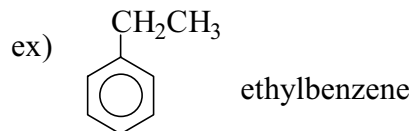
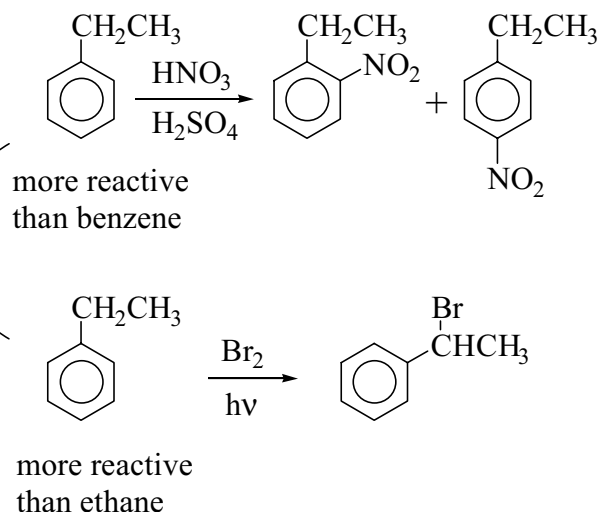


Chapter 16

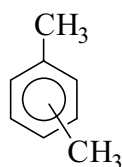
aliphatic + aromatic \Rightarrow arene



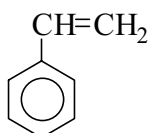
the reactivity and the orientation of each portion in the molecule are determined by the other portion



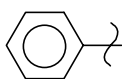
nomenclature : p551



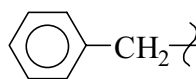
xylene



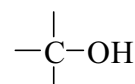
styrene



phenyl



benzyl



carbinol

Ar-X
aryl halide

Ar-R-X
aralkyl halide

(the chemistry is similar to that of alkyl halide)

arene : low polarity \Rightarrow soluble in non-polar solvents

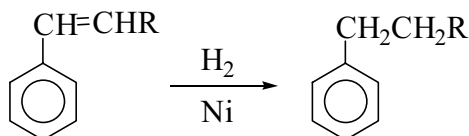
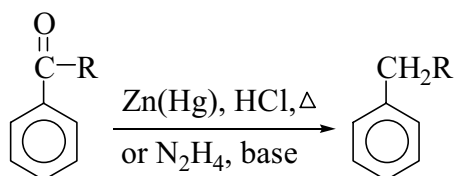
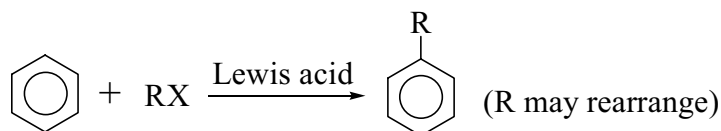
less dense than H₂O

more symmetric \Rightarrow higher m.p. \Rightarrow less soluble in a given solvent
(stronger intermolecular force)

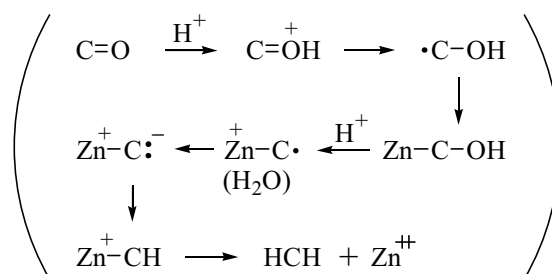
(Table 16-1)

Alkylbenzene

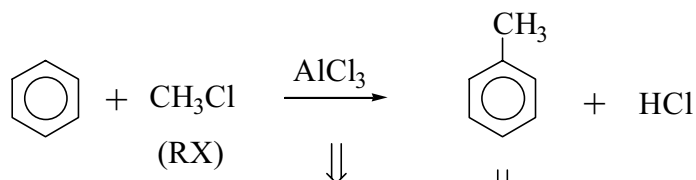
from Friedel-Crafts alkylation



(Clemmensen reduction
Wolff-Kishner reduction



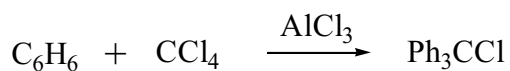
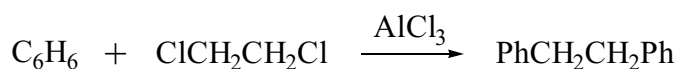
Friedel-Crafts alkylation

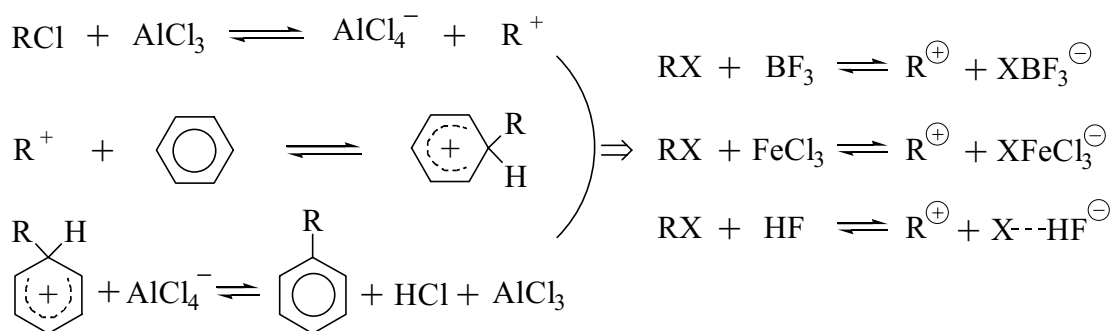


(RX)
 \Downarrow
 (alcohol and alkene may be used)
 \Downarrow
 BF₃
 HF
 H₂SO₄
 ⋮

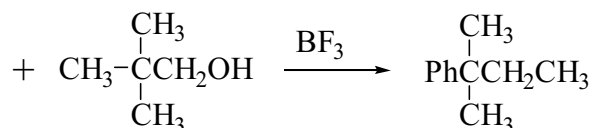
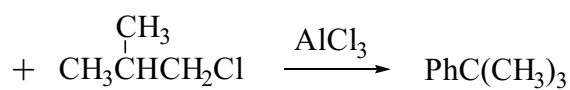
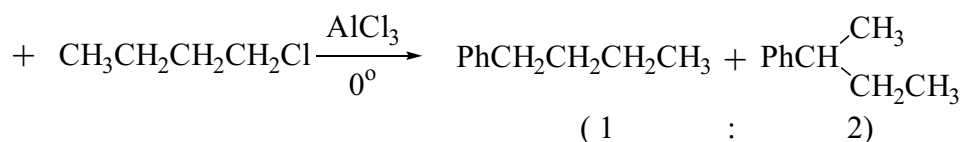
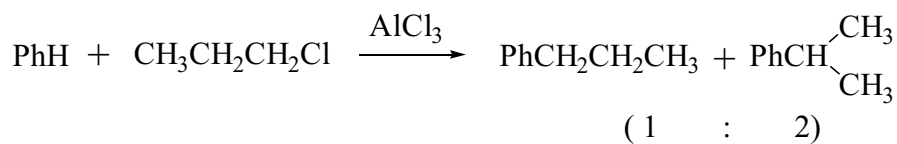
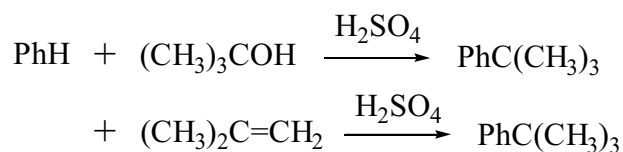
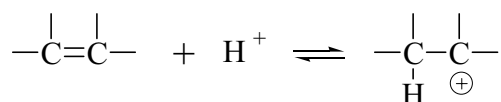
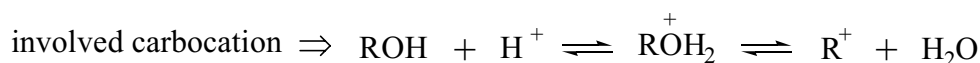
more reactive than \Rightarrow do the rxn with a large excess of reactant to prevent polyalkylation

(PhCH₂Cl is usable
ArX is not usable)





⇓



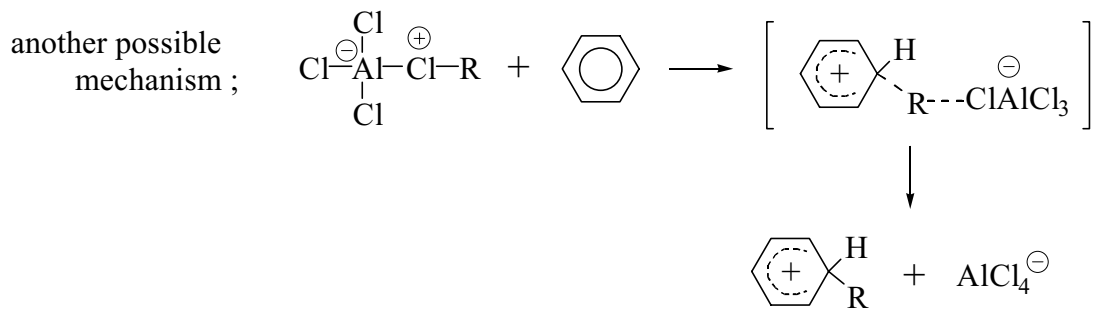
not via carbocation?

⇓

before rearrangement
it reacts with PhH.

⇐ primary carbocation is
unstable, so it is highly
reactive

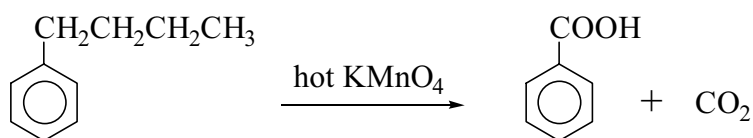
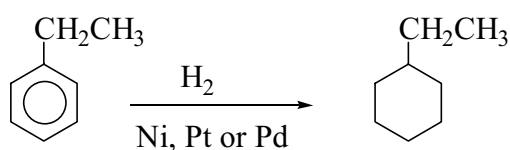
⇐ hard to answer



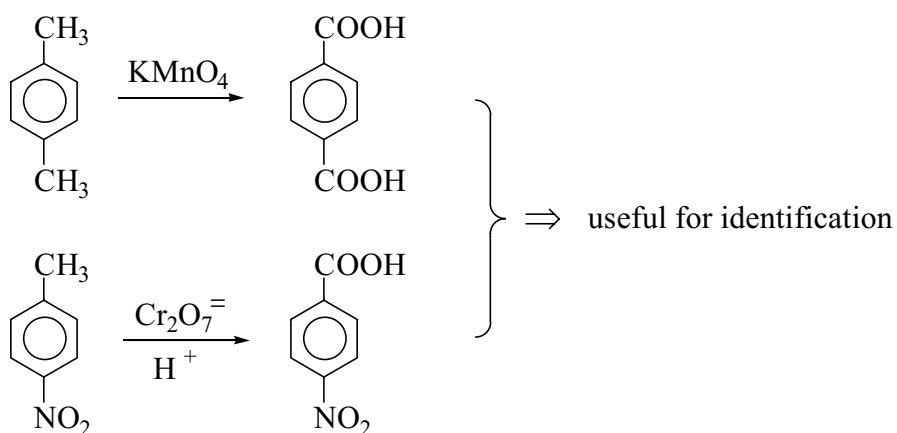
(especially for 1°-X and CH₃-X)

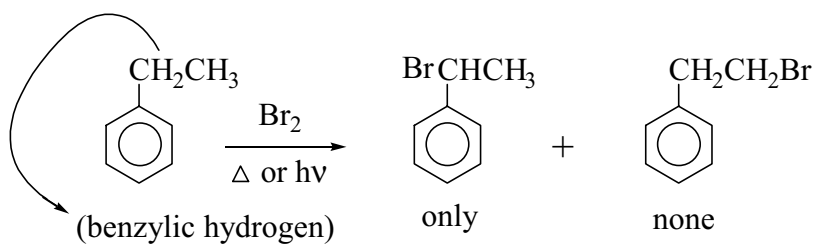
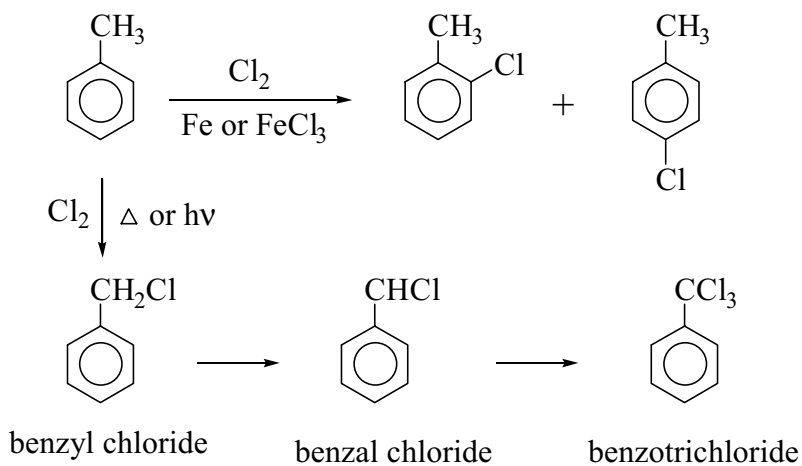
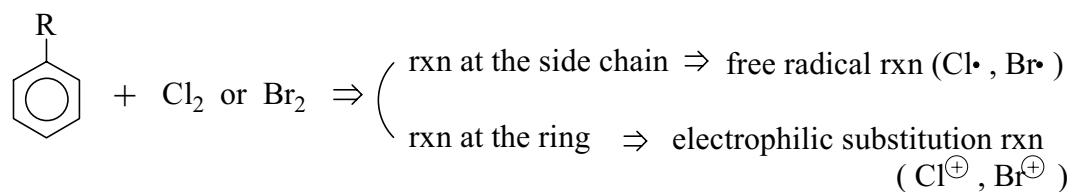
limitation of Friedel-Crafts alkylation

- 1) polyalkylation
- 2) rearrangement
- 3) ArX is not usable as alkylating reagent.
- 4) no rxn with less reactive aromatic compds than Ar-X
- 5) no rxn with Ar-NH₂, ArNHR, ArNR₂



cf) benzene & alkane are very resistant to the usual oxidizing reagents.

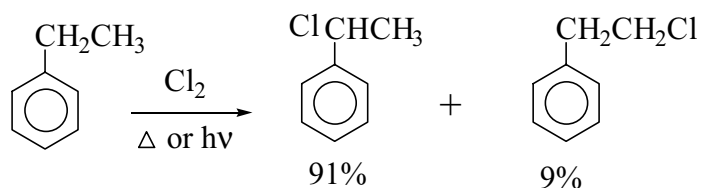




benzylic > allylic > 3° > 2° > 1° > CH₃• > vinylic

← more stable (by bond dissociation energy)

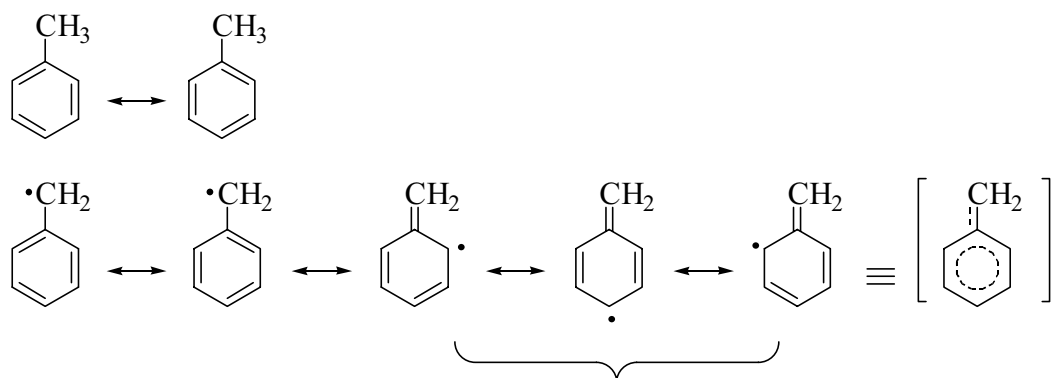
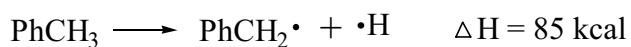
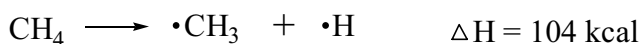
← easier to be formed (by rxns)



less selective ⇒ Cl• is more reactive than Br•

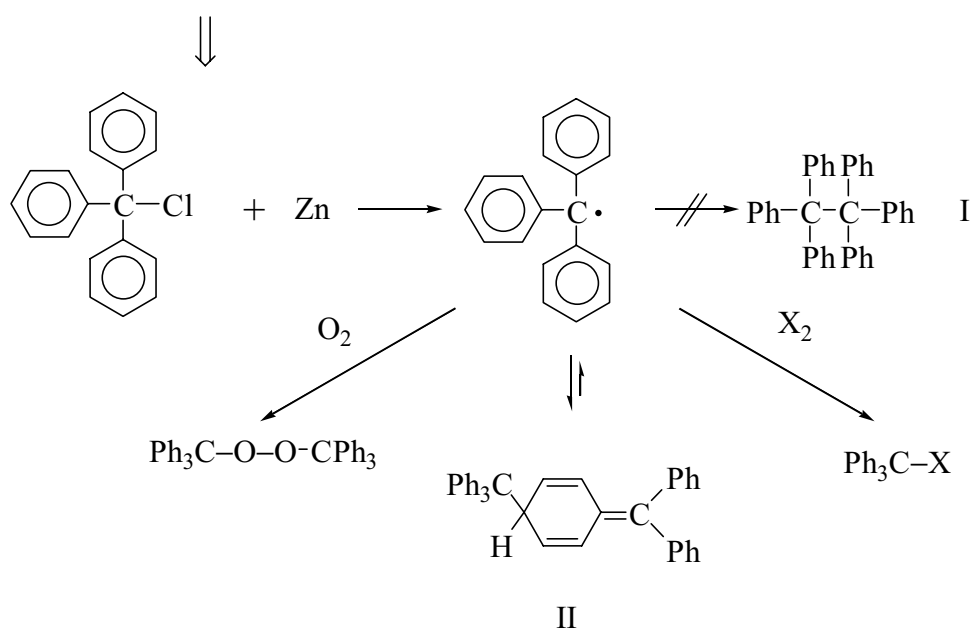
less free-radical character ⇐ early transition state

the factors stabilizing the benzyl radical have less effect on the transition state.



these resonance structures are responsible for the extra stabilization.

benzyl & allyl free radical are more stable than alkyl free radical, but extremely reactive and unstable.



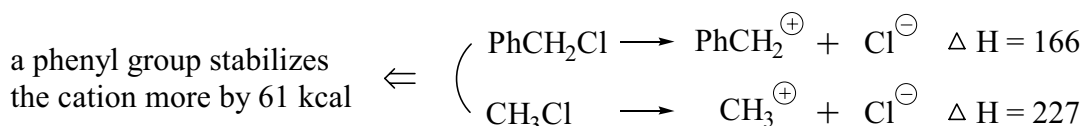
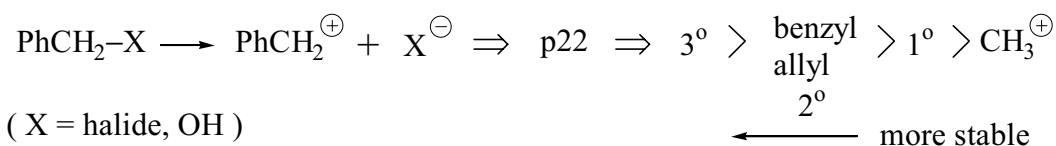
Why is II formed rather than I? \Rightarrow I : sterically much crowded.
 \Leftarrow II : sacrifice some aromaticity.
 steric effect wins over electronic effect. \Leftarrow sterically less crowded than I.

Why does II dissociate easily to triphenylmethyl radical ? \Rightarrow II : sterically crowded.
 triphenylmethyl radical : get more aromaticity.
 relieve steric strain.

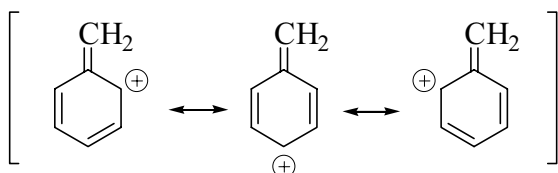


C-C single bond \approx 80 ~ 90 kcal

radical can be detected by paramagnetic resonance absorption (esr) \Leftarrow C-C in II \approx 11 kcal



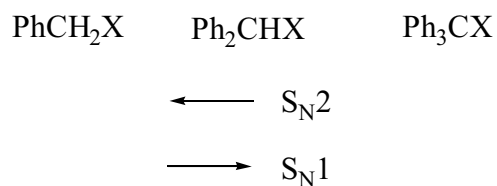
due to the contribution of



benzyl substrates

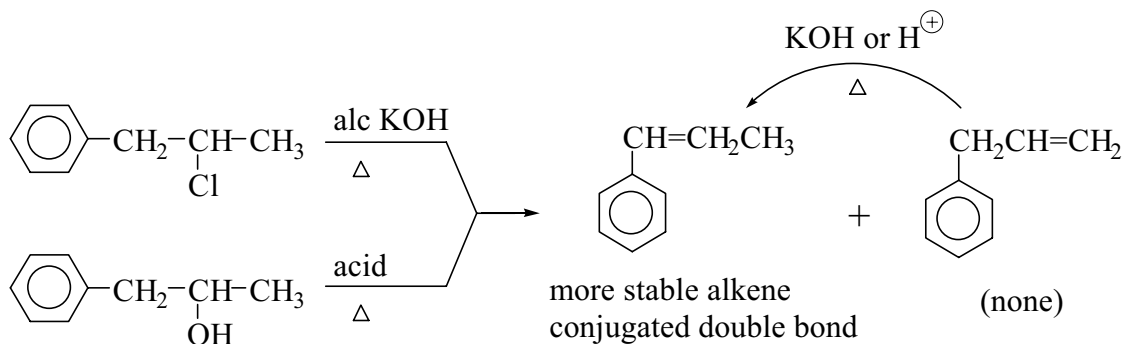
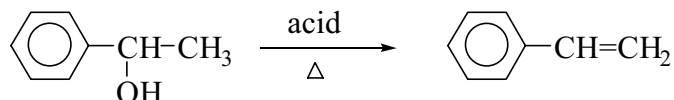
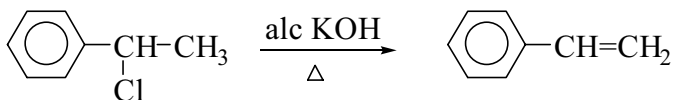
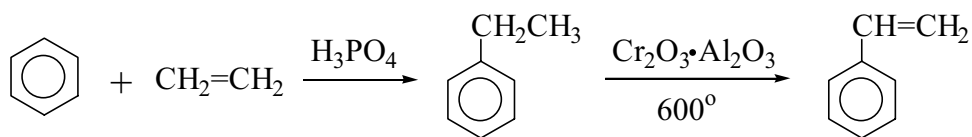
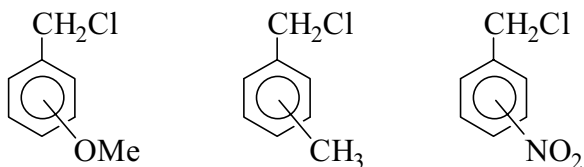
$\text{S}_{\text{N}}1$: as fast as 2° -substrates

$\text{S}_{\text{N}}2$: as fast as 1° -substrates (similar steric effect)

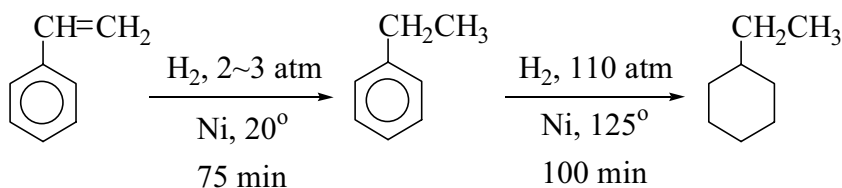


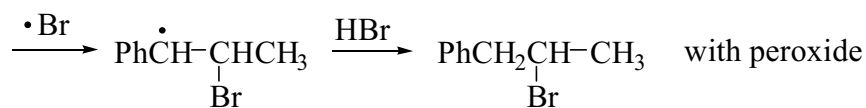
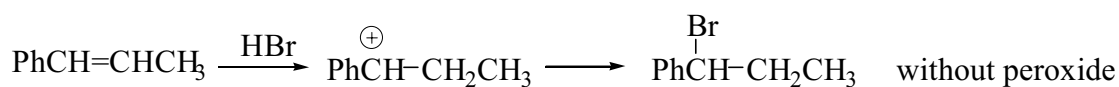
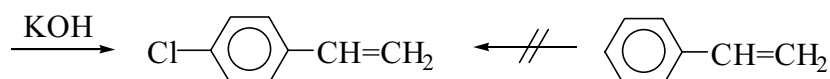
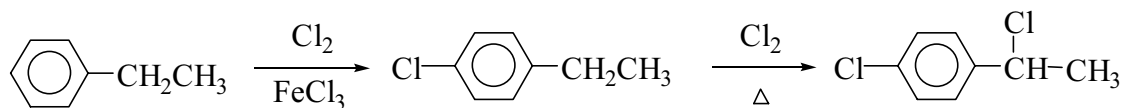
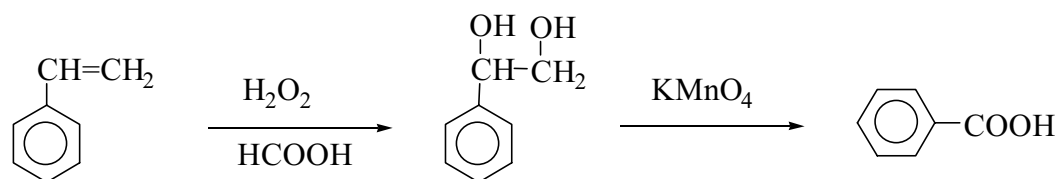
substituents on the ring (para & meta ; ortho exerts steric hindrance)
affect the rate of solvolysis greatly.

ex)



alkenylbenzene ; substitution in the ring
addition in the side chain \Rightarrow the double bond in the side chain
is more reactive





← more stable

↓

conjugated alkenylbenzene is more stable than simple alkene.

↓

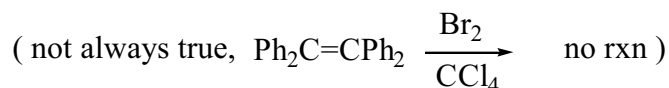
does addition to a conjugated alkenylbenzene occur faster than addition to a simple alkene?

↓

depends on E_a (depends on which is more stabilized, either reactant or transition state)

↓

generally conjugated alkenylbenzene is more reactive than simple alkene toward both ionic and free-radical addition.



alkynylbenzene

identification