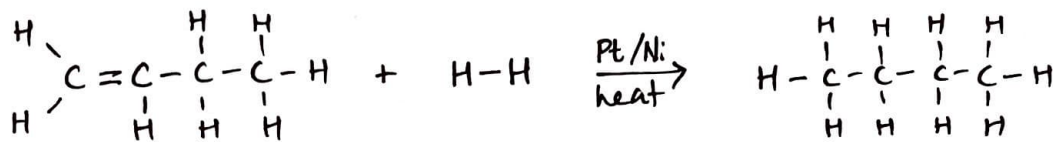
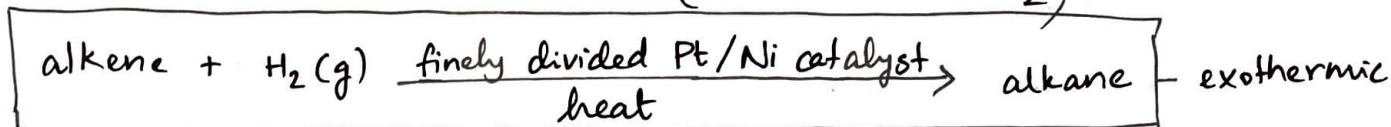
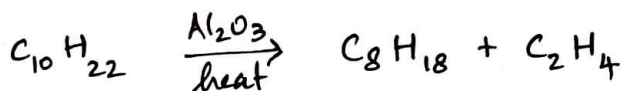
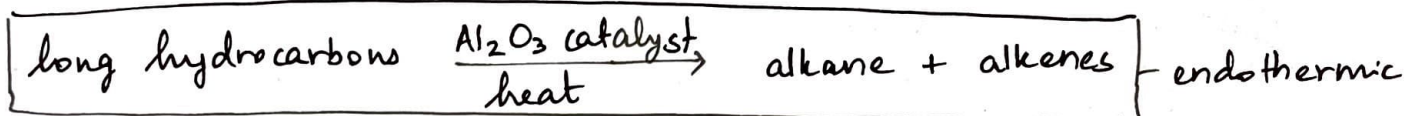


PRODUCTION OF ALKANES

1) HYDROGENATION OF ALKENES (ADDITION OF H₂)



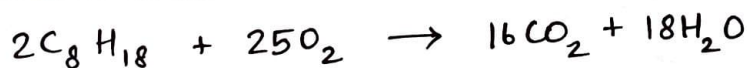
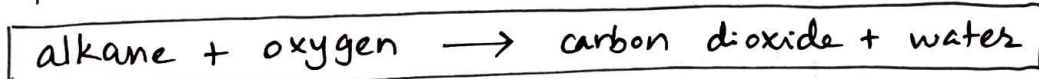
2) CRACKING



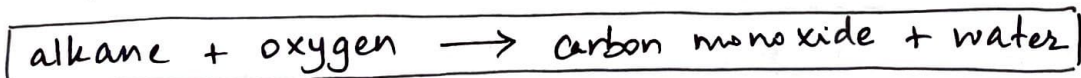
REACTIONS OF ALKANES

1) COMBUSTION

a) Complete Combustion

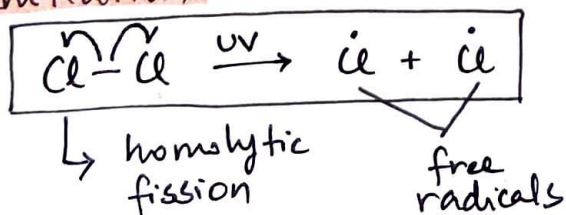


b) Incomplete Combustion

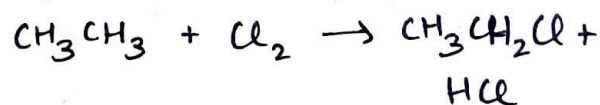


2) FREE-RADICAL SUBSTITUTION

i) Initiation



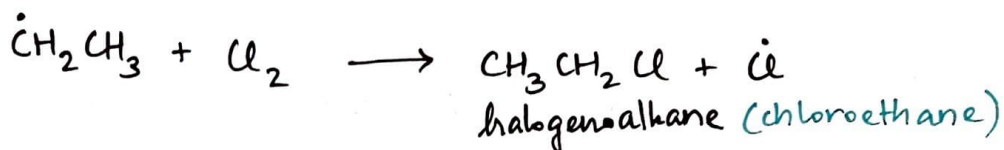
* overall reaction:



(ii) Propagation

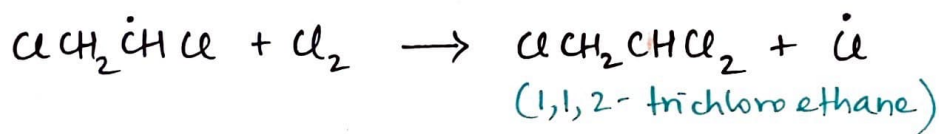
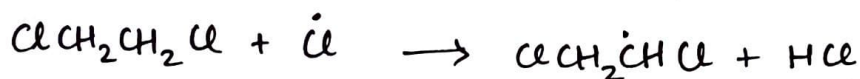
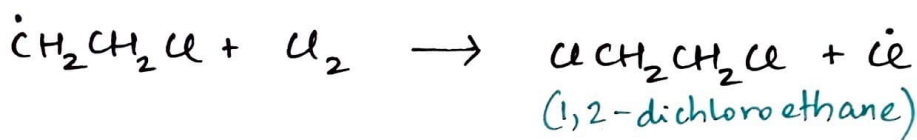
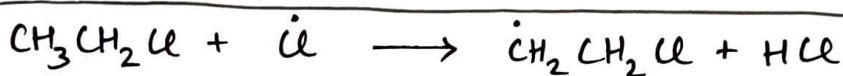


(homolytic fission of C-H bond; alkyl radical formed)



(free radical formed, which repeats cycle)

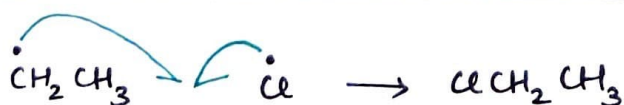
Further substitution:



⋮

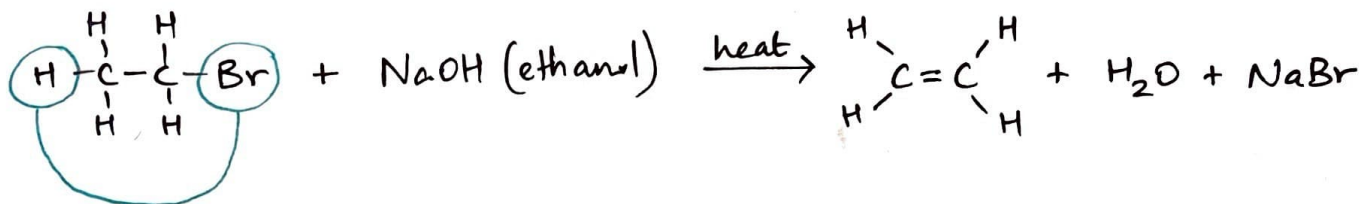
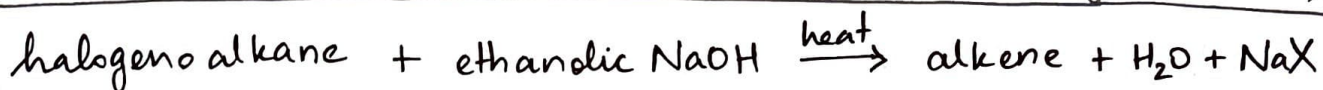
eventually C_2Cl_6 is formed

(iii) Termination



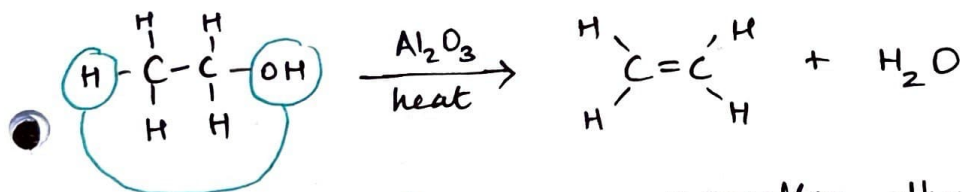
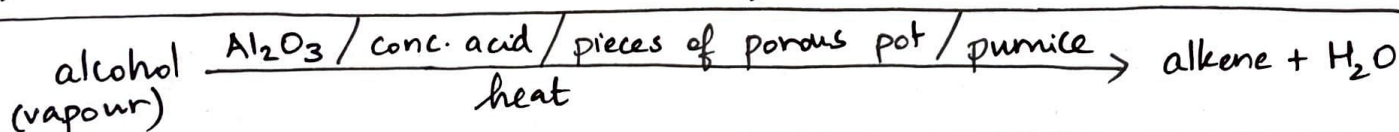
PRODUCTION OF ALKENES

1) ELIMINATION (of hydrogen halide from halogenoalkane)



- HBr eliminated
- heterolytic bond breaking of C-Br bond; Br takes both e^- & forms Br^- .
- ethanolic OH^- acts as a base & accepts H^+
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
- Br^- combines w/ Na^+ to form NaBr
 $\text{Na}^+ + \text{Br}^- \rightarrow \text{NaBr}$

2) DEHYDRATION (elimination of H_2O from alcohol)



- H_2O eliminated
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

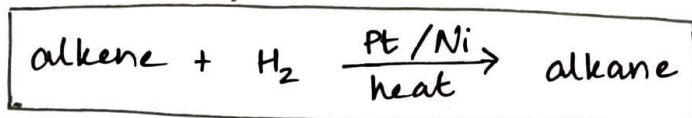
* smaller alkenes (ethene, propene, butene) = gases at room temp
 \therefore collected over water.

3) CRACKING

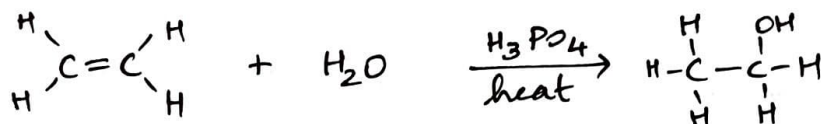
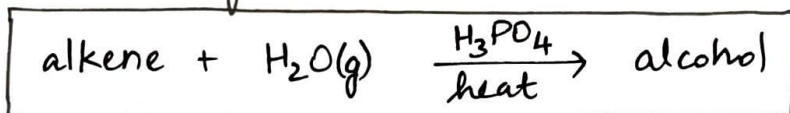
REACTIONS OF ALKENES

1) ELECTROPHILIC ADDITION - electrophile is added to double bond

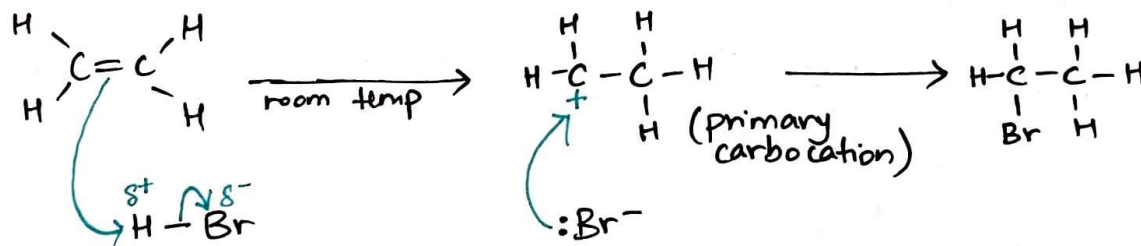
a) Addition of H_2 (Hydrogenation)



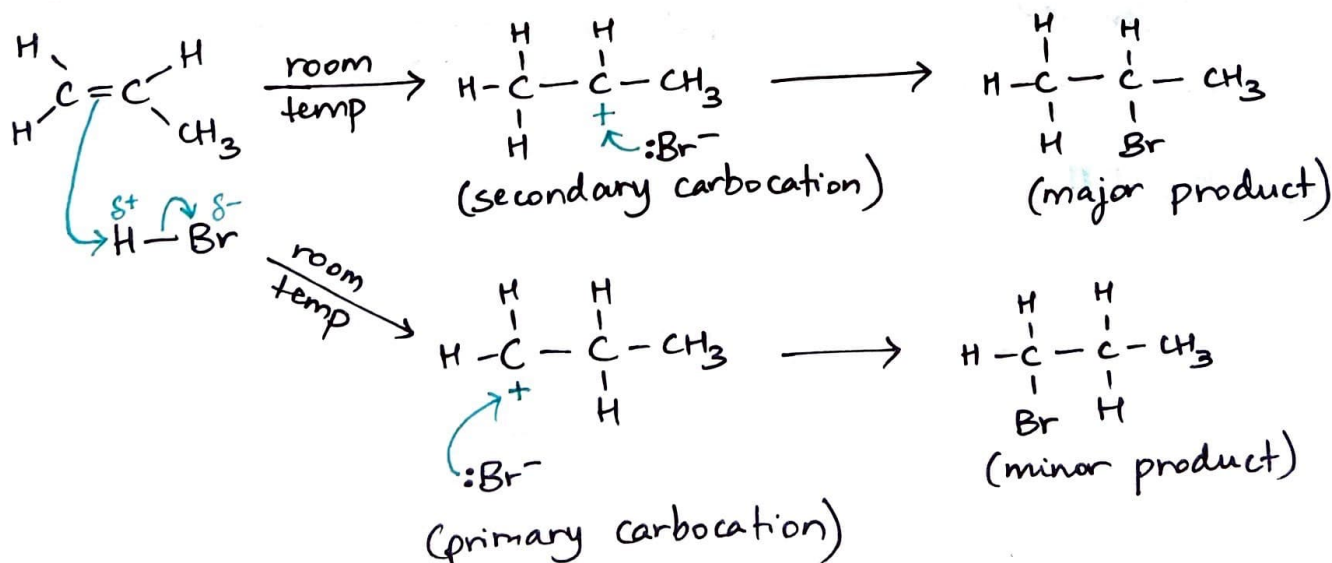
b) Addition of steam



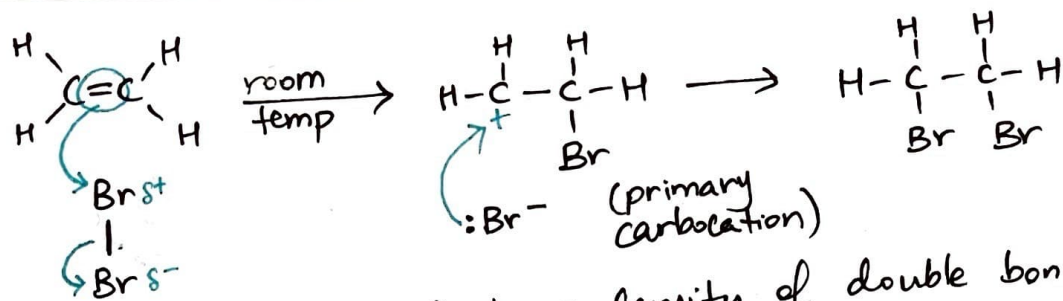
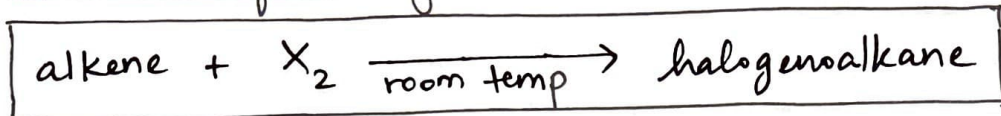
c) Addition of hydrogen halides (HX)



Markovnikov's rule: halogen ends up attached to most substituted C atom; applies to asymmetrical alkenes.



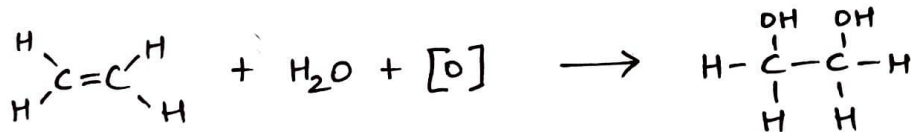
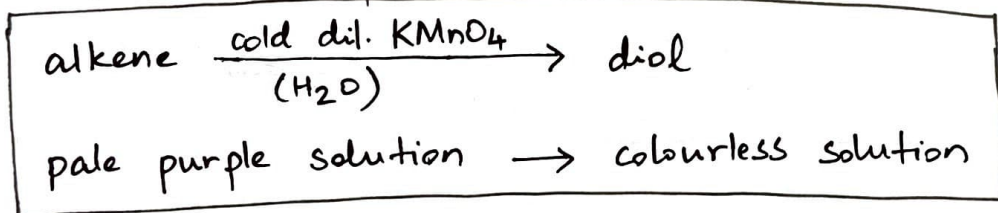
d) Addition of halogens



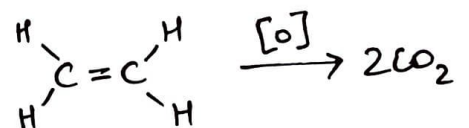
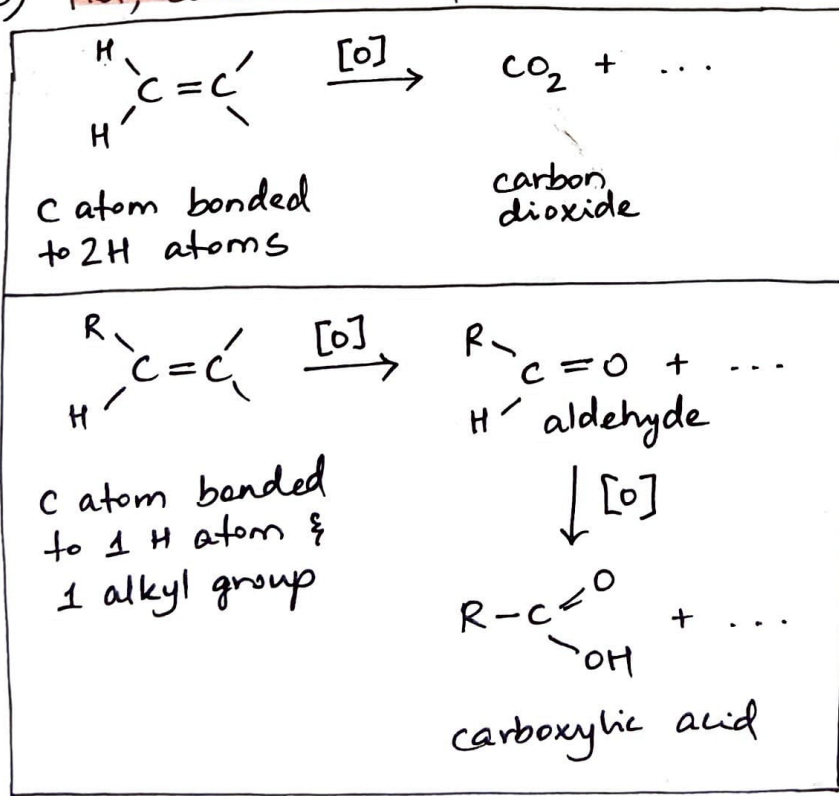
(induced dipole, as high e^- density of double bond repels e^- from the closest Br atom)

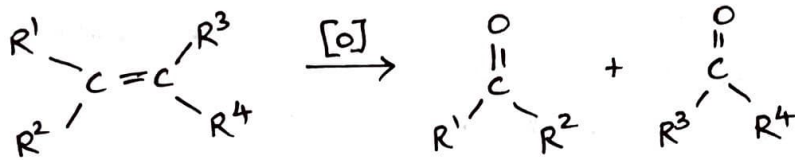
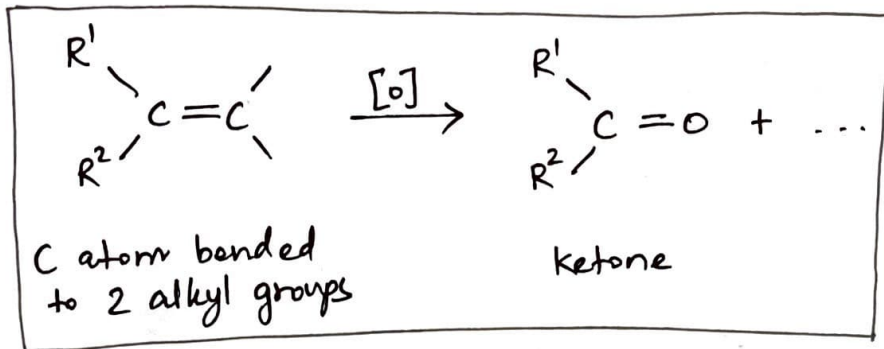
2) OXIDATION

a) Cold, dil. KMnO_4

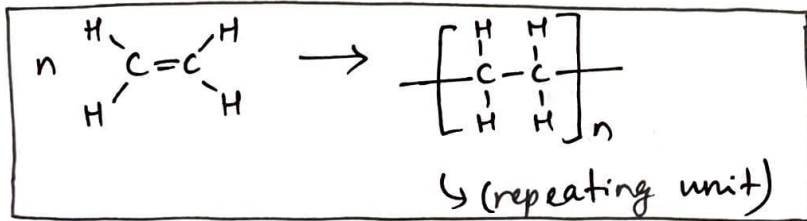


b) Hot, conc. KMnO_4





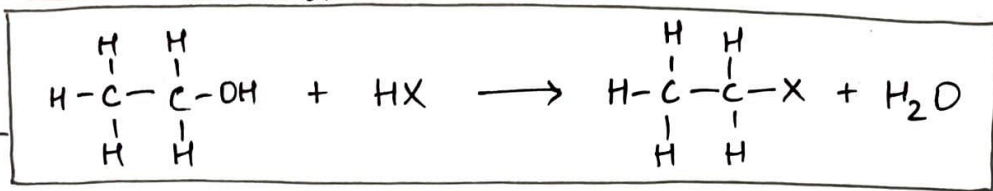
3) ADDITION POLYMERISATION



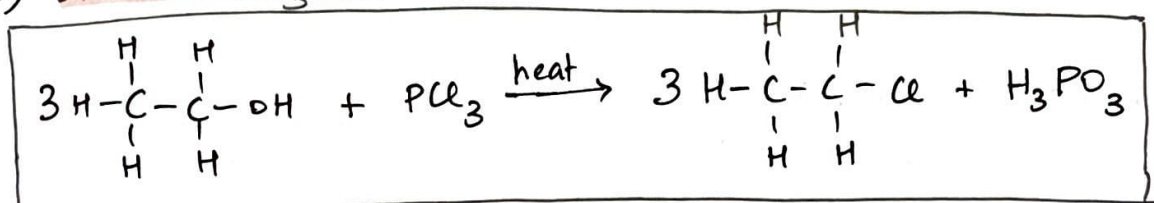
PRODUCTION OF HALOGENOALKANES

- 1) FREE-RADICAL SUBSTITUTION OF ALKANES
- 2) ELECTROPHILIC ADDITION (of hydrogen halides/halogens to alkenes)
- 3) SUBSTITUTION OF ALCOHOLS

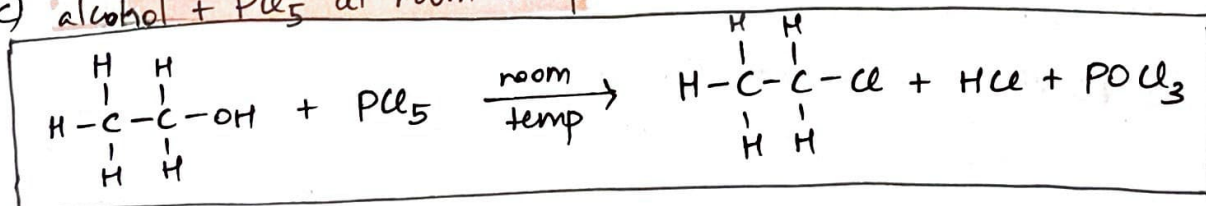
a) alcohol + HX (g)



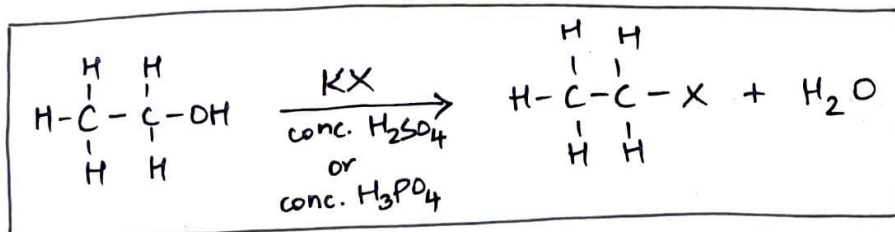
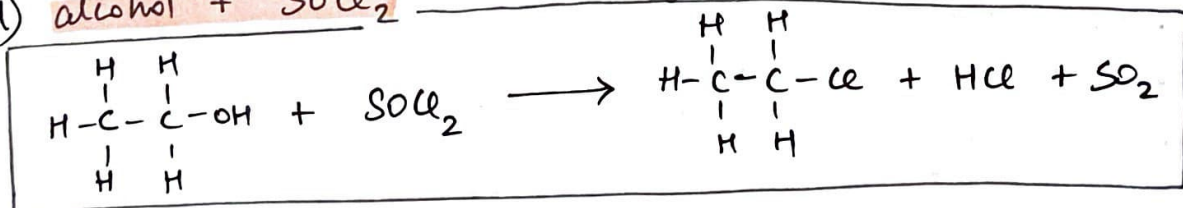
b) alcohol + PCl₃ + heat



c) alcohol + PCl₅ at room temp



d) alcohol + SOCl₂



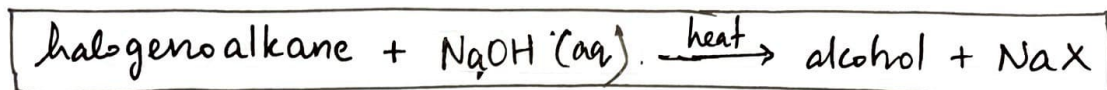
KCl + conc. H₂SO₄

conc. H₃PO₄

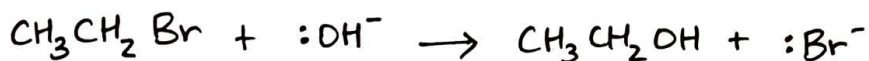
REACTIONS OF HALOGENOALKANES

1) NUCLEOPHILIC SUBSTITUTION - nucleophile attacks δ^+ C atom & replaces δ^- atom.

a) NaOH + heat



- OH^- ion = nucleophile
- OH^- replaces halogen



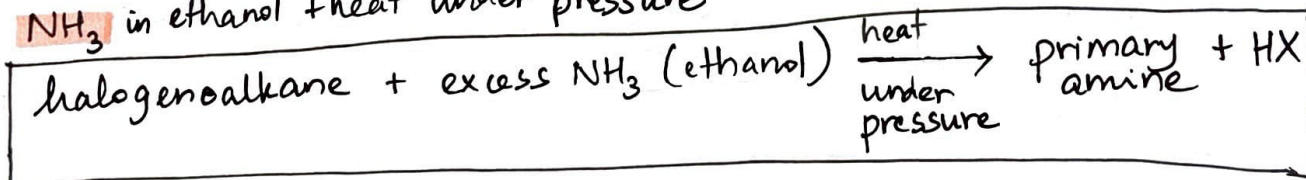
b) KCN in ethanol + heat



- CN^- = nucleophile
- CN^- ion replaces halogen
- an extra C atom is added to carbon chain



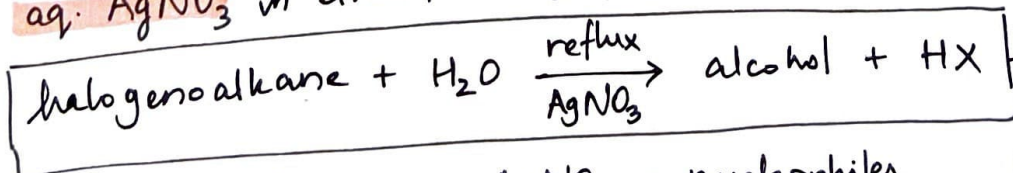
c) NH_3 in ethanol + heat under pressure



- NH_3 = nucleophile
- amine grp (NH_2) replaces halogen
- ammonia should be in excess otherwise primary amine produced can act as nucleophile, attack another halogenoalkane molecule to form secondary amine.



d) aq. AgNO_3 in ethanol \rightarrow halogenoalkanes have diff rates of hydrolysis so this reaction is used as a test to identify halogens in a halogenoalkane



- H_2O molecules in aq. AgNO_3 = nucleophiles
- H_2O replaces halogen

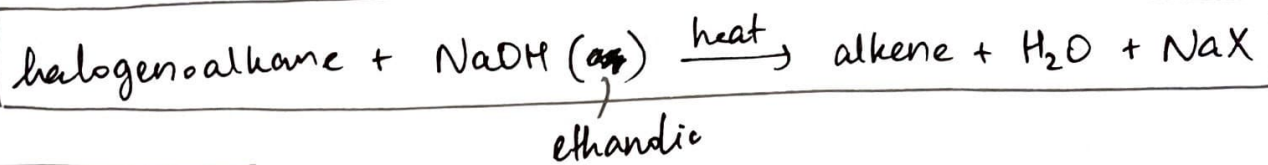


hydrolysis by measuring how long it takes for test tubes containing halogenoalkane & aq. AgNO_3 solutions to become opaque

$$\begin{array}{c} \delta^+ \text{O} \\ | \\ \text{H} - \text{O} - \text{H} \\ \delta^- \end{array}$$

* slower than nucl. sub. reac. w/ aq. alkali as OH^- is a better nucleophile: carries full formal $-ve$ charge. O atom in H_2O carries δ^- charge.

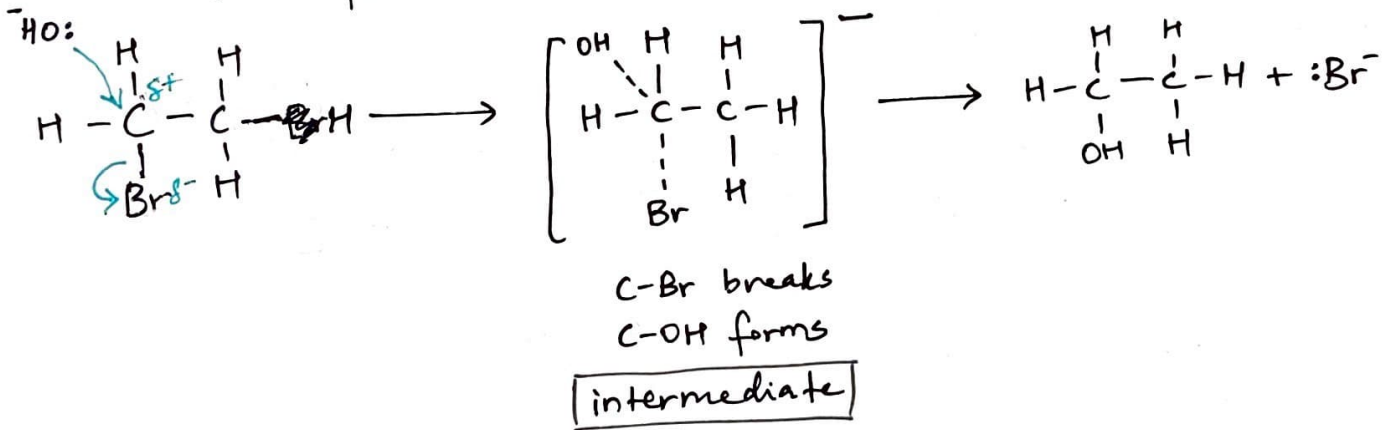
2) ELIMINATION



S_N1 & S_N2

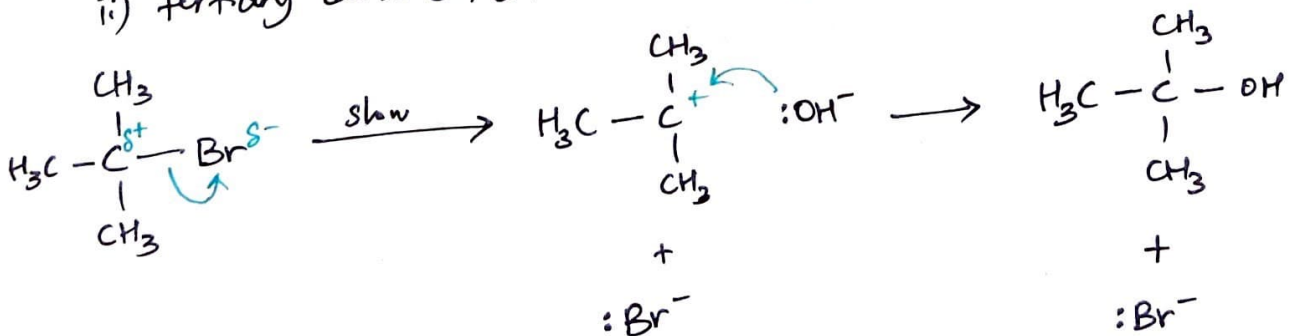
S_N2

- primary halogenoalkanes
- rate depends on conc. of halogenoalkane & nucleophile ions
- one step:
 - nucleophile donates e⁻ pair to δ⁺ carbon
 - at same time C-X bond breaks by heterolytic fission & X⁻ formed



S_N1

- tertiary halogenoalkanes
- rate depends on conc. of halogenoalkane
- 2 steps:
 - i) C-X bond breaks heterolytically & halogen leaves as X⁻ (slow & rate-determining step); tertiary carbo cation formed
 - ii) tertiary carbo cation attacked by nucleophile.



PRODUCTION OF ALCOHOLS

1) ELECTROPHILIC ADDITION (of steam to alkene)

2) OXIDATION OF ALKENES

(using cold dil. KMnO_4)

→ forms diol (2 OH grps)

→ $\text{C}=\text{C}$ double bond is not fully broken

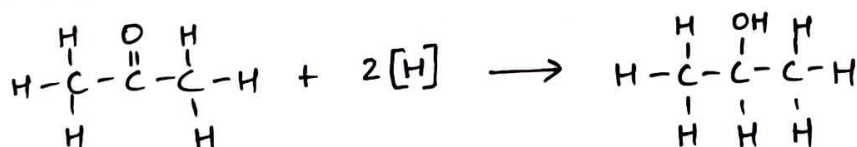
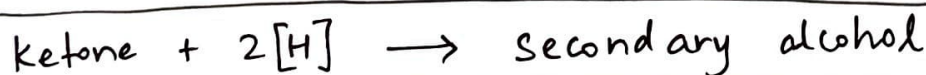
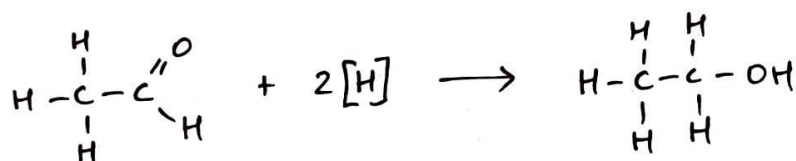
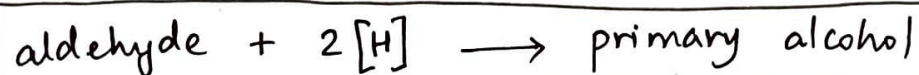
3) NUCLEOPHILIC SUBSTITUTION (of halogenoalkanes w/ aq. NaOH and heat)

4) REDUCTION OF ALDEHYDES & KETONES

• reducing agent = NaBH_4 or LiAlH_4

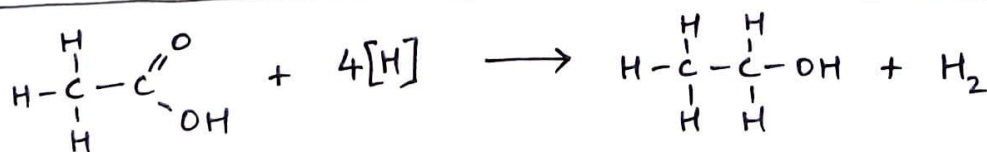
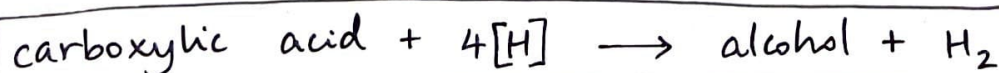
• aldehydes → primary alcohols

• ketones → secondary alcohols



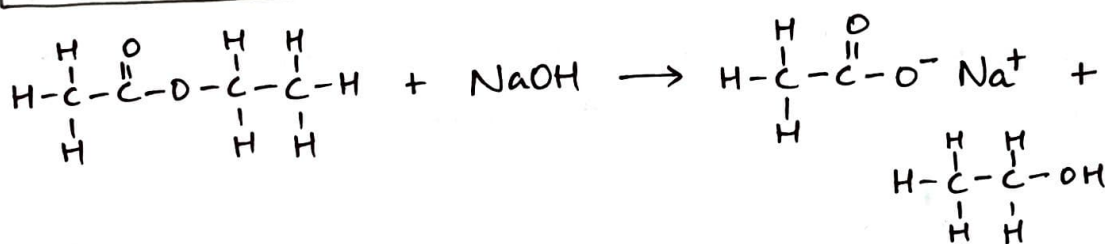
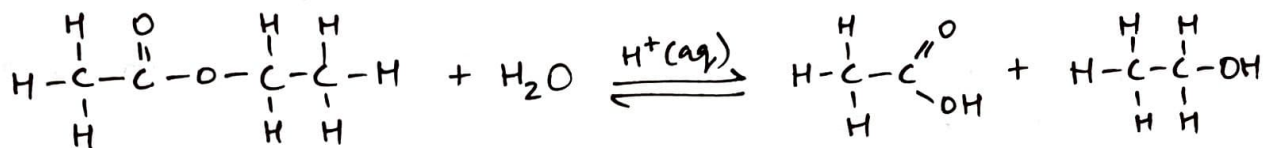
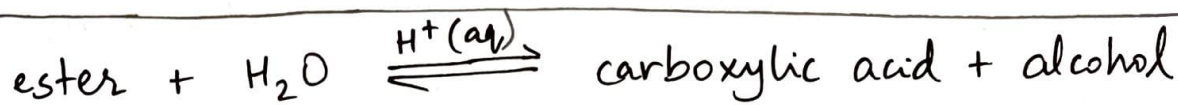
5) REDUCTION OF CARBOXYLIC ACIDS

• reducing agent = ~~NaBH_4~~ LiAlH_4



6) HYDROLYSIS OF ESTER

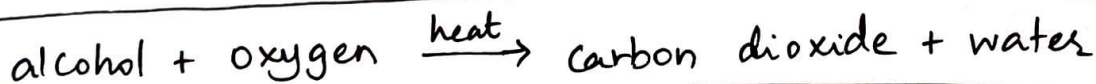
- dilute acid / alkali
- heat



REACTIONS OF ALCOHOLS

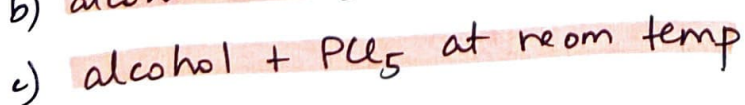
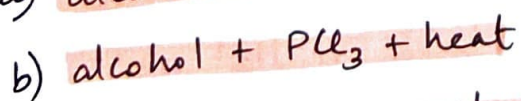
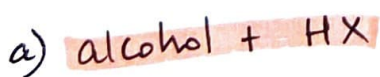
1) COMBUSTION

- complete combustion when ignited.

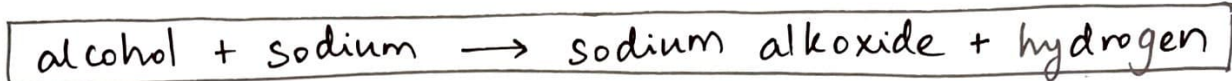


2) SUBSTITUTION (to form halogenoalkanes)

- OH grp replaced by halogen



3) REACTION WITH SODIUM - (Na(s))



(sodium ethoxide)

- when alcohol reacts w/ Na (reactive metal), O-H bond in OH grp breaks
- H₂ gas + basic compound (alkoxide) is formed, but reaction is less vigorous than Na + H₂O
- longer hydrocarbon chain in alcohol ⇒ less vigorous
- if excess alcohol is evaporated off, white crystalline solid of sodium alkoxide is left.

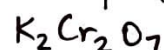
4) OXIDATION

• oxidising agents = acidified potassium dichromate (VI)

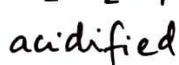
acidic medium

↓
H⁺ ions

↓
for reduction of the oxidising agent

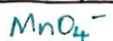


orange → green

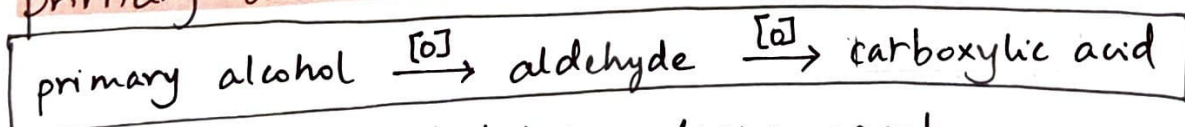


acidified potassium manganate (VII)

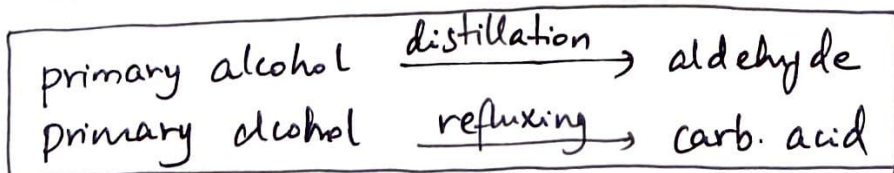
purple → colourless



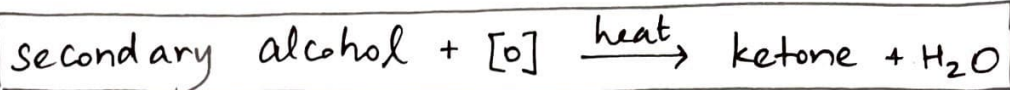
a) primary alcohols



- warm primary alcohol + oxidising agent
- aldehyde formed has lower b.p than alcohol so distilled off as soon as its formed.
- if not distilled off, further refluxing w/ excess oxidising agent will oxidise it to carb. acid.



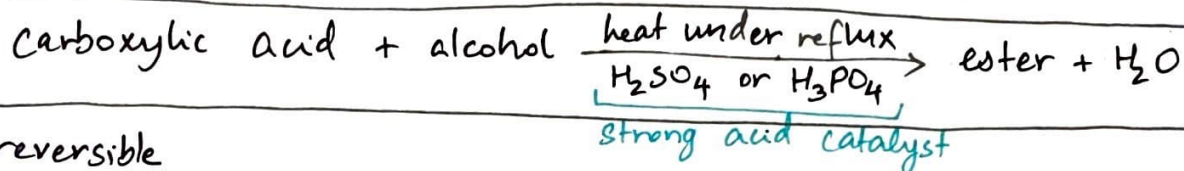
b) Secondary alcohols



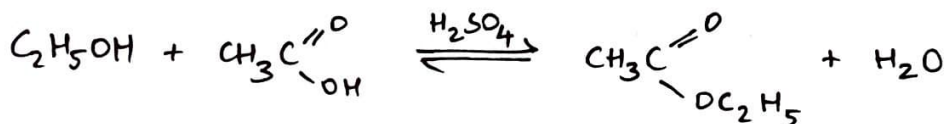
→ ketone is formed under distillation

5) DEHYDRATION (elimination of H_2O) to form alkene

6) ESTERIFICATION (condensation reaction)



reversible



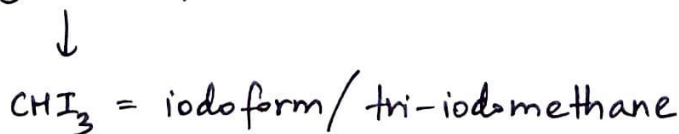
CLASSIFYING & TESTING FOR ALCOHOLS

1) alcohol + acidified $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow$ classifying alcohols

primary	green
secondary	green
tertiary	orange

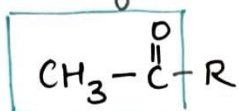
2) Iodoform test for alcohols

- reagent = I_2 in NaOH (aq); $\text{I}_2(\text{aq}) + \text{OH}^-(\text{aq}) =$ alkaline solution of iodine
- condition = warm
- positive test = yellow ppt

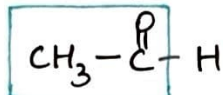


Compounds that give +ve result:

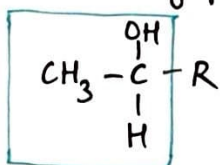
1) methyl ketones



2) ethanal

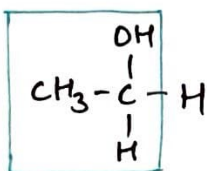


3) secondary alcohol that has CH_3 grp w/ C-atom that has $-\text{OH}$ grp attached to it.

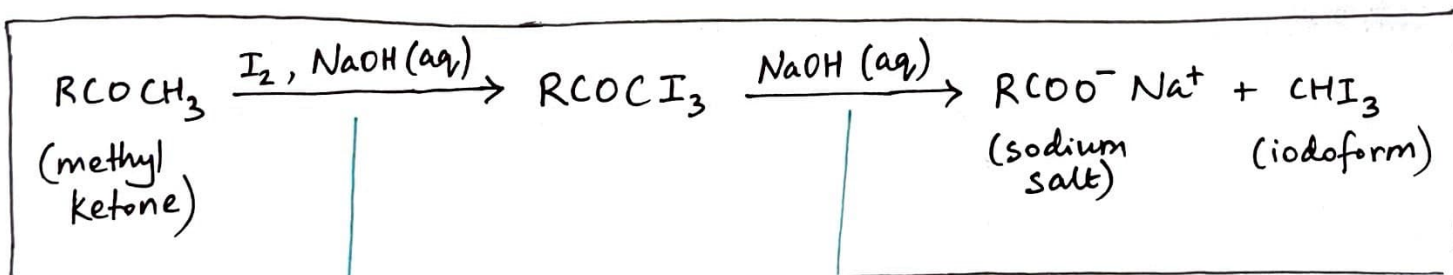


→ this secondary alcohol will oxidise to a methyl ketone

4) ethanol



→ ethanol is oxidised to ethanal



Step 1: HALOGENATION

→ all 3 H atoms in CH_3 grp are replaced for I atoms, forming $-\text{CI}_3$

Step 2: HYDROLYSIS

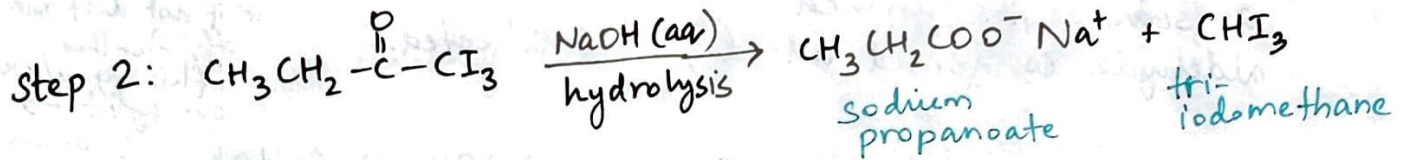
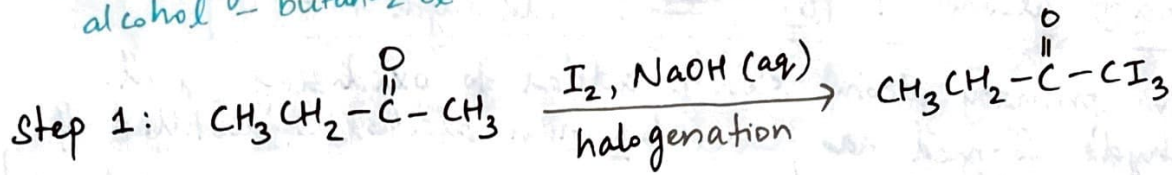
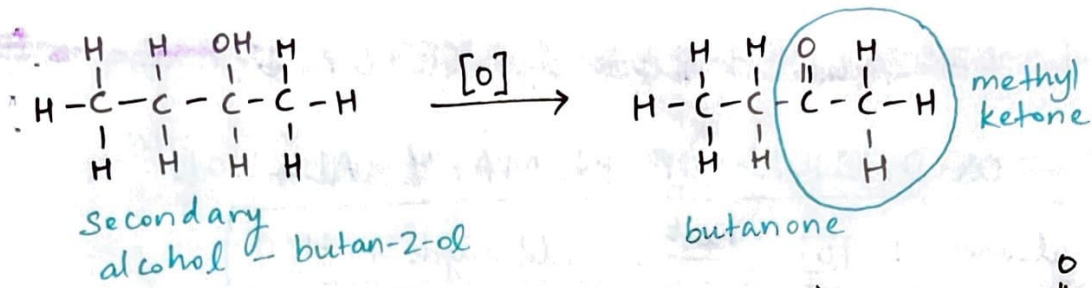
→ the intermediate compound is hydrolysed by alkaline solution, forming sodium salt + iodoform (yellow ppt)

Reaction is used to deduce position of a secondary alcohol:

→ if OH grp is on C atom nxt to CH_3 grp, it is oxidised to methyl ketone

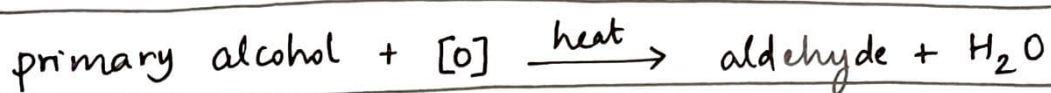
→ methyl ketone is halogenated & hydrolysed to form sodium salt + yellow ppt.

→ if no yellow ppt, secondary alcohol is NOT on a C atom nxt to methyl grp.



PRODUCTION OF ALDEHYDES & KETONES

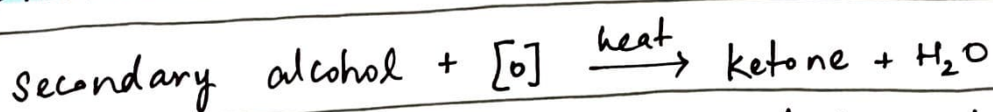
1) ALDEHYDE - OXIDATION OF PRIMARY ALCOHOL



- warm primary alcohol slowly added to oxidising agent.
- aldehyde formed has lower b.p than alcohol \therefore distilled off as soon as it's formed.
- aldehyde condensed into liquid & collected.

* if not distilled off, further refluxing w/ excess ox. agent \rightarrow carb. acid.

2) KETONE - OXIDATION OF SECONDARY ALCOHOL



- warm secondary alcohol slowly added to oxidising agent.
- ketone formed; doesn't need to be immediately distilled off as it cannot be further oxidised.

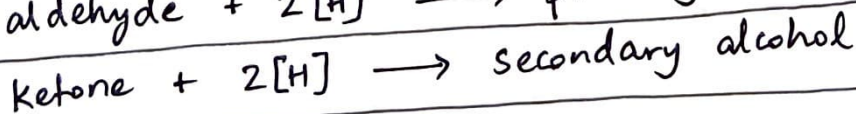
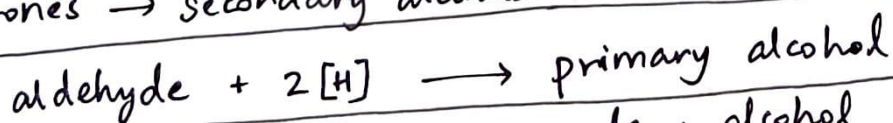
oxidising agents

acidified $\text{K}_2\text{Cr}_2\text{O}_7$	acidified KMnO_4
<ul style="list-style-type: none">• potassium dichromate (VI) acidified w/ dil. H_2SO_4• orange \rightarrow green ($\text{Cr}_2\text{O}_7^{2-}$) ($\text{Cr}^{3+}$) by reduction	<ul style="list-style-type: none">• potassium manganate (VII) acidified w/ dil. H_2SO_4• purple \rightarrow colourless (MnO_4^-) (Mn^{2+}) by reduction

REACTIONS OF ALDEHYDES & KETONES

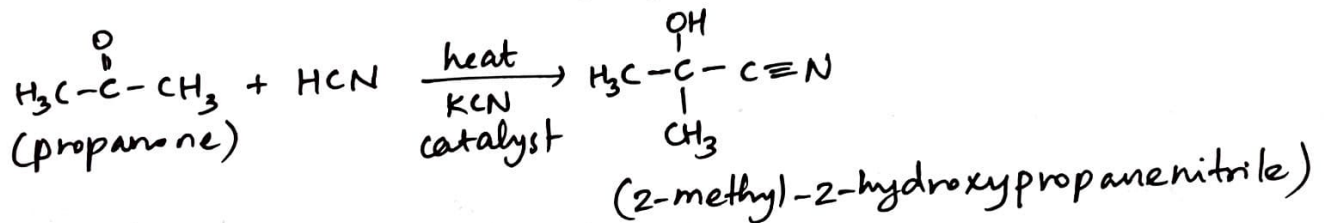
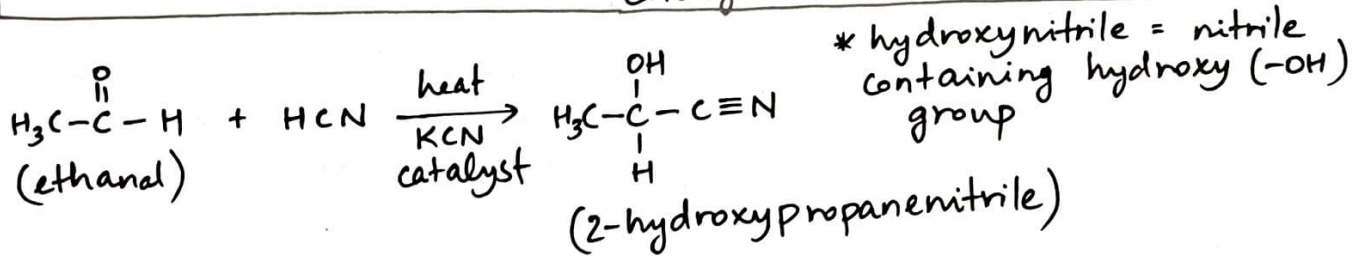
1) REDUCTION

- reducing agents: NaBH_4 , LiAlH_4
- aldehydes \rightarrow primary alcohols
- ketones \rightarrow secondary alcohols



2) NUCLEOPHILIC ADDITION WITH HCN

- nucleophile: cyanide ion (CN^-)
- nucleophile is added across $\text{C}=\text{O}$ bond



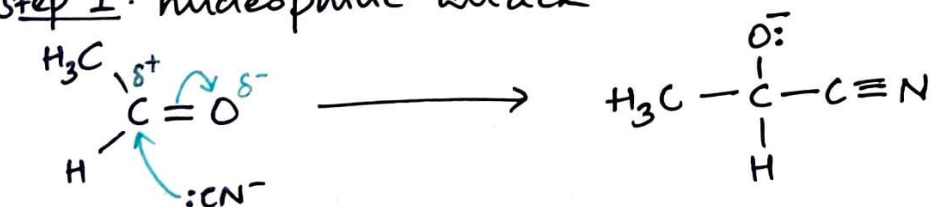
* nucleophilic addition of HCN to aldehyde = chiral hydroxynitrile always

nucleophilic addition of HCN to ketone = chiral hydroxynitrile maybe

Reaction mechanism

- carbonyl ($\text{C}=\text{O}$) grp is polarised.
- O atom more electronegative than C atom \therefore draws e^- density.
- C atom has δ^+ & O atom has δ^- charge.
- \therefore carbonyl C atom is susceptible to nucleophilic attack.

step 1: nucleophilic attack



* -ve charge on CN^- ion is on C atom NOT on N atom!!

(CN^- ion attacks carbonyl C atom)

step 2: protonation



\rightarrow -ve charged O atom in -ve reactive intermediate quickly reacts w/ aq. H^+ (from HCN / H_2O / dil. acid) to form 2-hydroxynitrile

TESTS FOR CARBONYL COMPOUNDS

1) 2,4-DNPH (2,4-dinitrophenylhydrazine)

- positive result: deep-orange ppt with aldehydes & ketones
- 2,4-DNPH + (C=O)grp = condensation reaction
- ppt formed can be purified by recrystallisation; mp of ppt is measured & compared to literature values to find out which specific aldehyde/ketone.

NOTE: carb. acids & esters give -ve result.

2) FEHLING'S SOLUTION

- oxidising agent.
- alkaline solution containing Cu^{2+} ions = oxidising agent.
- positive result: clear blue solution \rightarrow red ppt with aldehyde.
- aldehyde + Fehling's solution + heat = redox reaction
 - \rightarrow aldehyde oxidised to carb. acid
 - \rightarrow Cu^{2+} ions reduced to Cu^+ ions
 - \rightarrow opaque red ppt = copper (I) oxide (Cu_2O)
 - \rightarrow in alkaline conditions, carb acid neutralised to carboxylate ion (COOH loses proton to become COO^-)
 - \rightarrow COO^- will form a salt w/ +ve metal ion. eg. $\text{COO}^- \text{Na}^+$

NOTE: ketones give -ve result \because can't be oxidised.

3) TOLLENS' REAGENT

- oxidising agent.
- aq. alkaline solution of silver nitrate in excess ammonia solution: ammoniacal silver nitrate solution.
- positive result: silver mirror with aldehyde.
- aldehyde + Tollen's reagent + heat = redox reaction
 - \rightarrow aldehyde oxidised to carb. acid
 - \rightarrow Ag^+ ions reduced to Ag atoms
 - \rightarrow In alkaline conditions, carb. acid \rightarrow carboxylate ion \rightarrow salt.

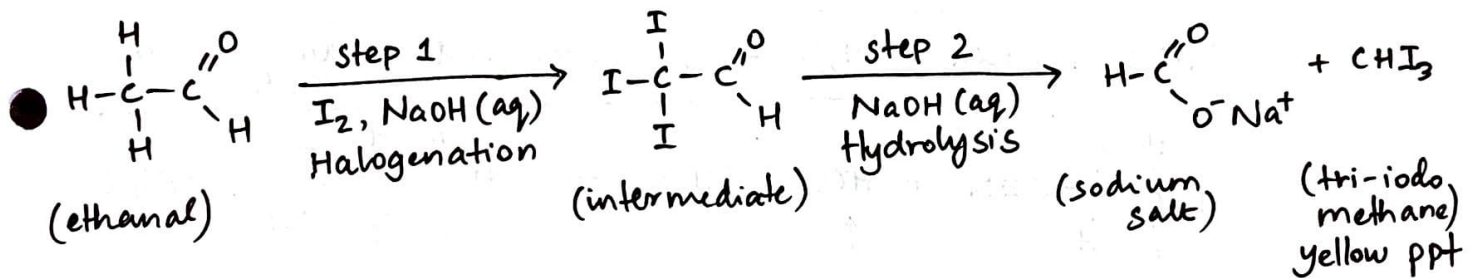
4.) IODOFORM TEST

- positive result: yellow ppt w/ methyl ketones & ethanal
compounds w/ $\text{CH}_3\text{CO-}$ grp

reagent + alkaline solution of iodine + heat

step 1: halogenation (all 3 H atom in $-\text{CH}_3$ grp replaced with I atoms = $-\text{CI}_3$)

step 2: hydrolysis (intermediate compound hydrolysed by alkaline solution to form sodium salt + yellow ppt)



PRODUCTION OF CARBOXYLIC ACIDS

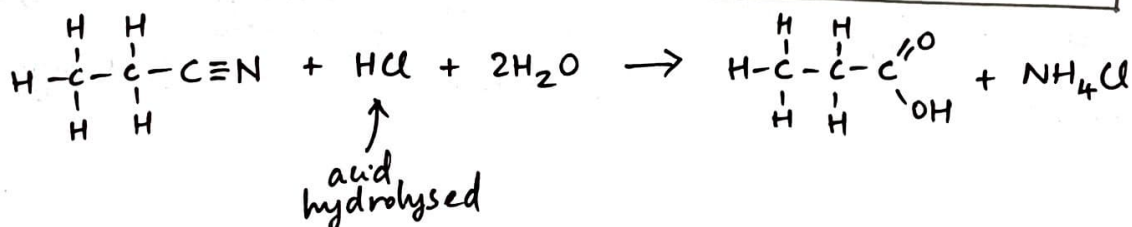
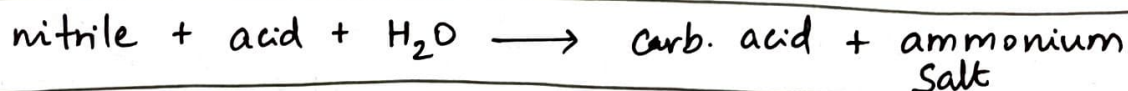
1) OXIDATION OF PRIMARY ALCOHOLS & ALDEHYDES

- oxidising agents: acidified $K_2Cr_2O_7$ / acidified $KMnO_4$
- reflux

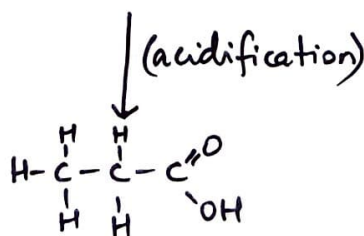
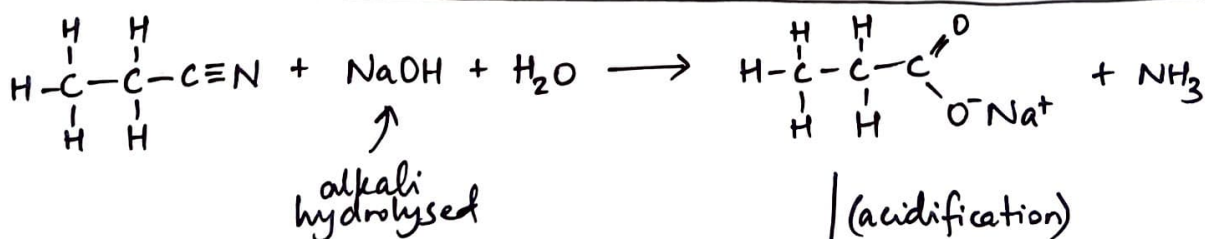
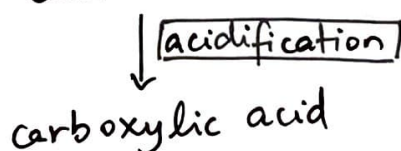
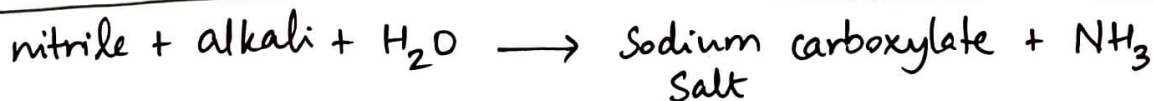


2) HYDROLYSIS OF NITRILES

a) using dilute acid

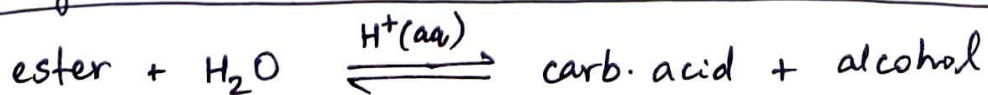


b) using dilute alkali + acidification



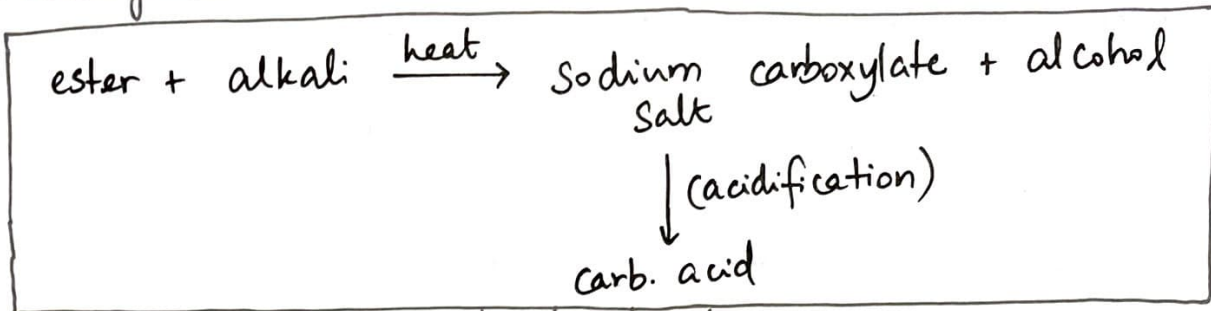
3) HYDROLYSIS OF ESTERS

a) using dilute acid

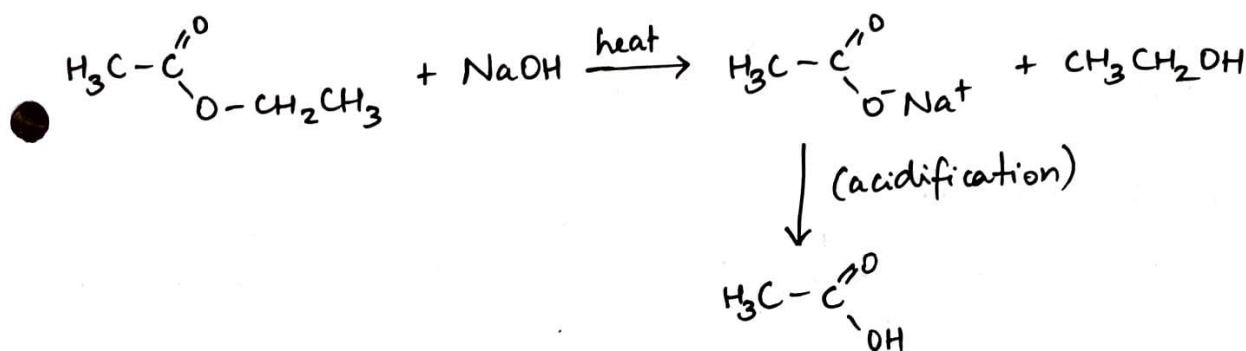
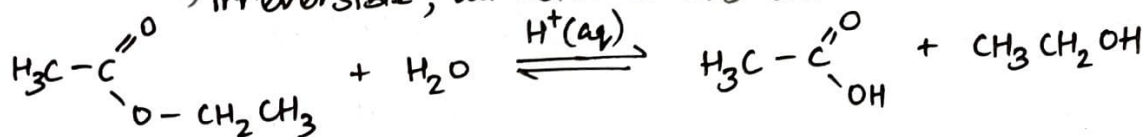


↳ reversible reaction where equilibrium established

b) using dilute alkali + acidification



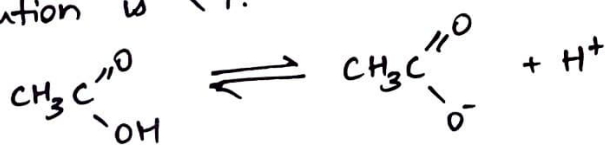
↳ irreversible; all ester breaks down.



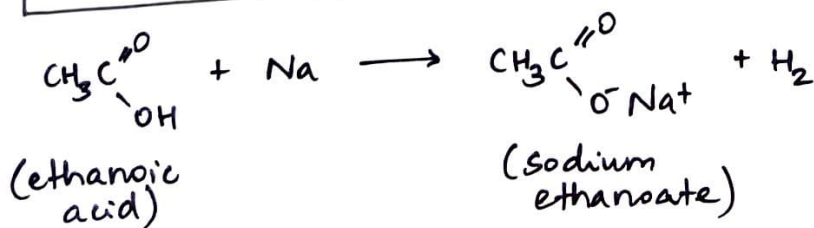
REACTIONS OF CARBOXYLIC ACIDS

→ weak acids; don't completely dissociate in H₂O
 → position of equilibrium lies to left & H⁺ conc. is much smaller than carb. acid conc.

→ pH of solution is < 7.

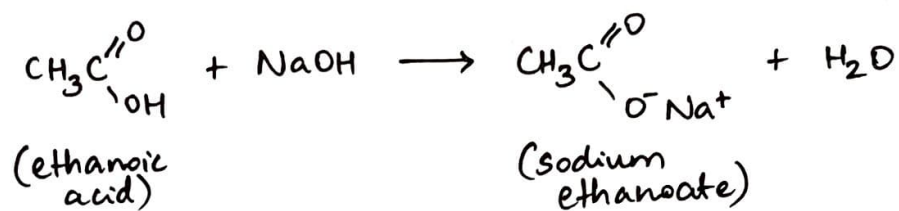


1) REDOX REACTIONS WITH REACTIVE METALS



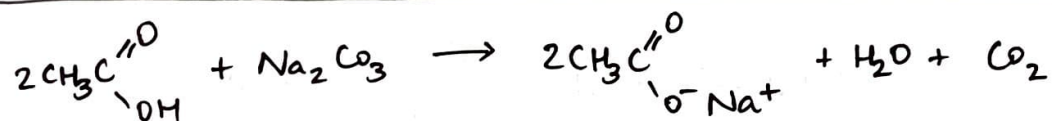
2) NEUTRALISATION REACTIONS WITH ALKALIS

carb. acid + alkali \rightarrow salt + water



3) ACID-BASE REACTIONS WITH CARBONATES

carb. acid + metal carbonate \rightarrow salt + H_2O + CO_2



4) ESTERIFICATION

carb. acid + alcohol $\xrightarrow[\text{Catalyst}]{\text{H}_2\text{SO}_4}$ ester + H_2O

catalyst:
conc. H_2SO_4

5) REDUCTION

carb. acid + $4[\text{H}] \rightarrow$ alcohol + H_2O

reducing agent: LiAlH_4 only

PRODUCTION OF ESTERS

1) ESTERIFICATION

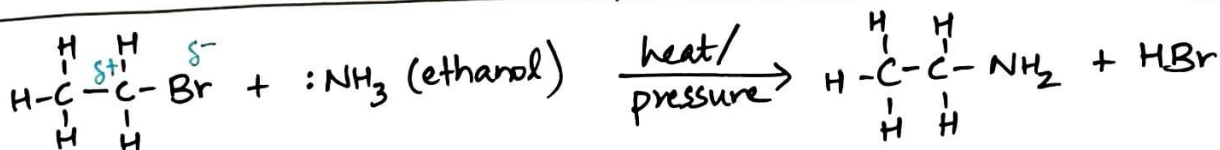
REACTIONS OF ESTERS

1) HYDROLYSIS

- using dilute acid + heat under reflux (reversible)
- using dilute alkali + heat under reflux (irreversible)

PRODUCTION OF AMINES

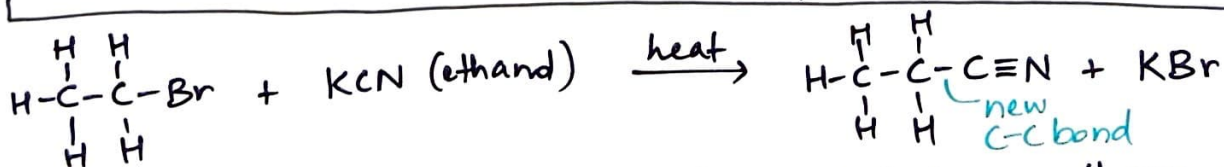
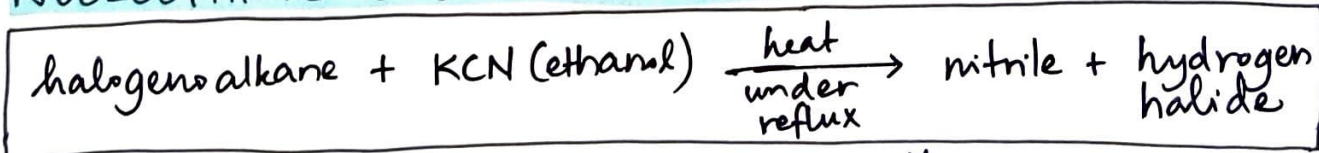
1) NUCLEOPHILIC SUBSTITUTION OF HALOGENOALKANES



- halogen atom more electronegative than C atom \therefore draws e^- density. $\text{C} = \delta^+$ & $\text{X} = \delta^-$ charge
- lone pair of e^- on N in NH_3 = nucleophile; it attacks δ^+ C.
- C-X bond broken & halogen substituted by $-\text{NH}_2$ grp.

PRODUCTION OF NITRILES

1) NUCLEOPHILIC SUBSTITUTION OF HALOGENOALKANES



- * KCN (ethanol) heated under reflux w/ halogenoalkane = nitrile
- KCN (aq) heated under reflux w/ halogenoalkane = alcohol

PRODUCTION OF HYDROXYNITRILES

1) NUCLEOPHILIC ADDITION OF ALDEHYDES & KETONES

REACTIONS OF NITRILES

1) HYDROLYSIS

a) using dil. acid

b) using dil. alkali + acidification

NOTE: formation of nitriles adds an extra C atom; hydrolysis of nitriles doesn't change no. of C atoms.