Haloalkanes:

Haloalkanes are generated by displacement of one or more hydrogen atoms of an alkane by halogen atom/s.

Classification & Nomenclature:

Monohaloalkanes:

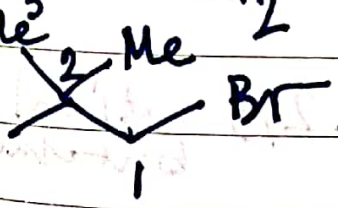
C_2H_5Cl Ethyl chloride

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ 2-bromopropane / trivially, Isopropyl bromide

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl$ 2-chloro-2-methylpropane / Trivially, tert-butyl chloride.

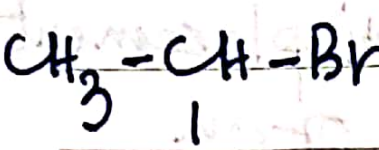
Dihaloalkanes:

$Cl-CH_2-CH_2-Cl$ 1,2-dichloroethane

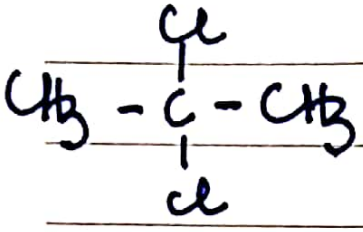


1,2-dibromo-2-methylpropane.

These are 1,2-dihalides / vicinal dihalides

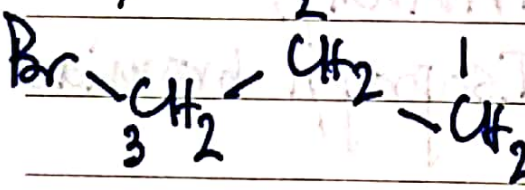


1,1-dibromoethane

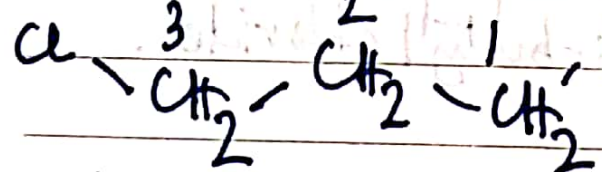


2,2-dichloropropane

These are geminal dihalides and are actually halogen analogs of carbonyl compounds.



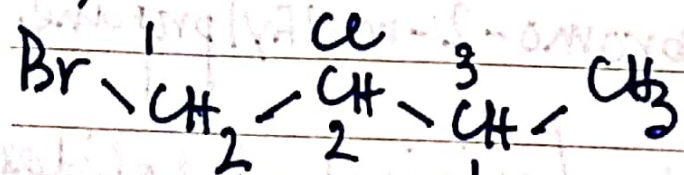
1,3-dibromopropane



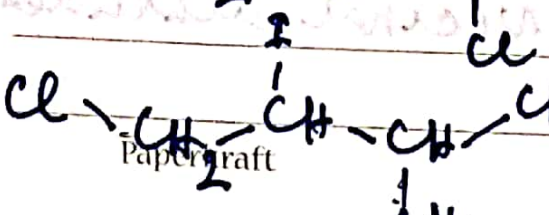
1-bromo-3-chloropropane

This is a mixed dihalide.

Polyhaloalkanes:



1-bromo-2,3-dichloro butane



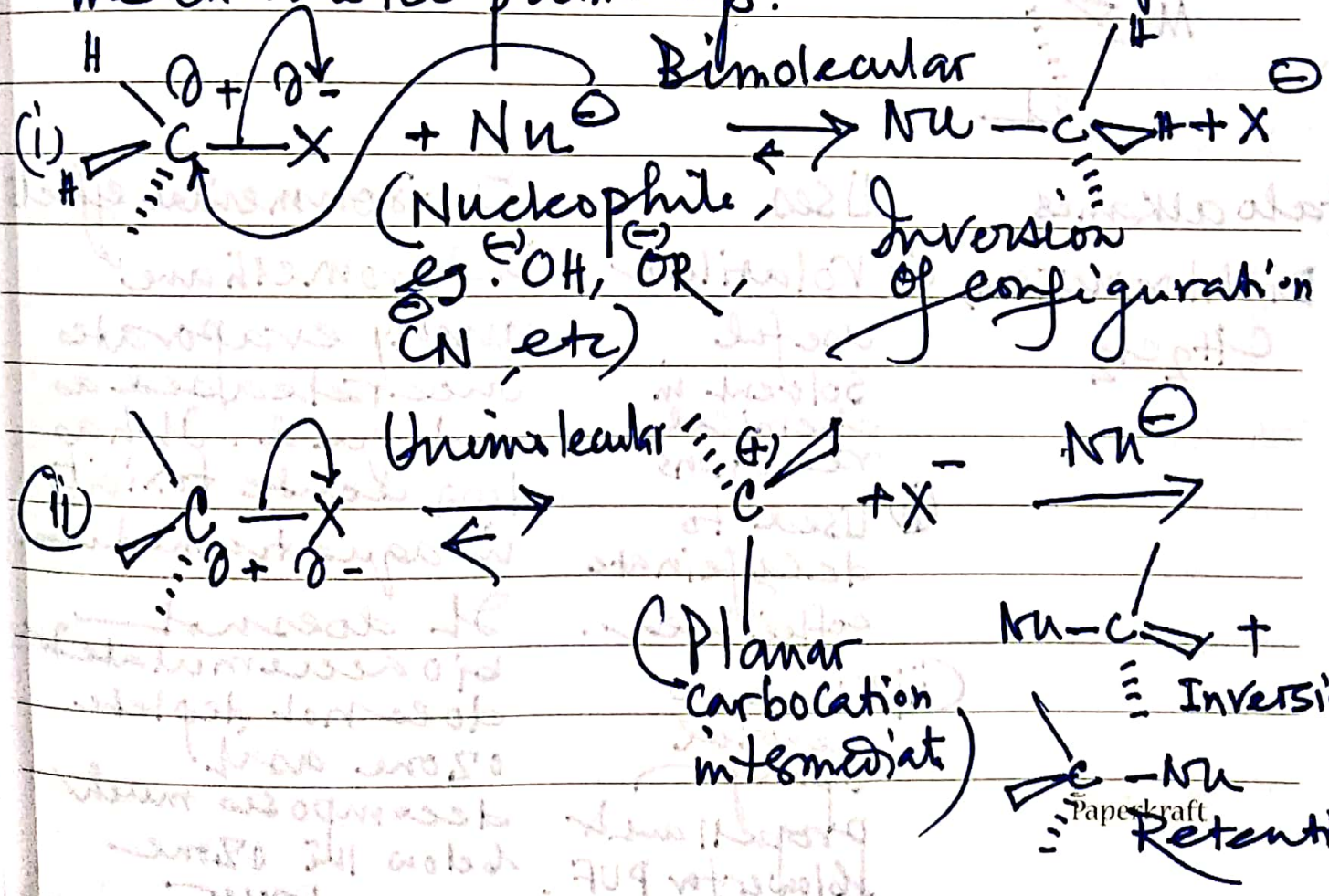
5-bromo-1-chloro-2-iodo-3-methylpentane.

δ+ δ−

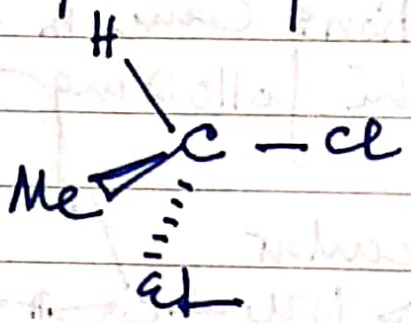
The C—X bond in a haloalkane is

polar due to greater electronegativity of the halogen compared to that of the carbon atom. The electropositive character of the α-C is transmitted upto the β-C. This dipolar nature of the C—X bond initiates nucleophilic substitution reactions at the α-C.

Such substitution reactions can, in a nutshell, proceed as per the following mechanistic pathways:



Less steric crowding and non-polar reaction medium favour the bimolecular (S_N2) pathway while more steric crowding and polar solvent favour the unimolecular (S_N1) pathway due of stabilization of the carbocation intermediate.
Alkyl halides which are devoid of molecular symmetry i.e. chiral are optically active, eg.



Haloalkanes	Uses	Environmental effects
1. Dichloromethane, CH_2Cl_2	(i) Volatile & useful solvent in chemical reactions (ii) Used to decaffeinate coffee & tea. (iii) Used as aerosol spray propellant & blowing for PUF.	Dichloromethane quickly evaporates once released as a liquid. It has low acute toxicity in aquatic medium. It does not bioaccumulate, does not deplete ozone as it decomposes much below the ozone layer.

Haloalkanes	Uses	Environmental effects.
i) Trichloromethane / $CHCl_3$ / chloroform	(i) Precursor of monochloro difluoro methane (CFC-22), a precursor of poly tetrafluoro ethylene (Teflon) $CHCl_3 + 2HF \rightarrow CHClF_2 + 2HCl$	Chloroform can cause health hazard when sufficiently concentrated. These include organ damage and heartbeat irregularities. It can acts as a potential respiratory depressant when inhaled. It is also strongly suspected of increasing the risk of cancer.
	(ii) Used as a solvent for fats, oils, etc. and in pesticide formulations.	
	(iii) Reagent in processes involving dichlorocarbene eg. Reimer – Tiemann formylation.	

Haloalkanes	Uses	Environmental effects.
(iv) Tetrachloromethane / CCl_4 / Carbon tetrachloride	(i) Acts as a chlorine source in Apel reach $R\text{-}OH \xrightarrow[CCl_4]{PPh_3} R\text{-}Cl$ (ii) Restoration of watermark on stamps (iii) As solvent.	(i) CCl_4 exposure causes CNS depression. (ii) Prolonged exposure leads to liver & kidney damage.
(v) Triiodomethane / CHI_3 / Iodoform	A yellow, crystalline solid, used as an antiseptic component of medication for skin diseases. In contact with organic matter, it decomposes to give free iodine which acts as an antiseptic.	Exposure to iodoform may cause nausea, dizziness, CNS depression, heart, Kidney & liver damage

Haloalkanes	Uses	Environmental effects.
(v) Freons/ chlorofluoro carbon compounds	As stable, non flammable low toxicity gases or liquids and have been generally used as refrigerants and aerosol propellants. They include the CFCs & HCFCs ($HCFCl_2$). CFCs cause Ozone depletion.	Freons are considered as significant environmental pollutants. They cause depletion of ozone layer and expose the earth surface to UV radiation. They are potential greenhouse gases as well.

$CFCl_3 \rightarrow F\overset{(\cdot)}{C}Cl_2 + Cl^{(\cdot)}$

$Cl^{(\cdot)} + O_3 \rightarrow Cl-O^{(\cdot)} + O_2$.

$2ClO^{(\cdot)} \rightarrow Cl-O-O-Cl$

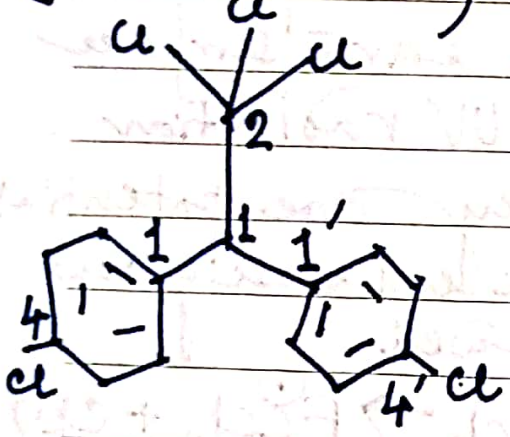
$Cl-O-O-Cl \rightarrow Cl-O-O^{(\cdot)} + Cl^{(\cdot)}$

$Cl-O-O^{(\cdot)} \rightarrow ClO^{(\cdot)} + O_2$

repeat ...

Haloalkanes Uses

DDT, Dichlorodiphenyltrichloroethane/ 1,1'-(2,2,2-Trichloroethane-1,1-diyl) bis (4-chlorobenzene)



Also,
1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl) ethyl] benzene

Broad Spectrum Insecticide and pesticide

Environmental effects.

A persistent organic pollutant that is readily adsorbed in soils and sediments leading to long term sources of exposure affecting organisms.

Preparation of haloalkanes:

(i) Photohalogenation of alkanes:
The method generates multiple halogenated products from a single precursor and hence has little synthetic value.

$$Cl_2 \xrightarrow{h\nu} Cl(\cdot) + Cl(\cdot)$$

$$Cl(\cdot) + H-CH_3 \rightarrow H-Cl + (\cdot)CH_3$$

$$Cl-Cl + (\cdot)CH_3 \rightarrow CH_3-Cl + Cl(\cdot)$$

$$Cl(\cdot) + H-CH_2-Cl \rightarrow H-Cl + (\cdot)CH_2-Cl$$

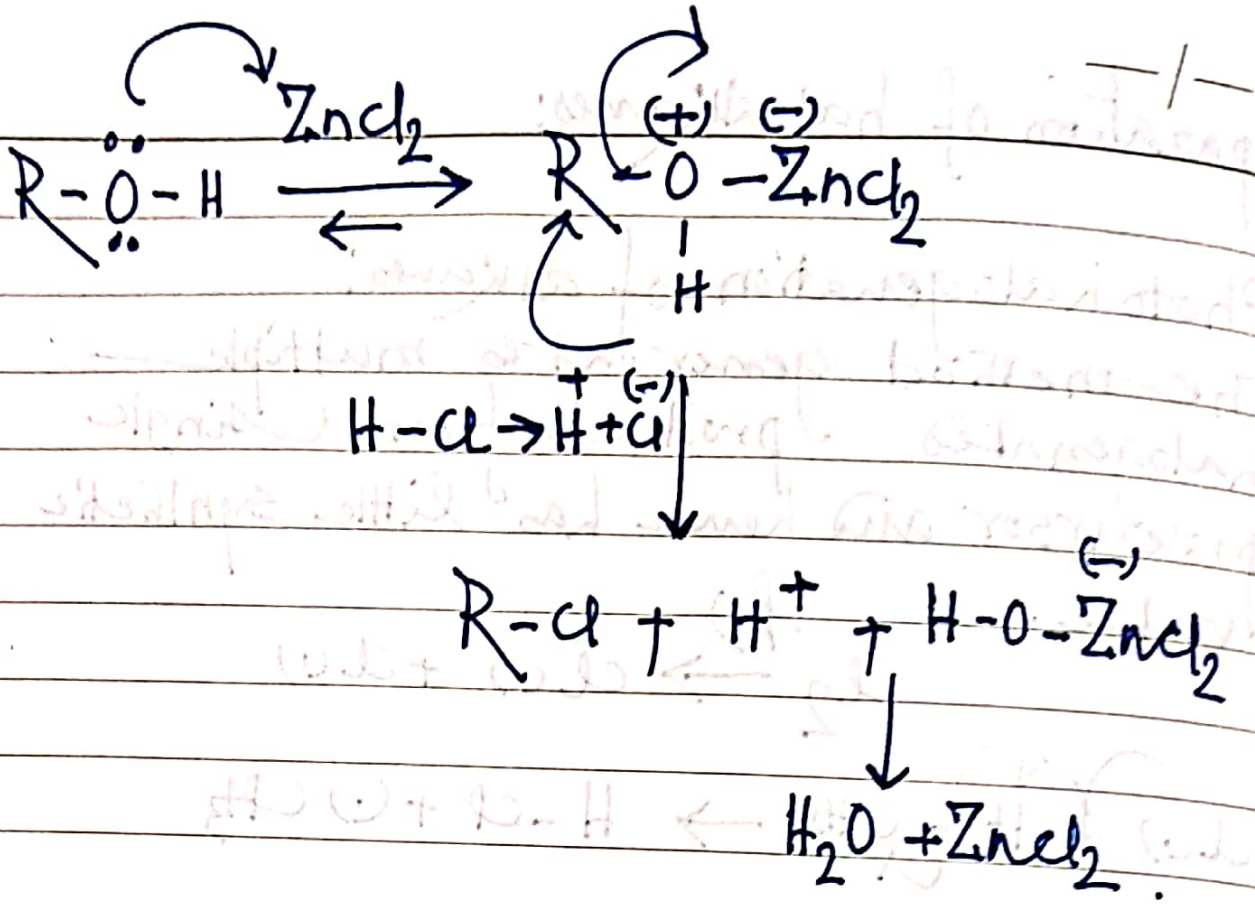
$$Cl-Cl + (\cdot)CH_2-Cl \rightarrow Cl(\cdot) + Cl-CH_2-Cl$$

... and so on.

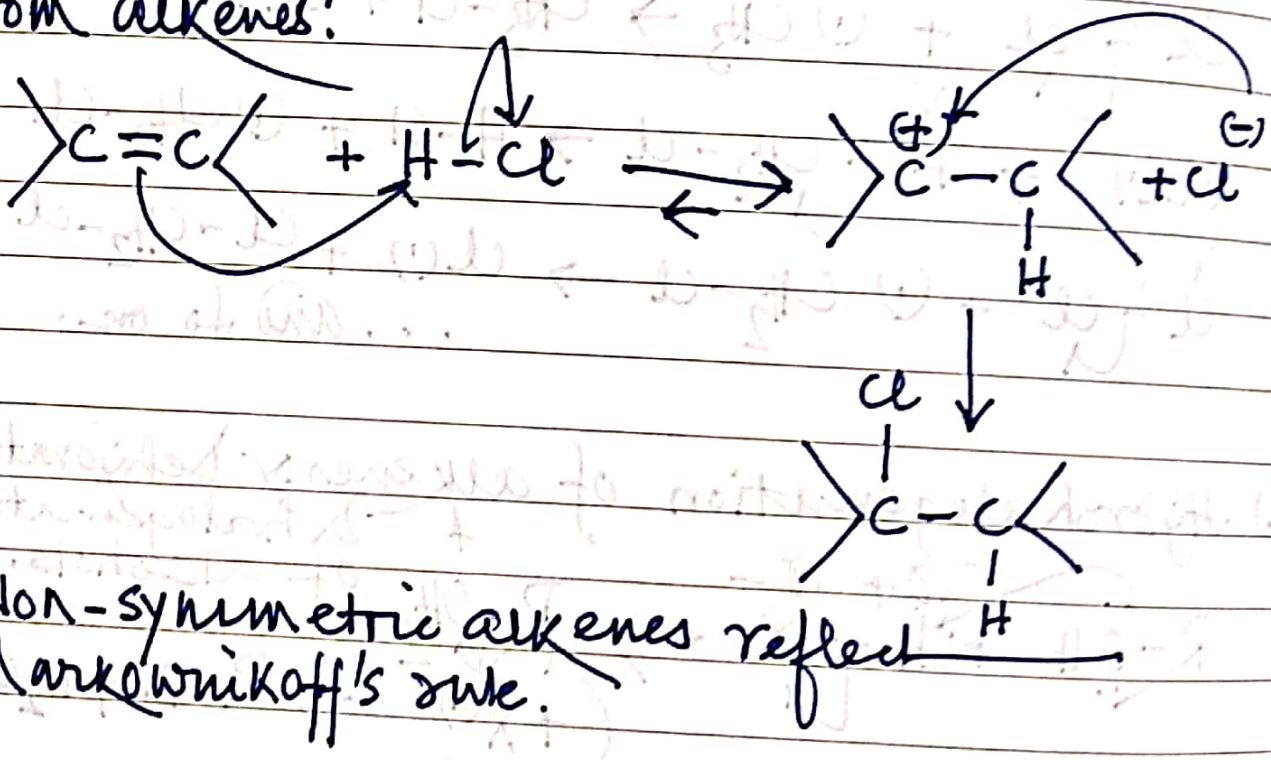
(ii) Hydrohalogenation of alkenes or Dehydration + Halogenation of alcohols.

$$R-\ddot{O}H + H-X \rightarrow R-\overset{+}{O}H_2 + X^{(-)} \rightarrow R-X + H_2O$$

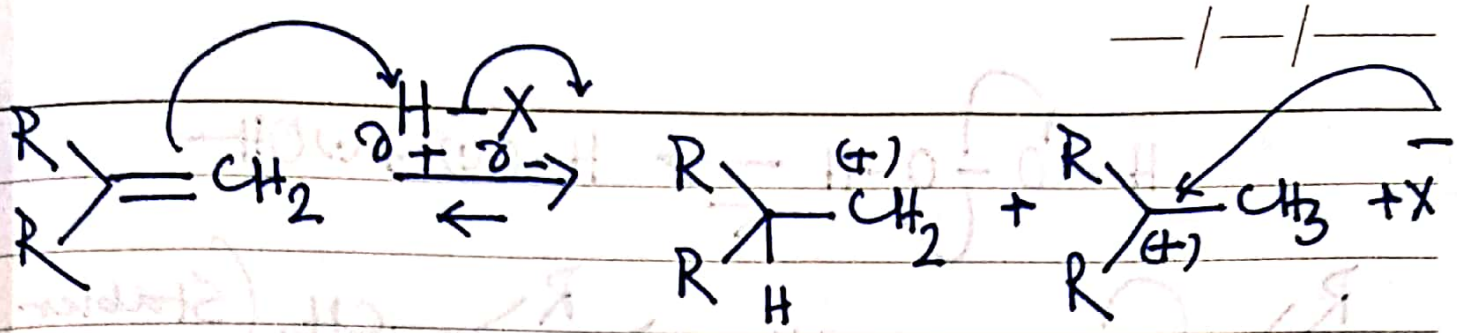
The process may be catalysed by anhydrous $ZnCl_2$ which acts as a Lewis Acid.



From alkenes:

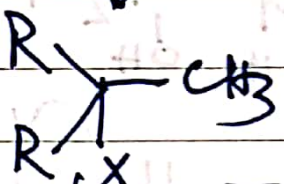


Non-symmetric alkenes reflect Markownikoff's rule.



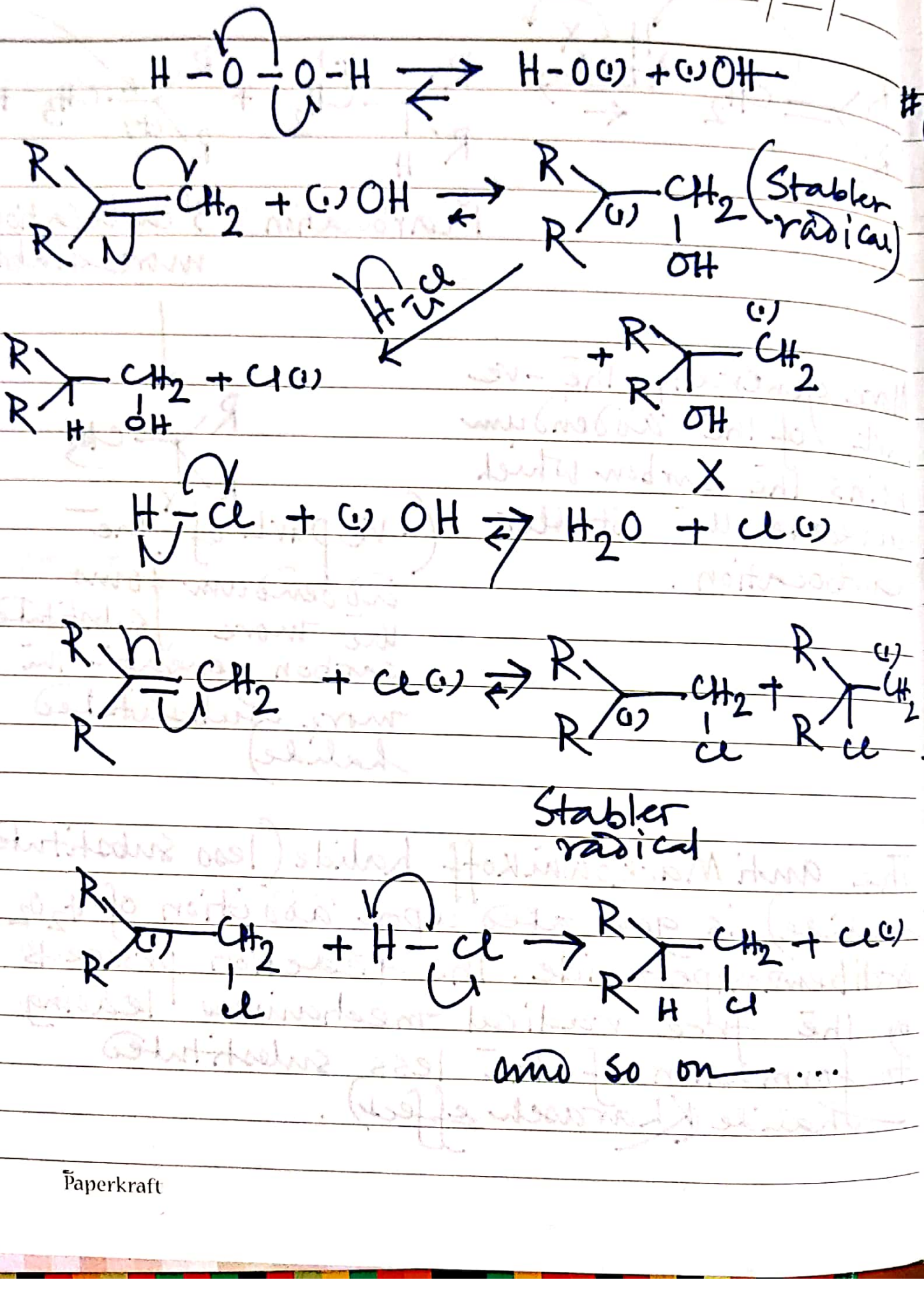
1° Carbocation 3° Carbocation, more stable.

More generally, the -ve part of the addendum joins the Carbon which generates the stabler carbocation.

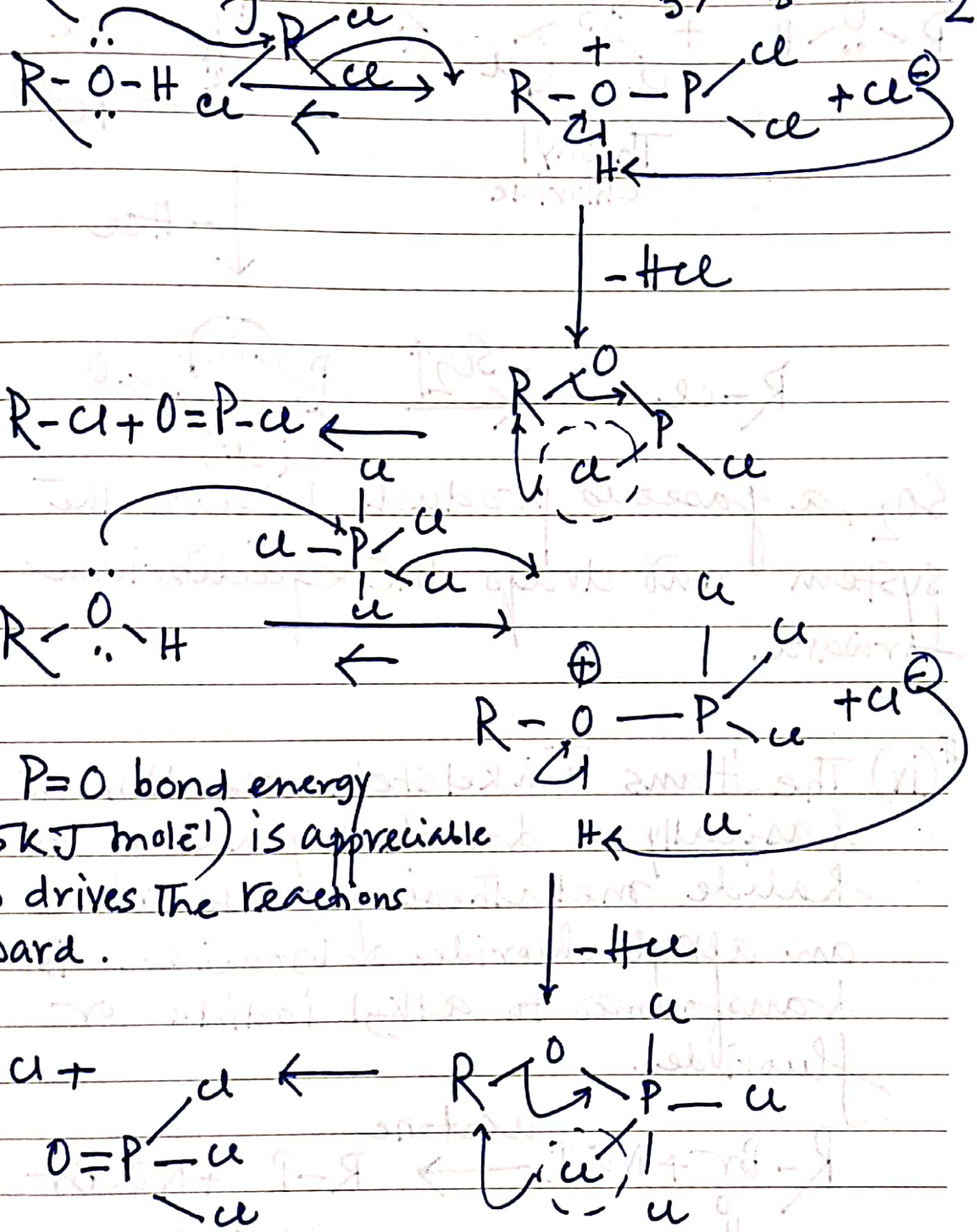


(-ve part of the addendum joins the more substituted carbon, generating the more substituted halide)

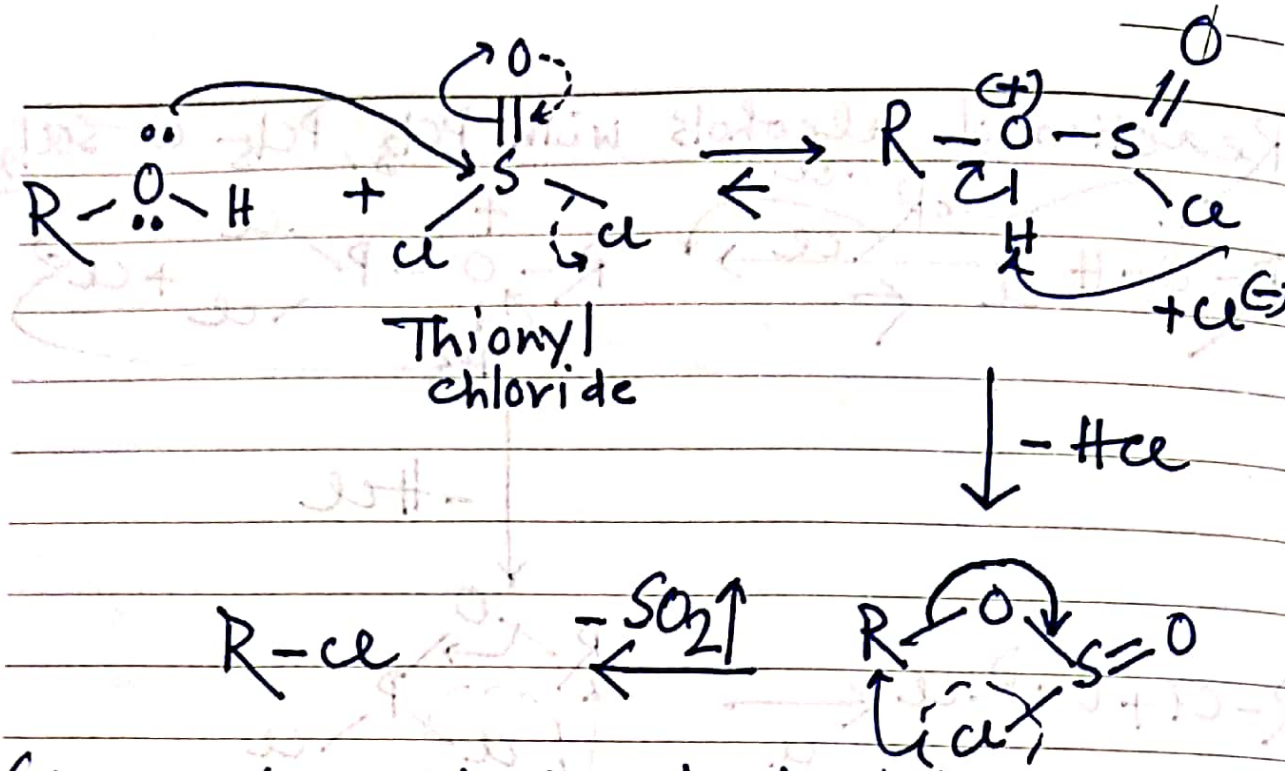
The anti Markownikoff halide (less substituted halide) is generated upon addition of H_2O_2 or dibenzoylperoxide. The reaction proceeds by the free radical mechanism leading to formation of the less substituted halide (Kharasch effect).


Stabler radical
and so on ...

(iii) Reaction of alcohols with PCl_3, PCl_5 or $SOCl_2$:



The P=O bond energy (575 kJ mole^{-1}) is appreciable and drives the reactions forward.



SO_2, a gaseous product, leaves the system and drags the equilibrium forward.

#(iv) The Hans Finkelstein reaction is basically a transhalogenation or halide metathesis process where an alkyl chloride or bromide is transformed to alkyl iodide or fluoride.

$$R-Br + NaI \xrightarrow{\text{acetone}} R-I + NaBr$$

$$EtO_2C-(CH_2)_4-Cl + NaI \xrightarrow{\text{acetone}} EtO_2C-(CH_2)_4-I + NaCl$$

The reaction is driven forward due to precipitation of the less soluble KBr or KCl in acetone.

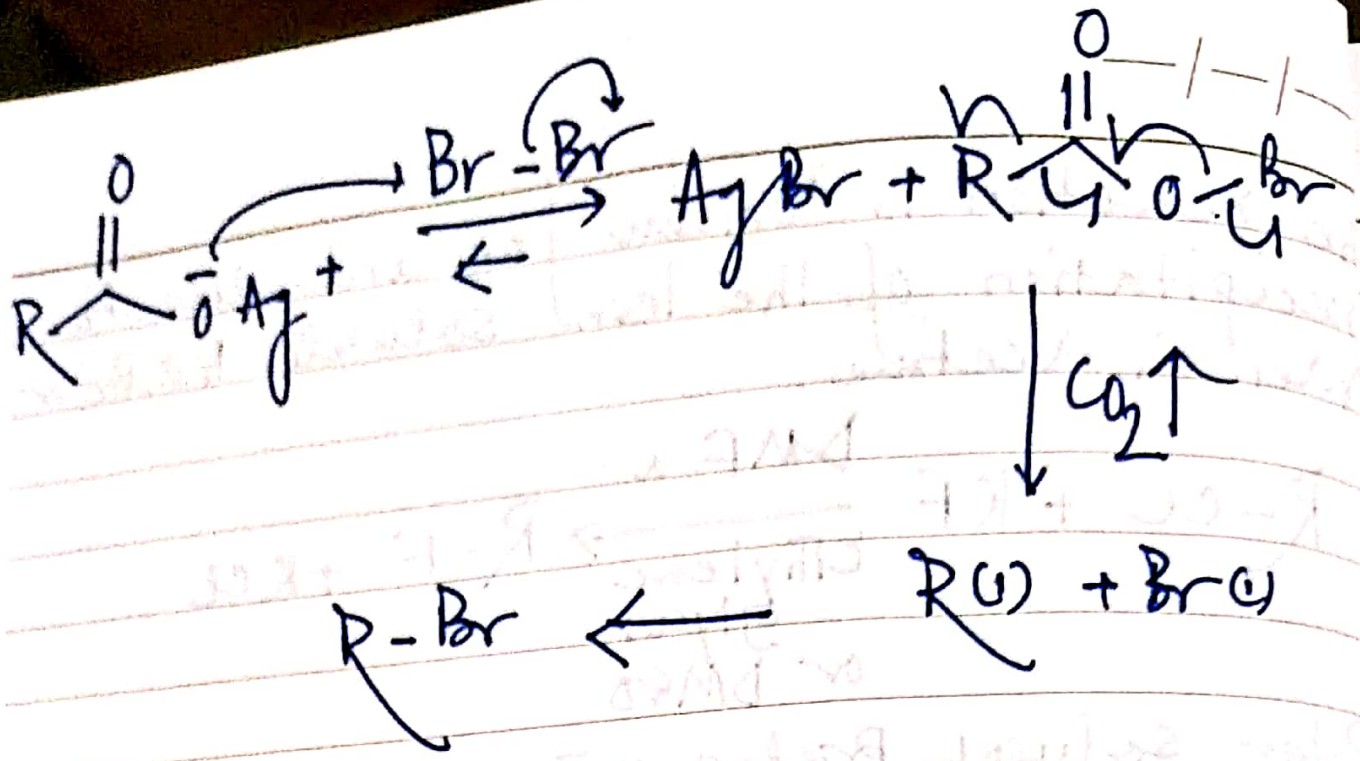
$$R\text{-}Cl + KF \xrightarrow[\text{Ethylene glycol or DMSO}]{\text{DMF or}} R\text{-}F + KCl$$

Polar solvent prefers the more polar product.

(v) The Borodine-Hunsdiecker reaction:

In this method, Ag(I) salts of carboxylic acids react with halogens to yield alkyl halides. The reaction proceeds through homolysis of the C–C bond by a radical chain mechanism.

$$R\text{-}C(=O)\text{-}O^{-}Ag^{+} + Br_2/CCl_4 \rightarrow CO_2 + AgBr + R\text{-}Br$$



#(vi) The Kochi reaction:

In this method, a carboxylic acid is subjected to oxidative degradation with a Pb(IV) reagent, eg. $Pb(OAc)_4$. The method is suitable for synthesis of 2° & 3° halides.