

Physical Properties of Haloalkanes

1. Boiling point orders

1. $R - I > R - Br > R - Cl > R - F$
2. $CH_3 - (CH_2)_2 - CH_2Br > (CH_3)_2 CHCH_2Br > (CH_3)_3 CBr$
3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is



3. Dipole moment decreases as the electronegativity of the halogen decreases.

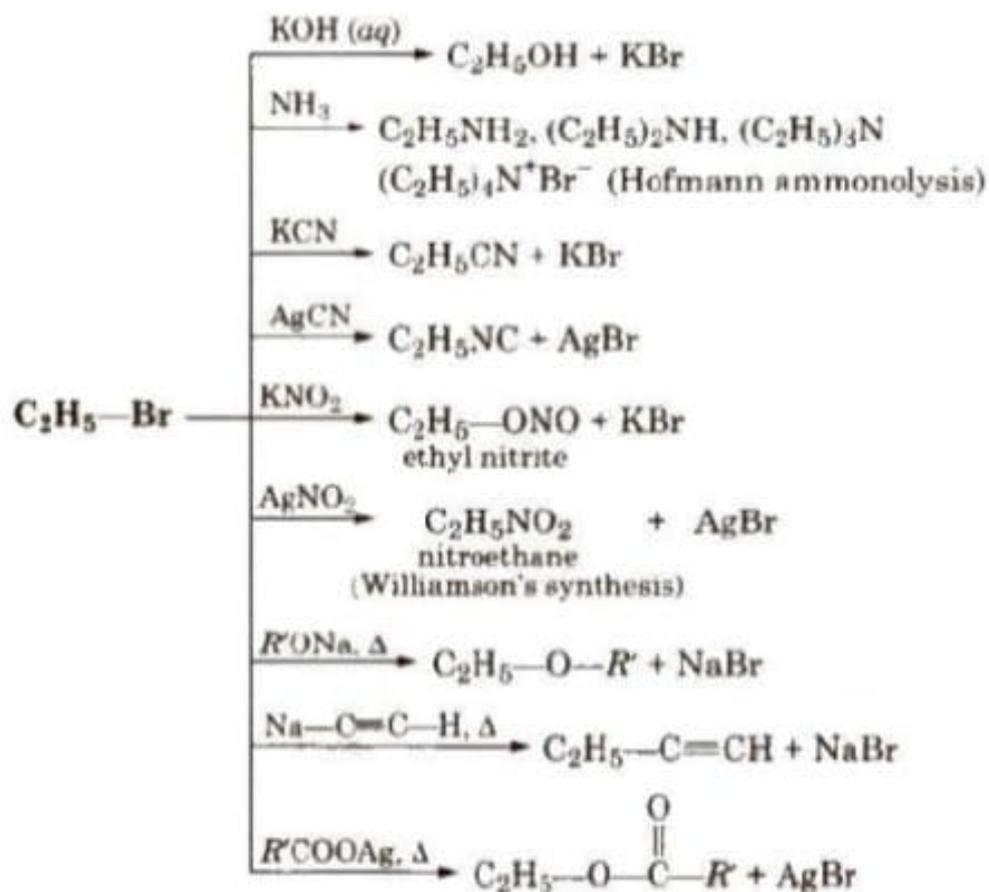
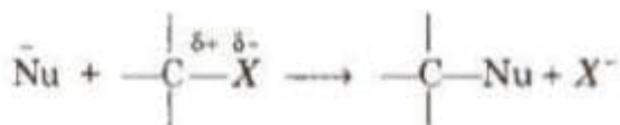
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is



Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)

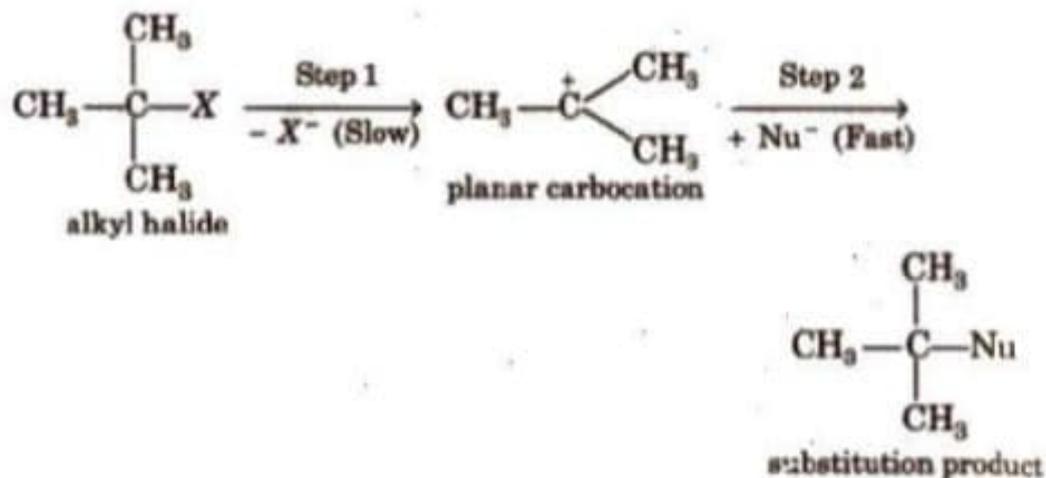


kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO₂ form R-ONO while AgNO₂ produces R-NO₂ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

(a) **S_N1** type (Unimolecular nucleophilic reactions proceed in two steps:



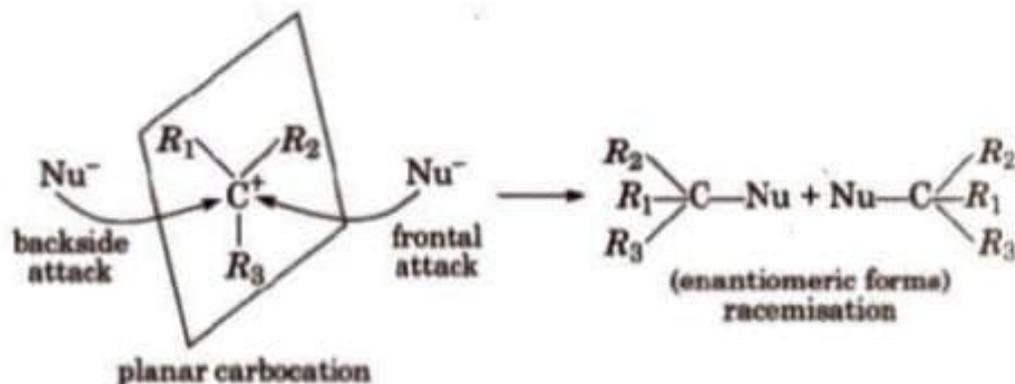
Rate, $r = k [\text{RX}]$. It is a first order reaction.

Reactivity order of alkyl halide towards $\text{S}_{\text{N}}1$ mechanism



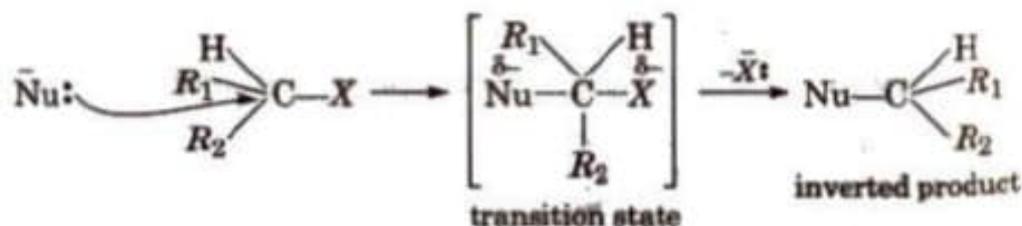
Polar solvents, low concentration of nucleophiles and weak nucleophiles favour $\text{S}_{\text{N}}1$ mechanism.

In $\text{S}_{\text{N}}1$ reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



(b) $\text{S}_{\text{N}}2$ type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with $r = k[\text{RX}][\text{Nu}]$.

During $\text{S}_{\text{N}}2$ reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



Reactivity of halides towards S_N2 mechanism is

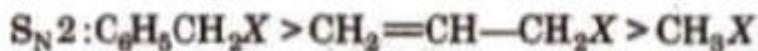
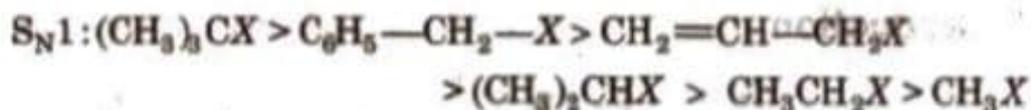


Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

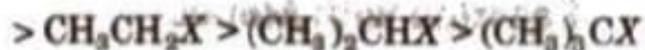


Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

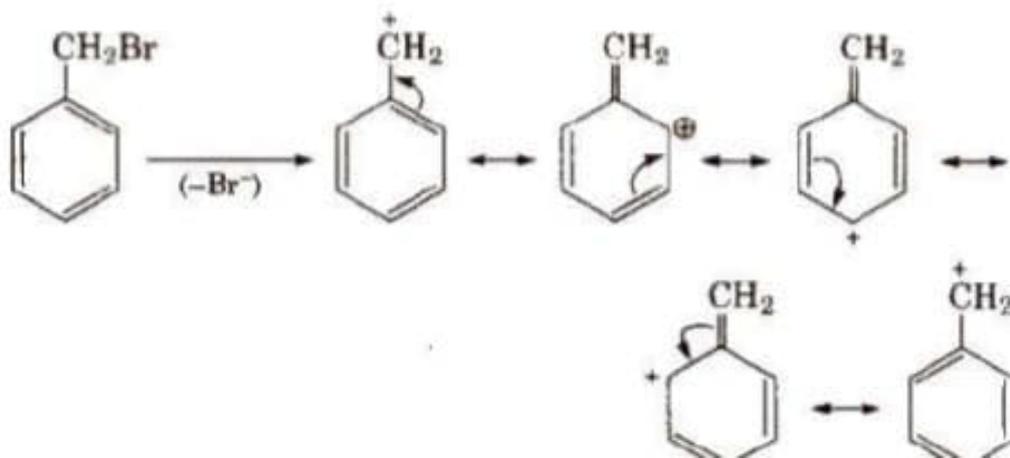
Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order



resonance stabilised

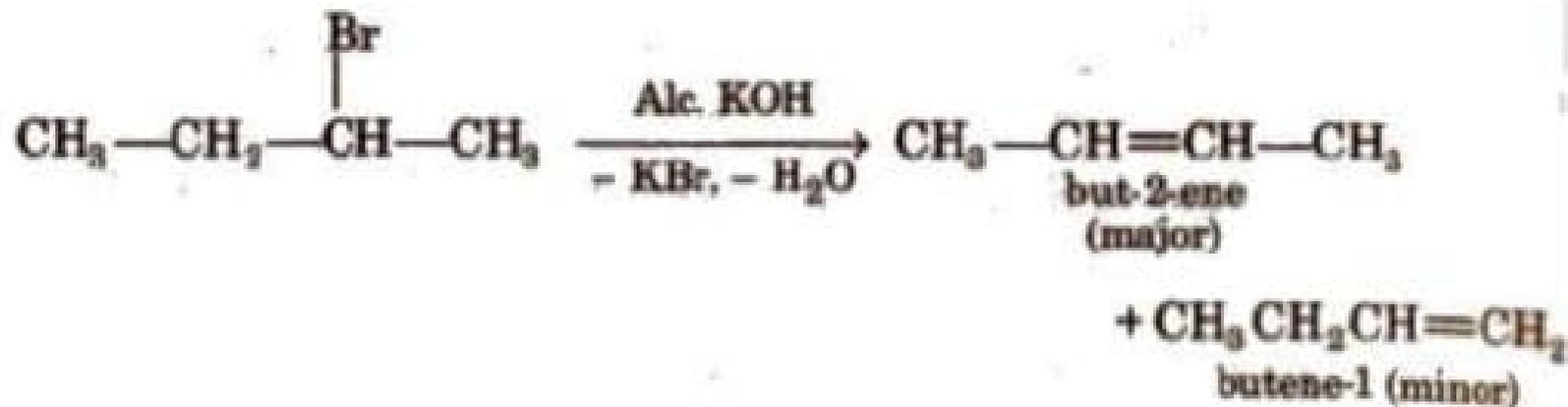


Resonating structure of benzyl carbocations are



2. Elimination Reactions

Dehydrohalogenation is a β - elimination reaction in which halogen is from α -carbon atom and the hydrogen from the α -carbon according to Saytzeff rule, e.g.,



Ease of dehydrohalogenation among halides



i.e.,

