

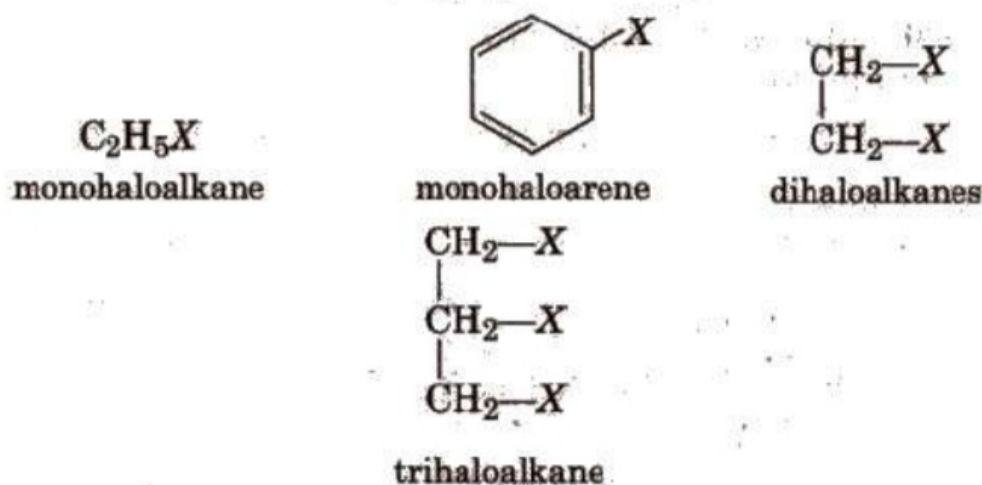
Chemistry Notes for class 12 Chapter 10

Haloalkanes and Haloarenes

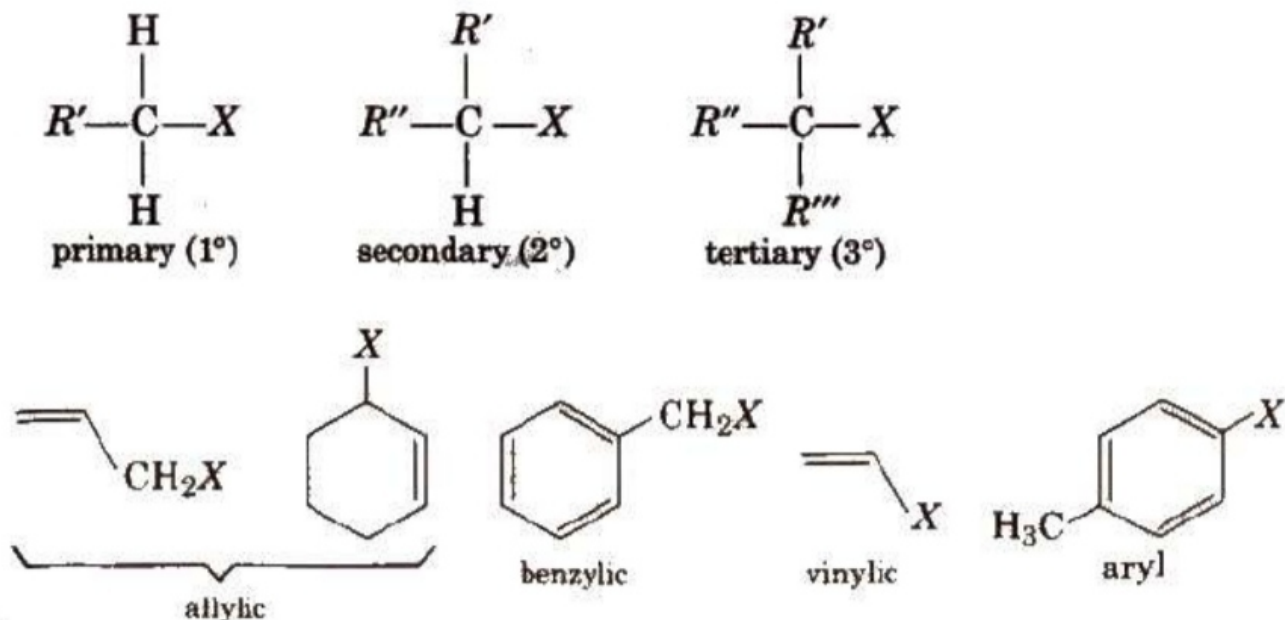
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification of Halogen Derivatives

On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,

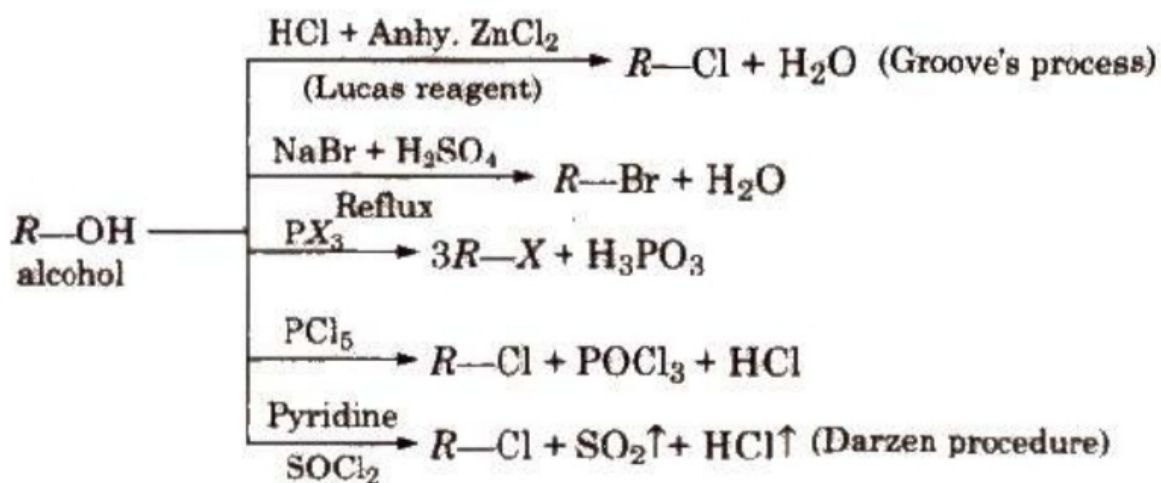


On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1° , 2° , 3° , allylic, benzylic, vinylic and aryl derivatives, e.g.,



General Methods of Preparation of Haloalkanes

1. From Alcohols

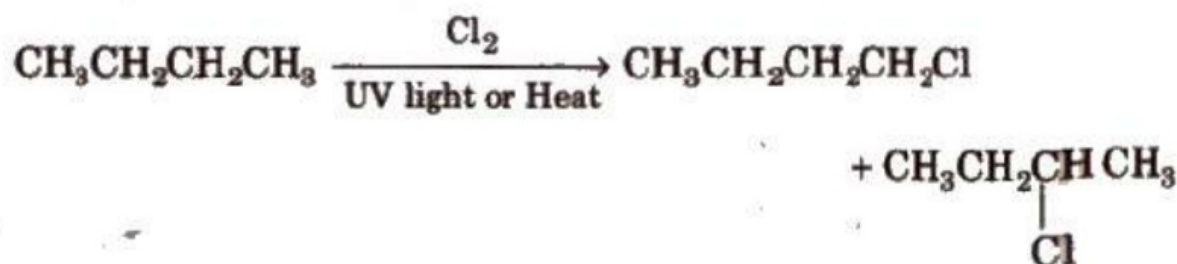


In Groove's method, ZnCl_2 is used to weaken the C-OH bond. In case of 3° alcohols, ZnCl_2 is not required.

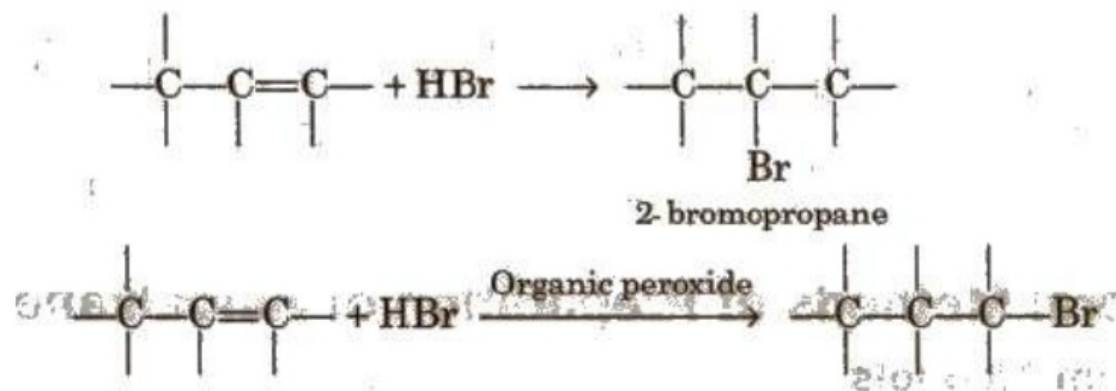
The reactivity order of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$.

Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products (SO_2 and HCl) are gaseous and escape easily.

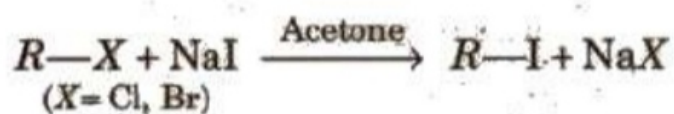
2. Free Radical Halogenation of Alkanes



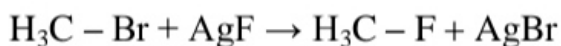
Addition of Hydrogen Halides on Alkenes



1. Finkelstein Reaction

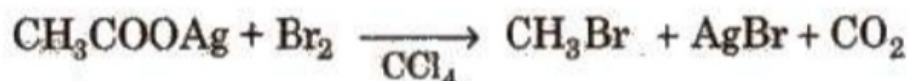


2. Swarts Reaction



Hg_2F_2 , COF_2 and SbF_3 can also be used as a reagent for Swarts reaction.

3. Hunsdiecker Reaction

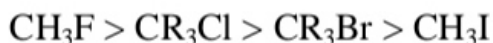


Physical Properties of Haloalkanes

1. Boiling point orders

1. $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$
2. $\text{CH}_3-(\text{CH}_2)_2-\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHCH}_2\text{Br} > (\text{CH}_3)_3\text{CBr}$
3. $\text{CH}_3\text{CH}_2\text{CH}_2 > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3\text{X}$

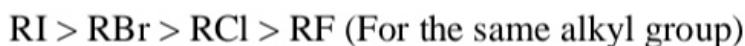
2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is



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

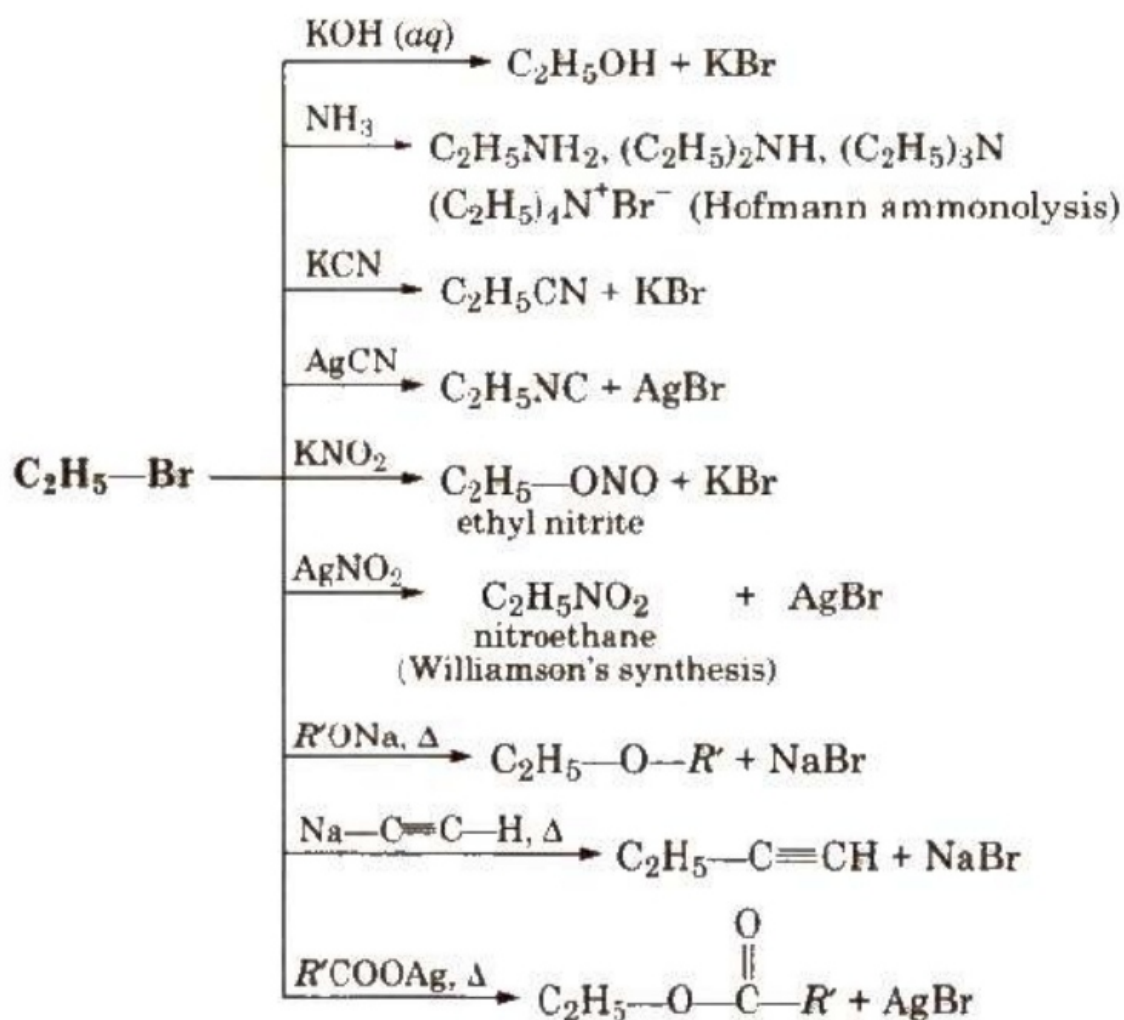
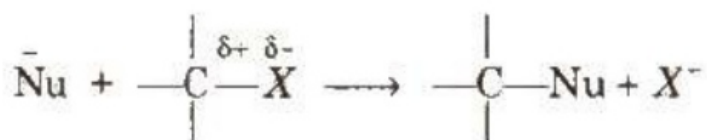
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is



Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)

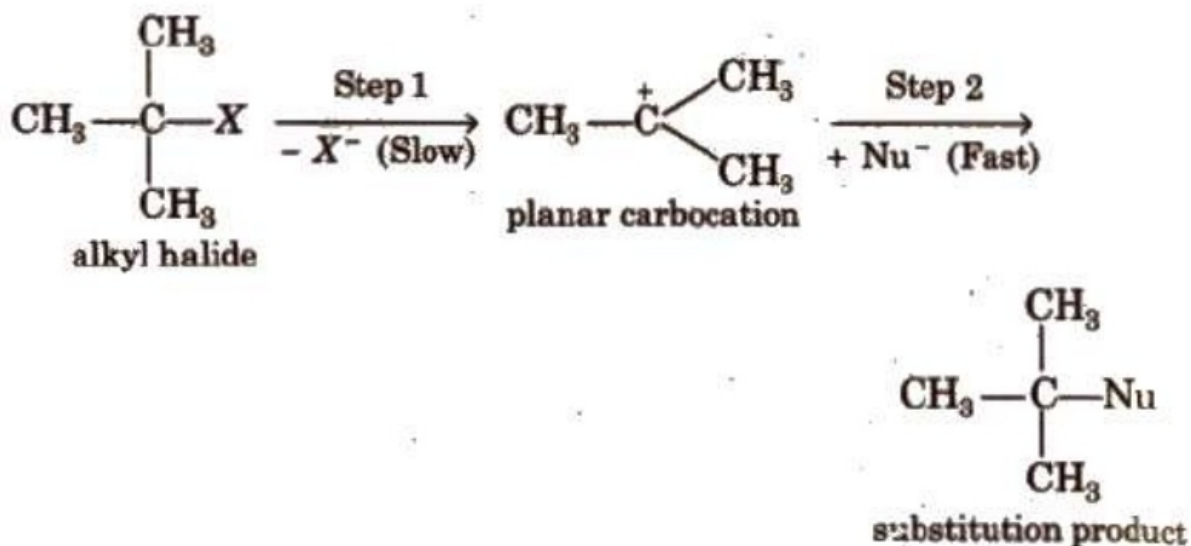


kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

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.

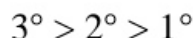
Nucleophilic substitution reactions are of two types

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



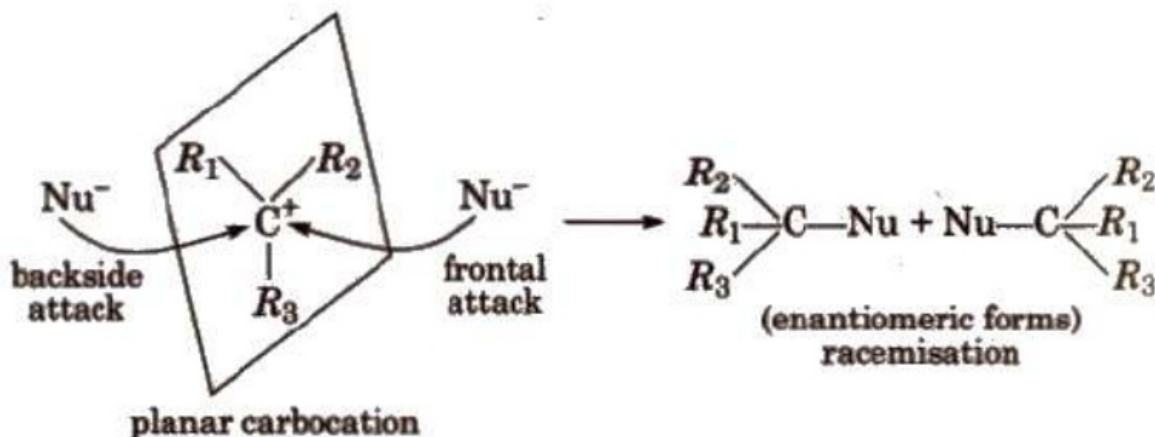
Rate, $r = k [RX]$. It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism



Polar solvents, low concentration of nucleophiles and weak nucleophiles favour S_N1 mechanism.

In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



(b) S_N2 type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with $r = k[RX] [Nu]$.

During S_N2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,