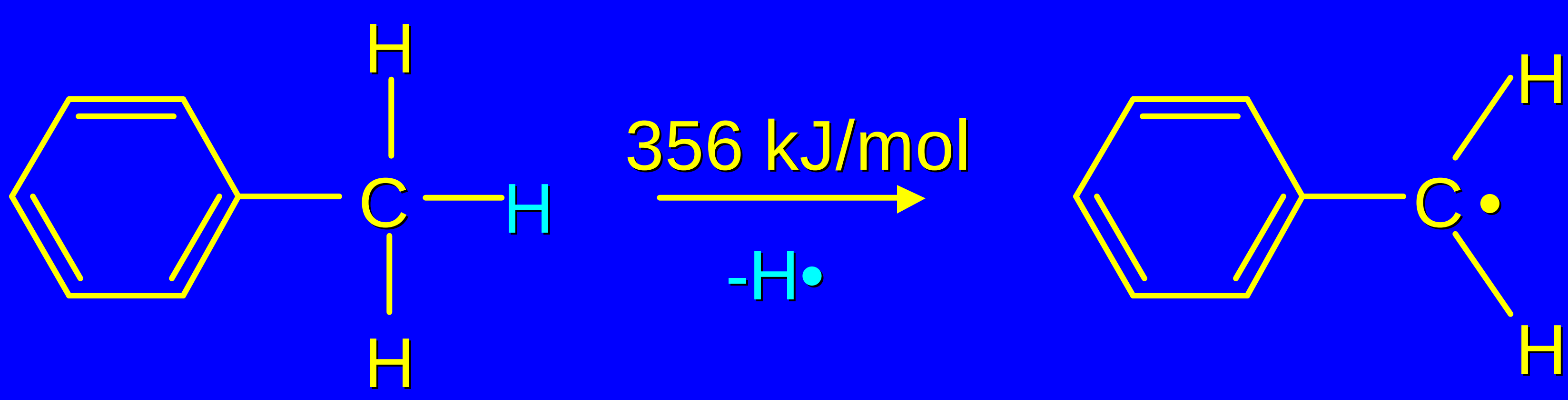
$$R—H \longrightarrow R\bullet + \bullet H$$

and is about 400 kJ/mol for alkanes.

The more stable the free radical R•, the weaker the bond, and the smaller the bond-dissociation energy.

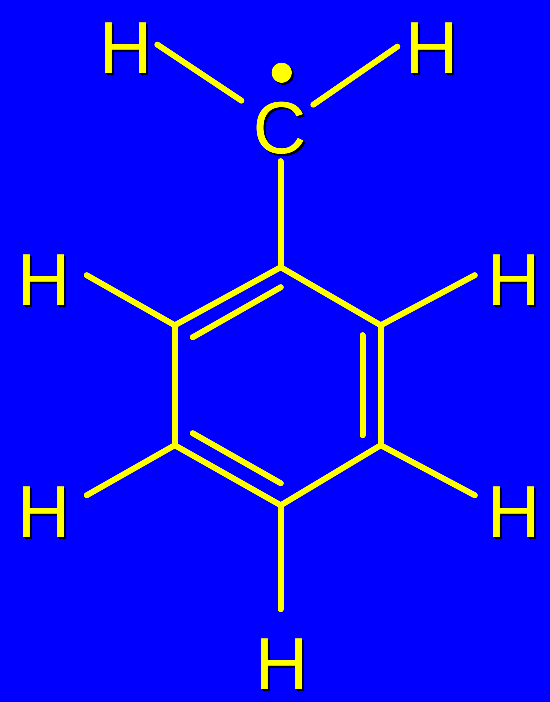
*Bond-dissociation energies of propene and toluene*



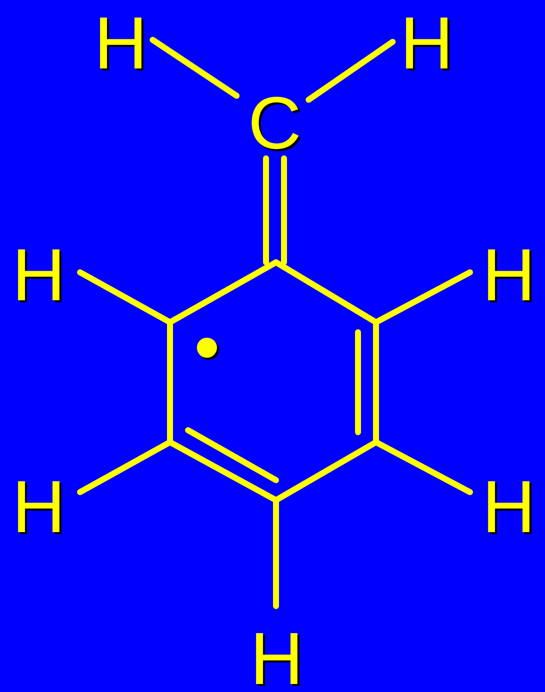

Low BDEs indicate allyl and benzyl radical are more stable than simple alkyl radicals.

# *Resonance in Benzyl Radical*



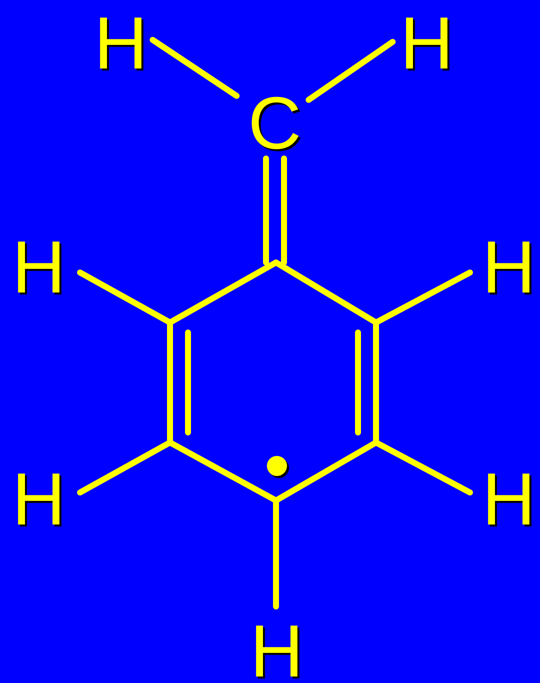

unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

# *Resonance in Benzyl Radical*



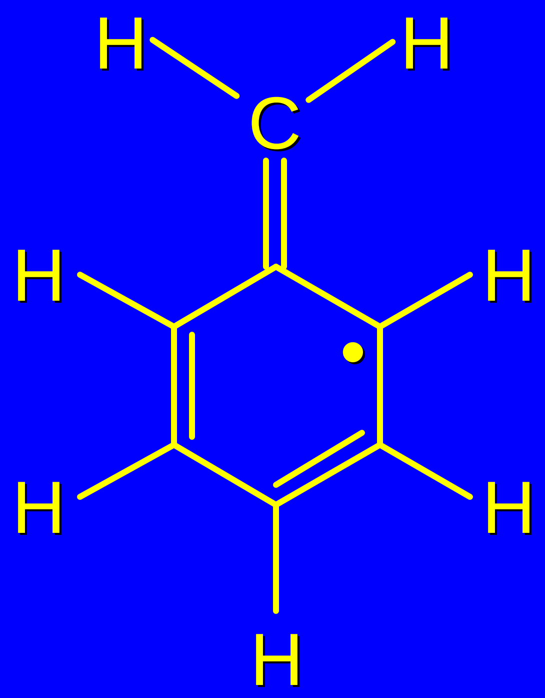

unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

# *Resonance in Benzyl Radical*




unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

*Resonance in Benzyl Radical*

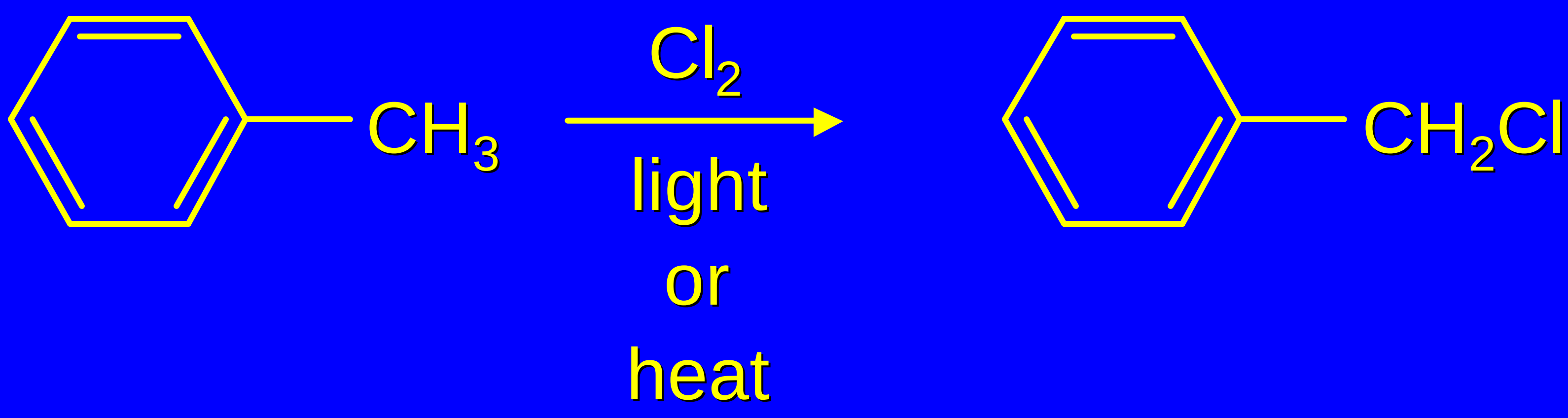



unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

# *Free-radical chlorination of toluene*

industrial process

highly regioselective for benzylic position

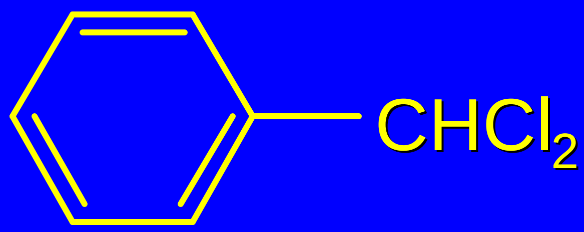


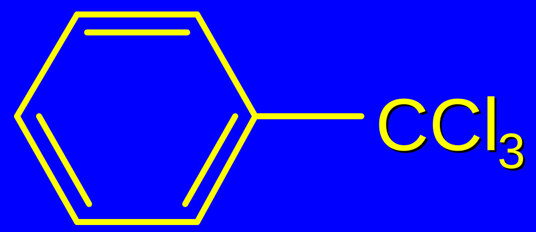

Toluene

Benzyl chloride

*Free-radical chlorination of toluene*

Similarly, dichlorination and trichlorination are selective for the benzylic carbon. Further chlorination gives:

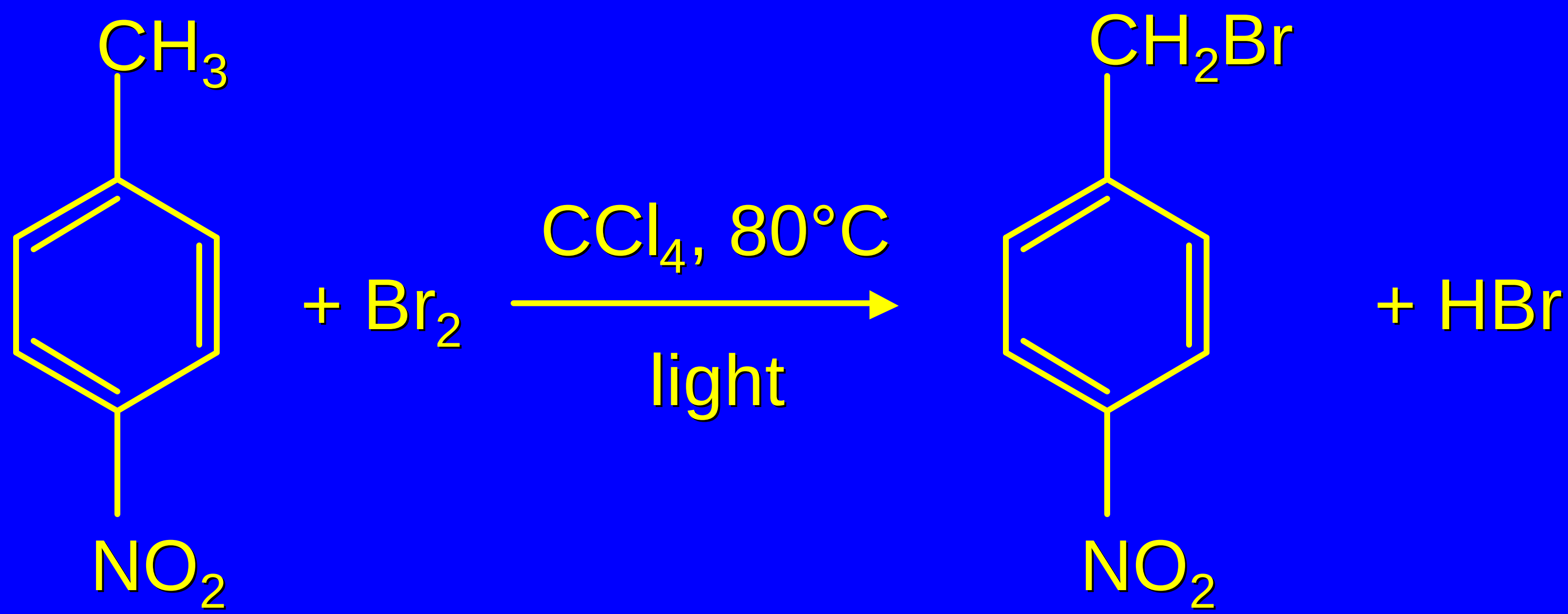



(Dichloromethyl)benzene (Trichloromethyl)benzene

# *Benzylic Bromination*

is used in the laboratory to introduce a halogen at the benzylic position

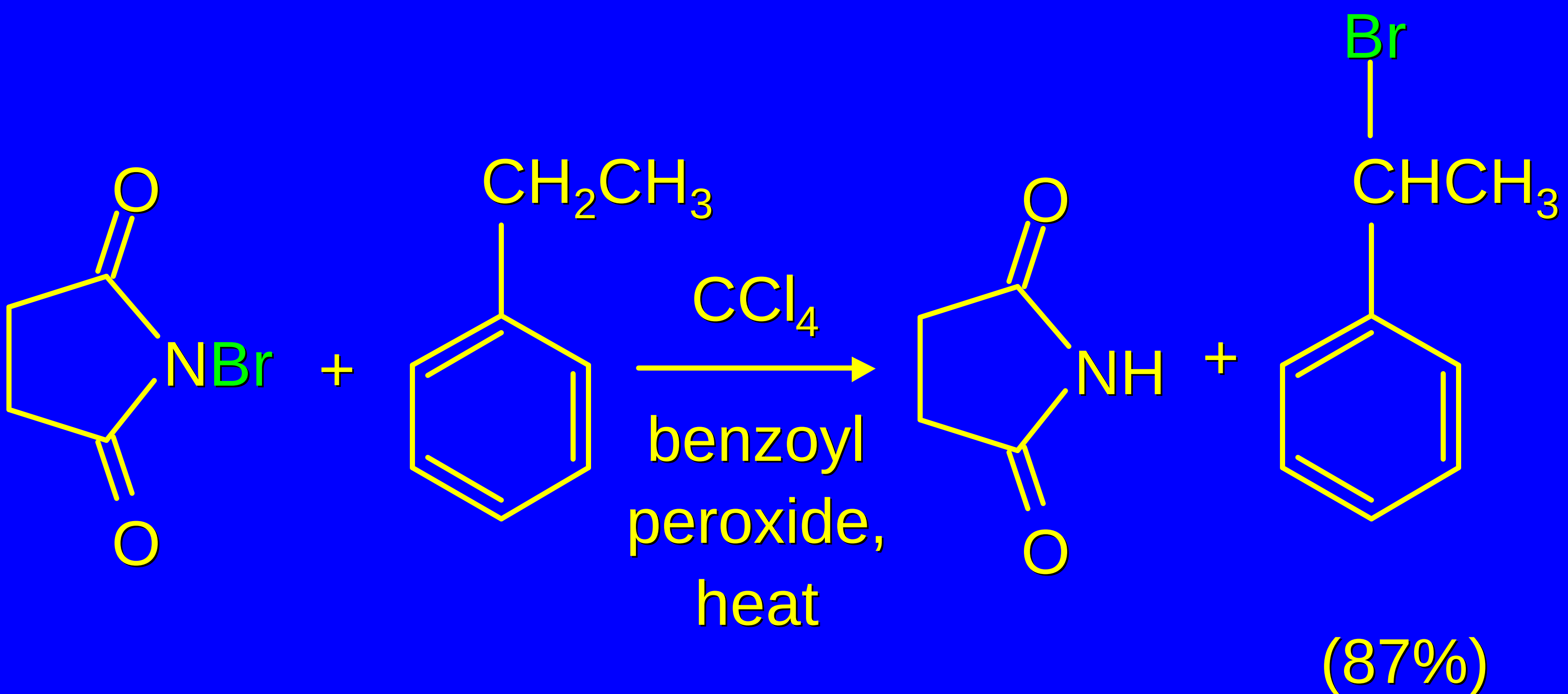



*p*-Nitrotoluene

*p*-Nitrobenzyl bromide (71%)

## *N-Bromosuccinimide (NBS)*

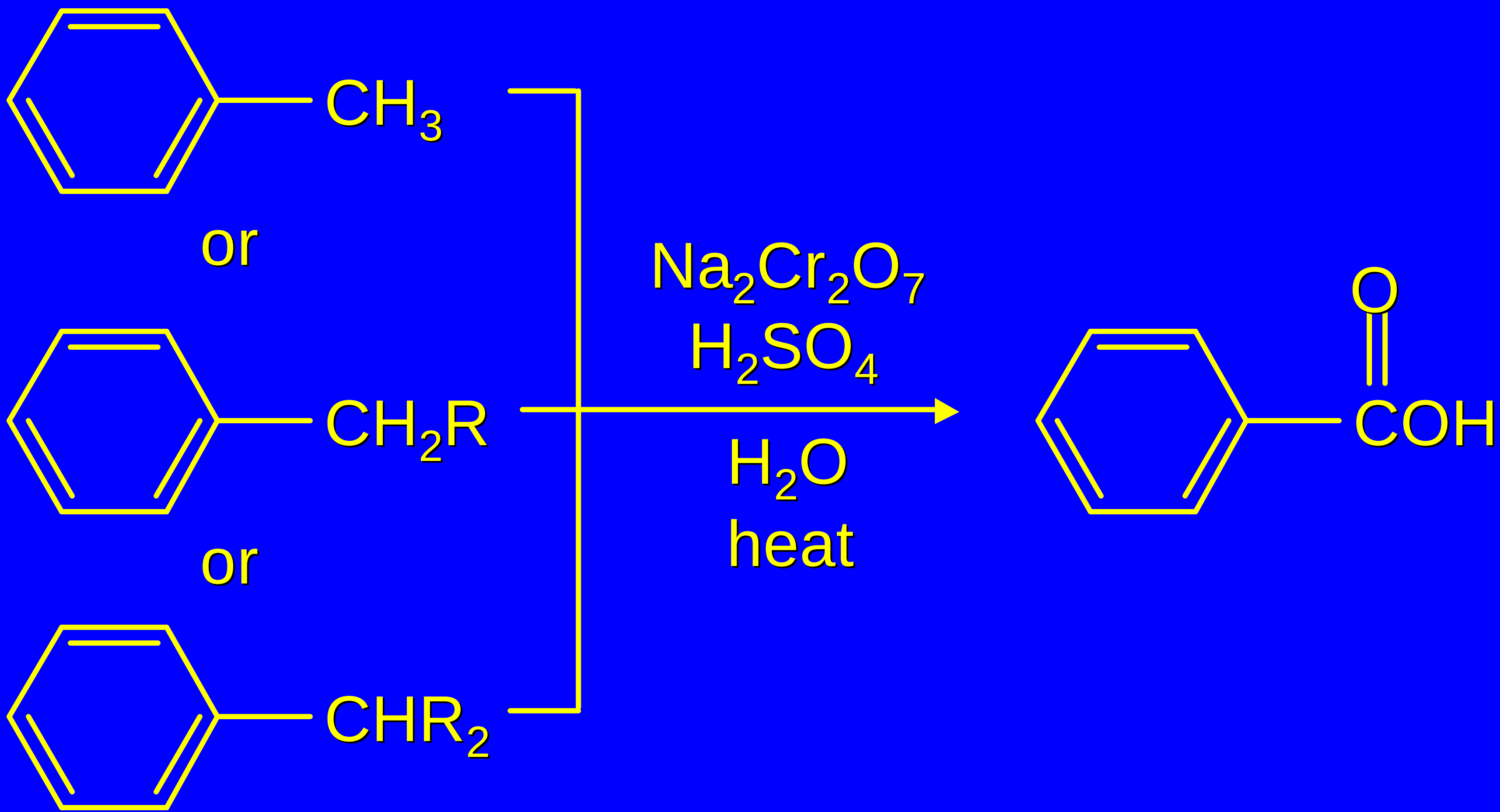
is a convenient reagent for benzylic bromination



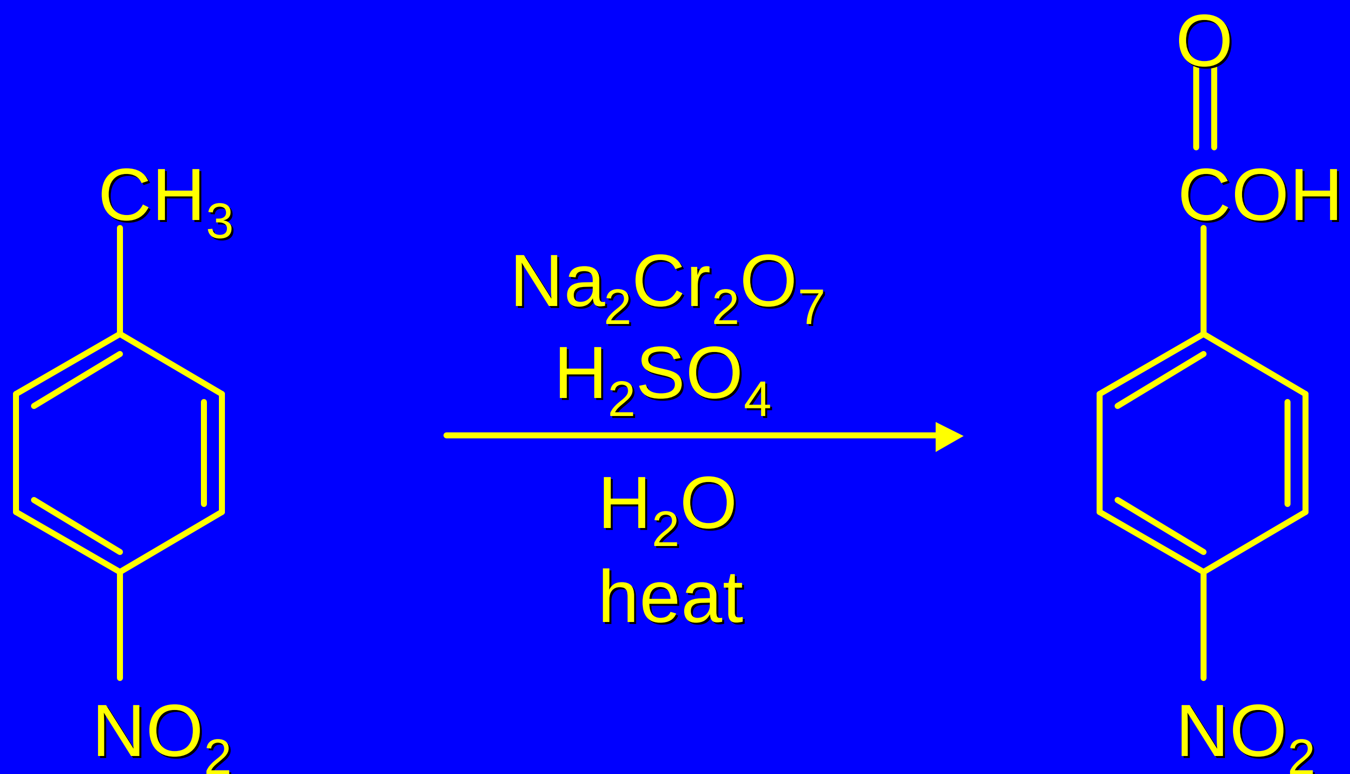
# 11.13

# Oxidation of Alkylbenzenes

## *Site of Oxidation is Benzylic Carbon*



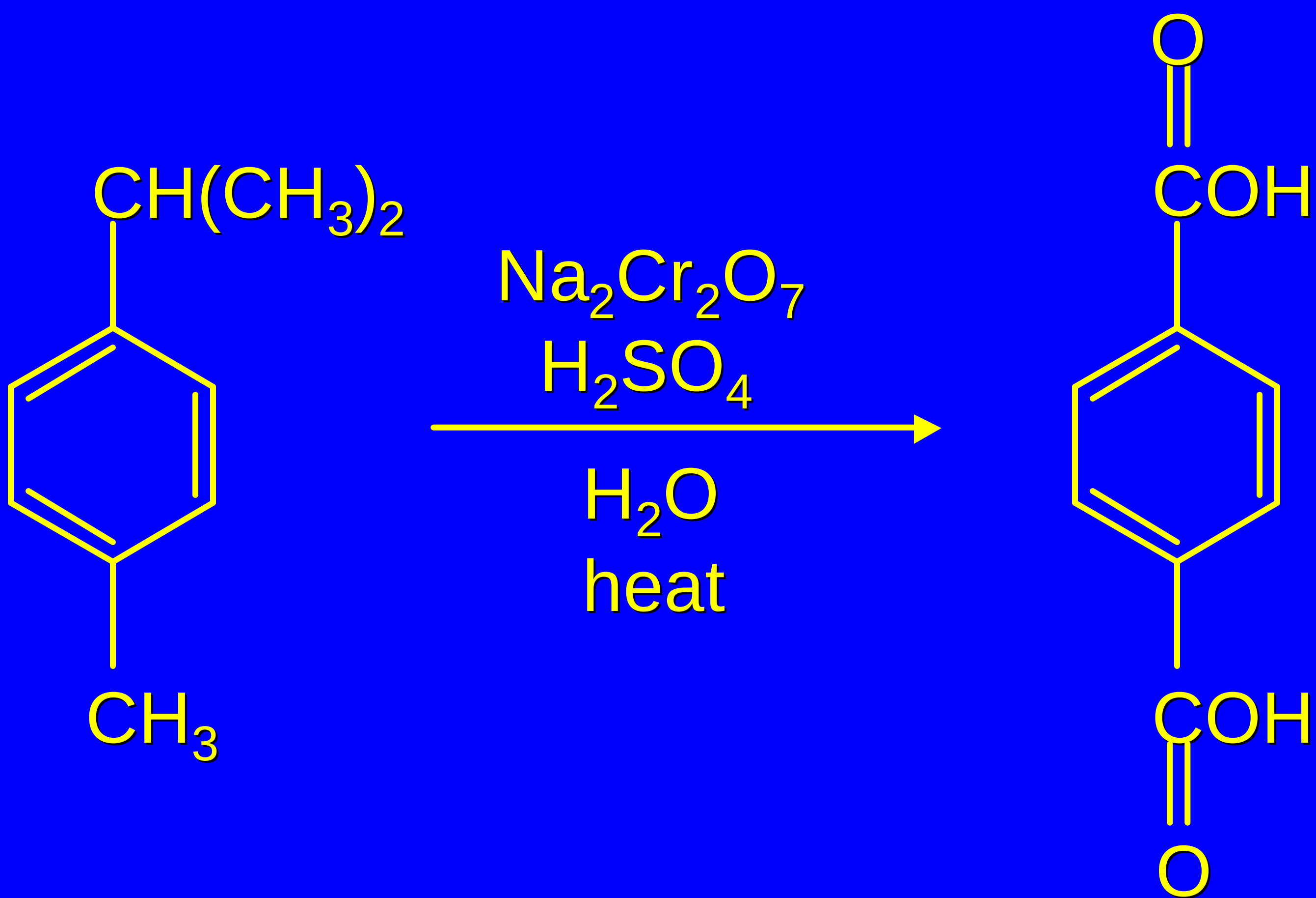
*Example*




*p*-Nitrotoluene

*p*-Nitrobenzoic acid (82-86%)

## *Example*

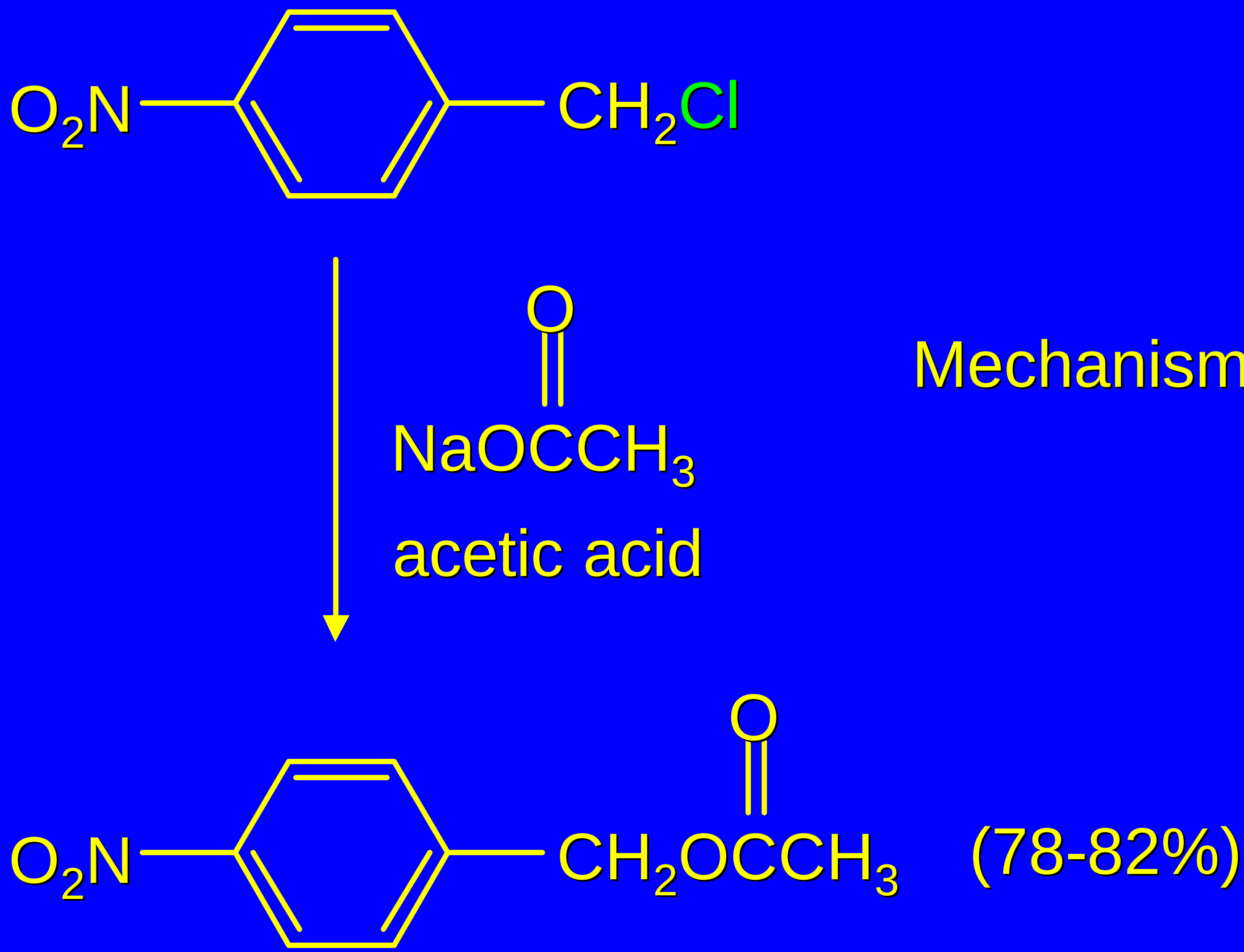



(45%)

# 11.14

# Nucleophilic Substitution in Benzylic Halides

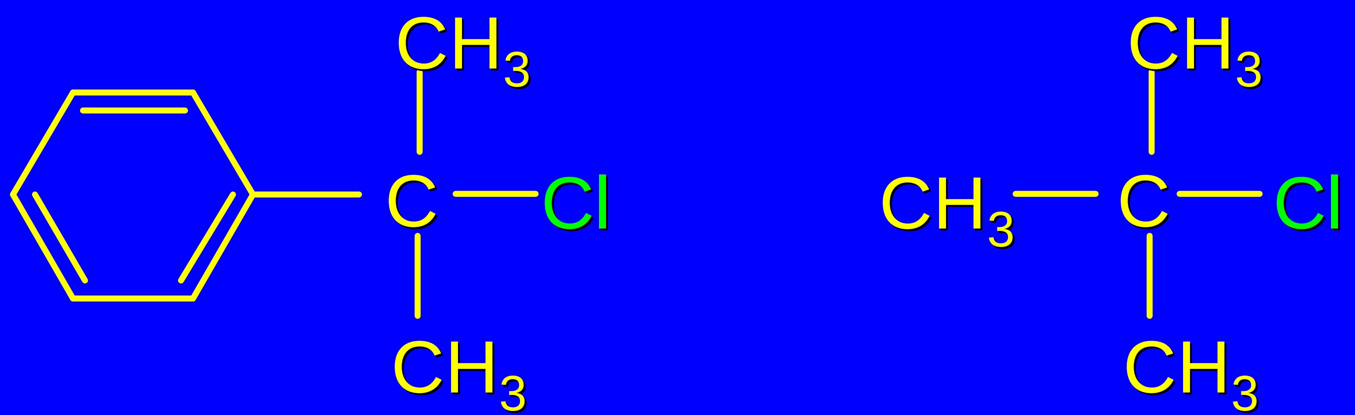
# *Primary Benzylic Halides*




Mechanism is $S_N2$

## *What about $S_N1$?*

Relative solvolysis rates in aqueous acetone

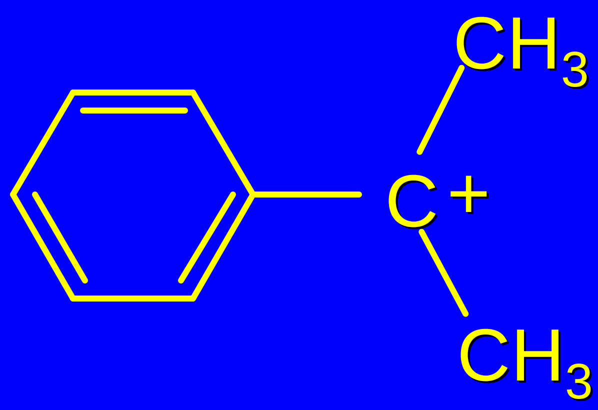


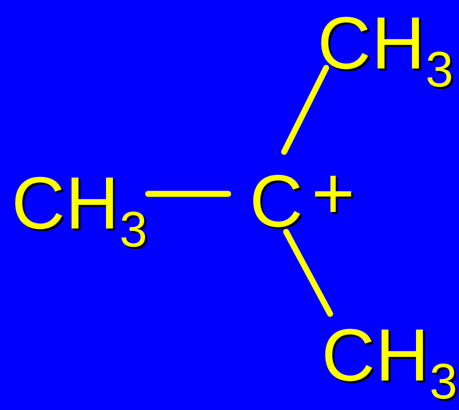

600 1

tertiary benzylic carbocation is formed more rapidly than tertiary carbocation; therefore, more stable

# *What about $S_N1$?*

Relative rates of formation:

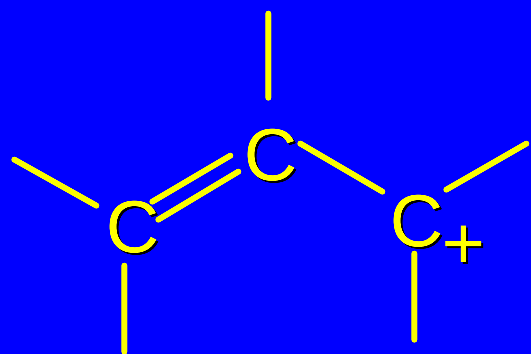


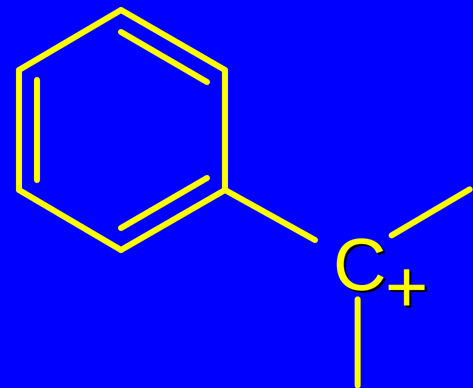

more stable

less stable

## *Compare.*



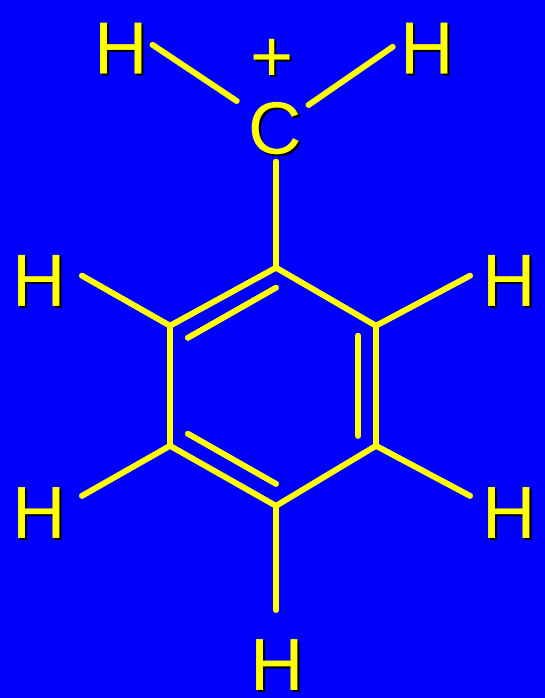

*allylic carbocation*




*benzylic carbocation*

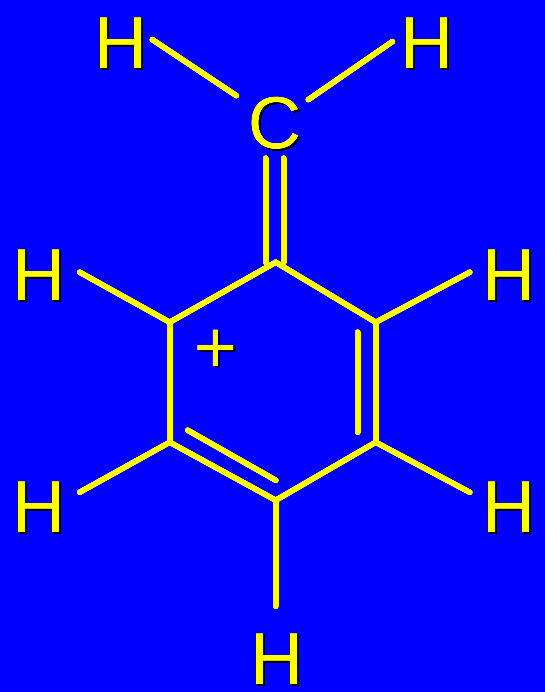
benzylic carbon is analogous to allylic carbon

# *Resonance in Benzyl Cation*



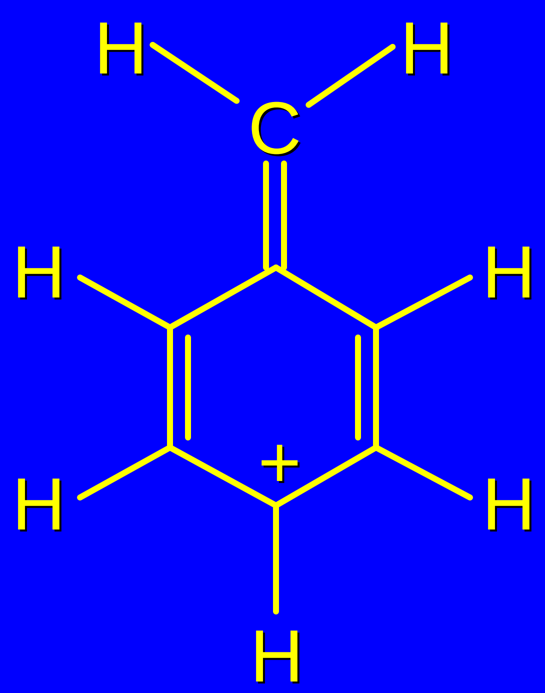

unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

## *Resonance in Benzyl Cation*



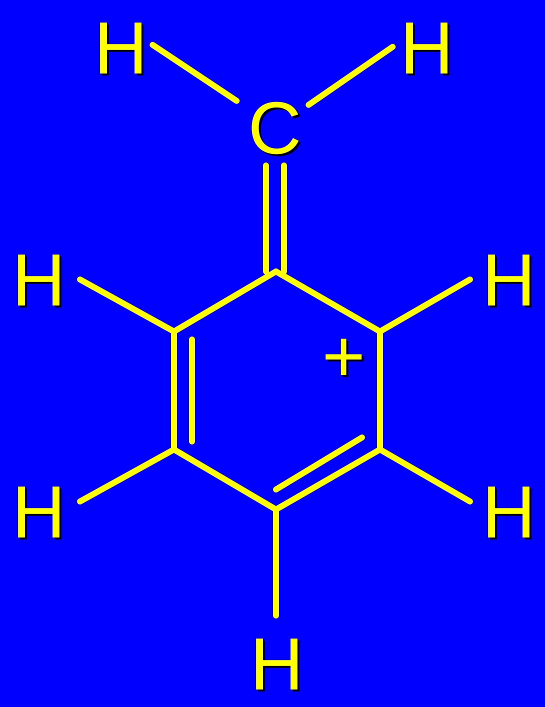

unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

## *Resonance in Benzyl Cation*



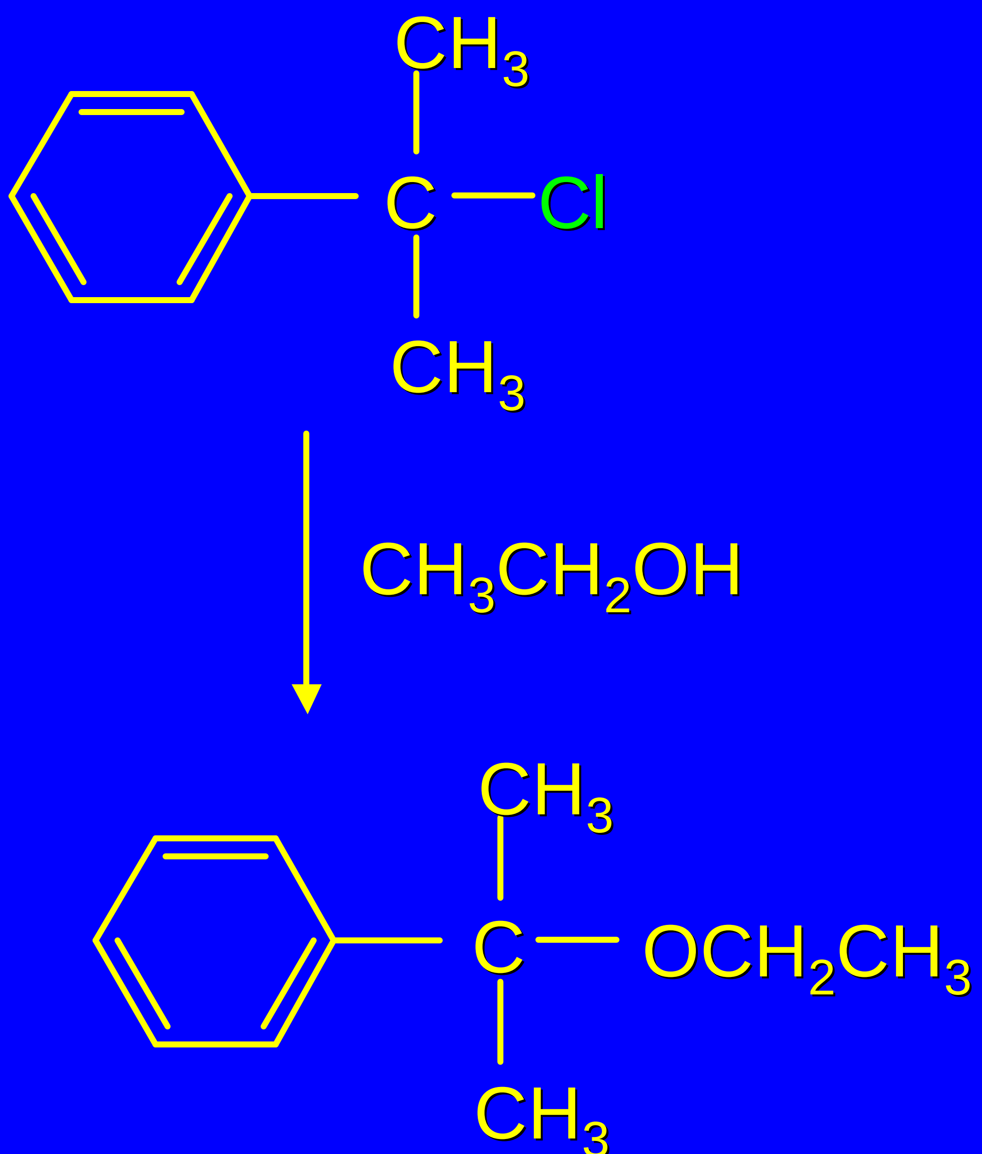

unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

# *Resonance in Benzyl Cation*




unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it

# *Solvolysis*




(87%)