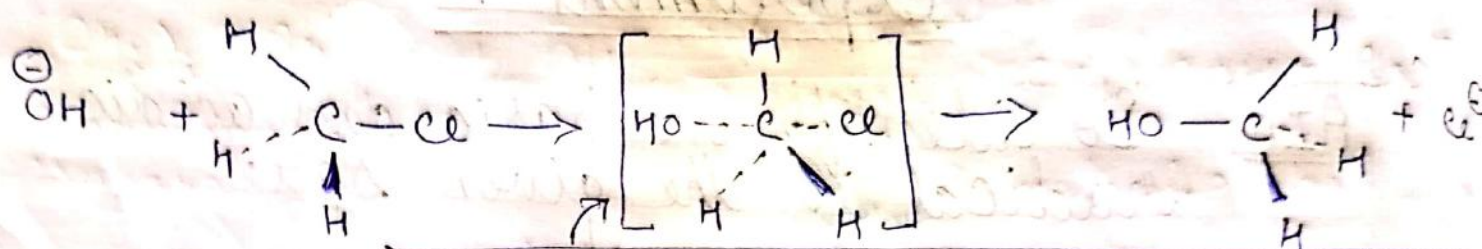


Mechanism of nucleophilic substitution reaction.

a) Substitution nucleophilic bimolecular (S_N2)

(Fig 10.2), (Fig 10.2)



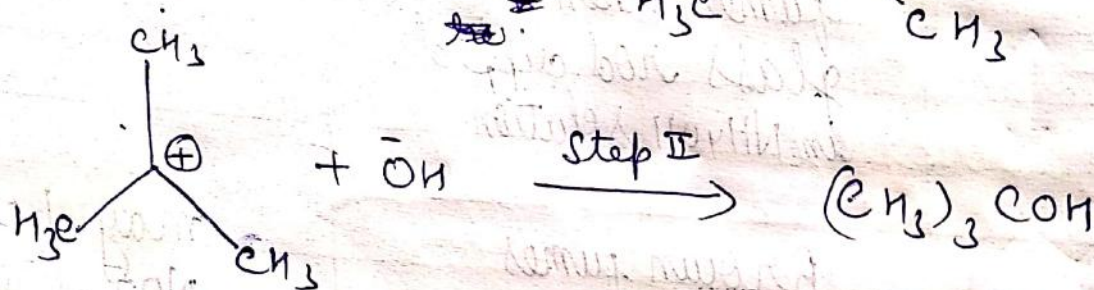
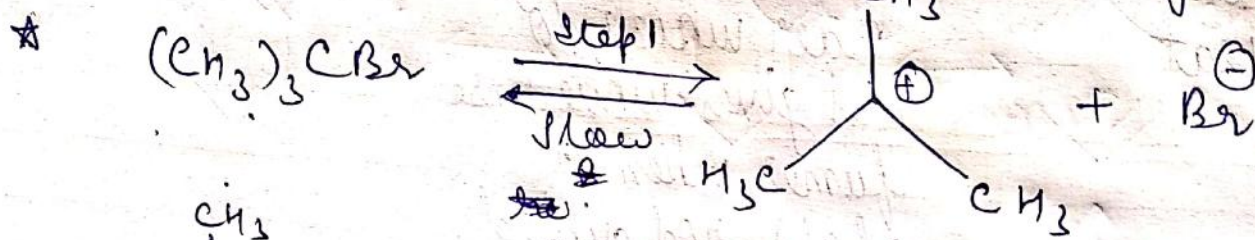
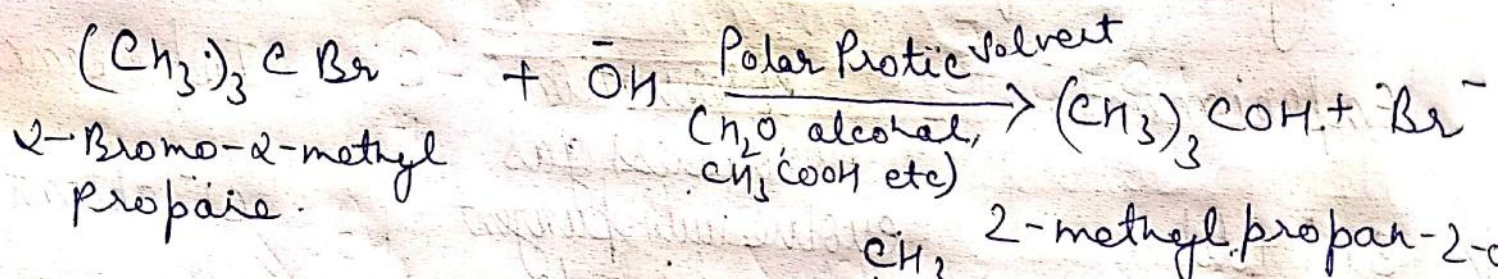
Transition state:

- Bond between the nucleophile ~~and~~ (OH) and the carbon starts forming, ~~and~~ bond between Cl^- (leaving group) and Carbon weakens.
- Transition state are unstable and cannot be isolated.

- i) It depicts a bimolecular nucleophilic displacement (S_N2) reaction. Rate of reaction depends on concentration of both reactants.
- ii) The incoming nucleophile (OH^-) interacts with alkyl halide causing the Carbon-halide bond to break while forming a new Carbon- OH bond.
- iii) As this happens, the configuration of carbon atom under attack inverts as an umbrella in strong wind. This process is called inversion of configuration.
- iv) ~~Since~~ In transition state, the carbon atom is simultaneously bonded to incoming nucleophile and outgoing leaving group is unstable as carbon is bonded to five atoms.
- v) Tertiary halides are least reactive because bulky groups hinder approaching nucleophile.

n) Order of reactivity: Primary halide > Secondary halide > tertiary halide.

b) Substitution nucleophilic unimolecular (S_N1)

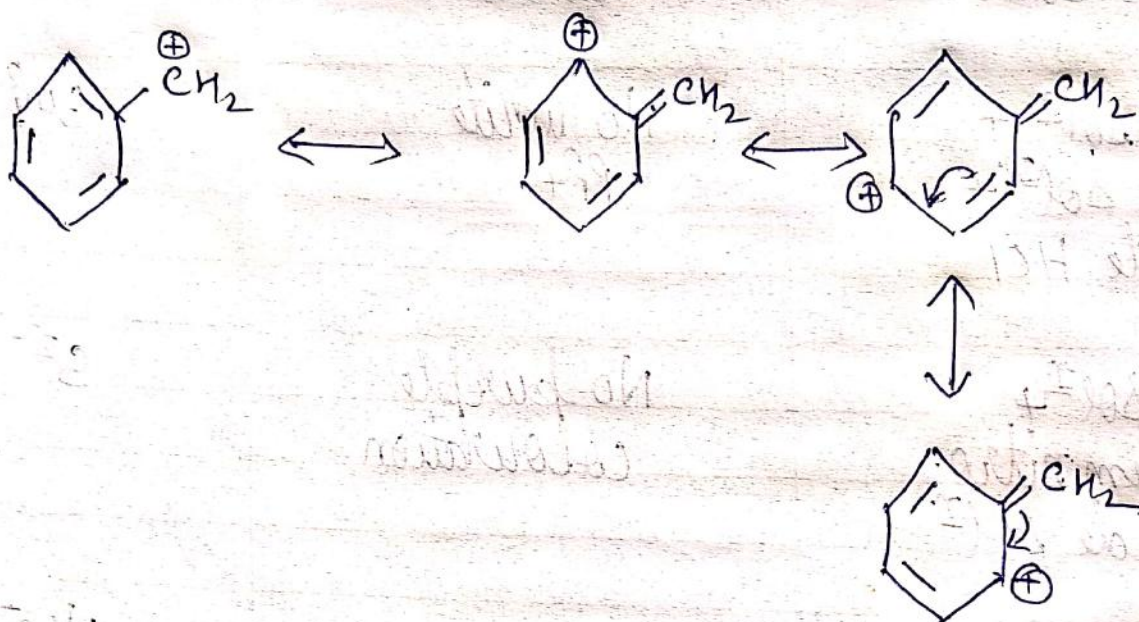
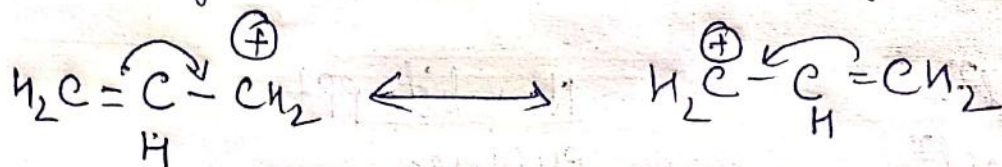


$\Rightarrow S_N1$ occurs in 2 steps. In step I, the polarized C-Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II.

\Rightarrow Step I, it involves the C-Br bond breaking for which the energy is obtained through solvation of halide ion with proton of protic solvent. Rate of reaction depends on concentration of one reactant (ie. alkyl halide).

\Rightarrow Greater the stability of carbocation, greater will be its ease of formation of alkyl halide with faster rate.

iv) Allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation gets stabilised through resonance.



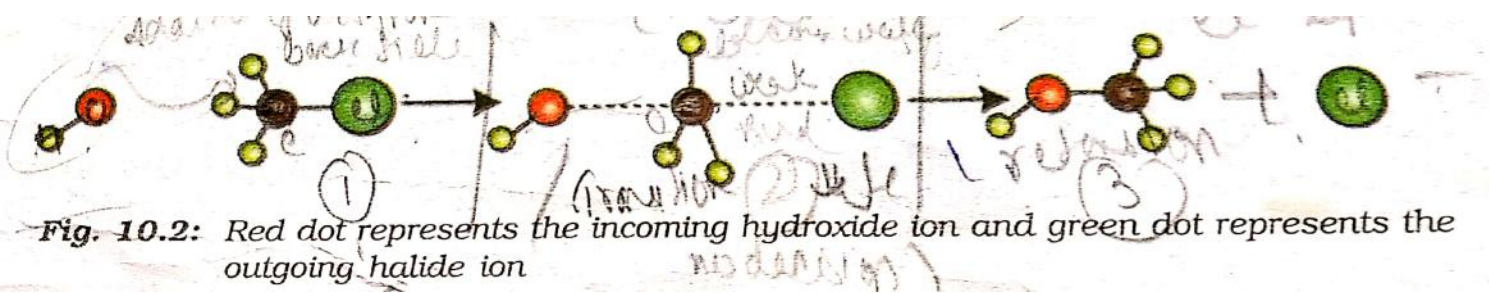
Therefore,

For S_N2

Stability - Tertiary halide, secondary halide, Primary, CH_3X halide



For S_N1



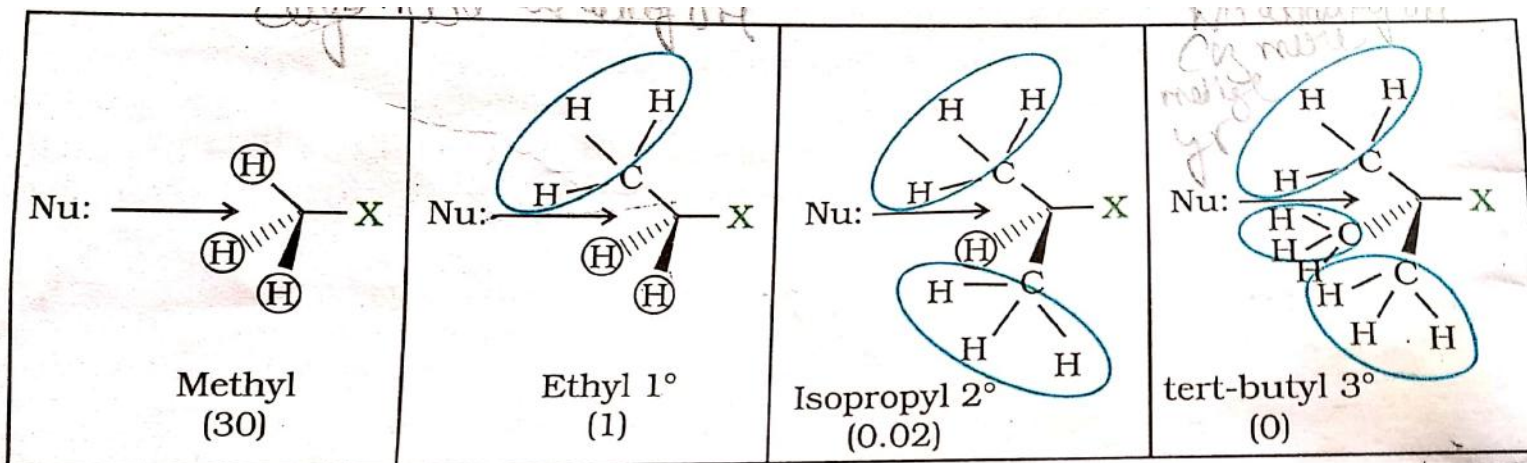


Fig.10.3: Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis