Alcohols

WHAT ARE ALCOHOLS ?

- → -OH group
- → $C_nH_{2n+1}OH$
- → used as solvent for perfumes, manufacture of plastics, as a fuel.
- → when naming, prefix = 'hydroxy' if in carboxylic acid.
- → other wise, -OH in lowest C number
- → 1°, 2°, 3°, see how many alkyl group on C containing -OH

PHYSICAL PROPERTIES

- → bp ↑, solubility in water ↑
  - ↳ ∵ -OH group can form H-bonds w/ alcohol or H_2O molecules
- → molecular mass ↑, solubility ↓
  - ↳ solubility ↓ when no. of C ↑
  - ↳ C-H chain (non-polar part) ↑, solubility ↓ ∴ less polar
- → "straight" chain isomers bp ↑, ∵ vdw ↑

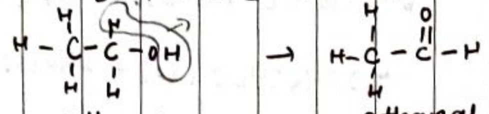
CHEMICAL PROPERTIES

- → O atom has 2 lone pairs ∴ alcohol is
  - → weak base
  - → proton acceptor } base = lp donor/ H^+ acceptors
  - → nucleophile
- → can use lone pair e^- to attack +ve centres
- → can undergo oxidation, elimination, substitution.

OXIDATION (1° alcohols)

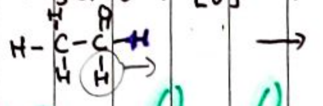
- → 1° & 2° undergo oxidation
- → 3° not oxidized (must have H & OH on a C to oxidise)
- → 1° alcohol → aldehyde → carboxylic acid

→ $C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$



ethanal ← further oxidised

→ $CH_3CHO + [O] \rightarrow CH_3COOH + H_2O$ ethanoic acid

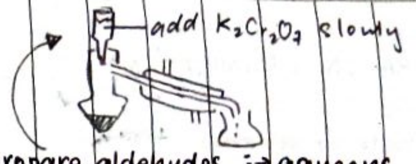


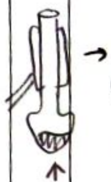
* do not use $KMnO_4$, cuz too strong, will directly become carboxylic acid.

* turns from orange to green

* redox reaction.

- → to prepare aldehydes ∴ aqueous $K_2Cr_2O_7$ in dilute H_2SO_4
  - → continuous distillation + heat
- → to prepare carboxylic acids : → excess aqueous $K_2Cr_2O_7$ in dilute H_2SO_4
  - → heat under reflux

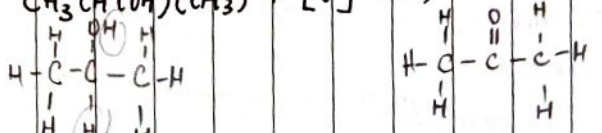




→ aldehyde condenses back into mixture & gets oxidised further.

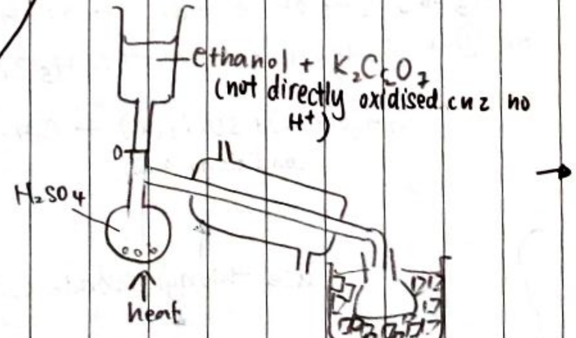
OXIDATION (2° alcohols)

- → 2° alcohols → ketone
- → $CH_3CH(OH)(CH_3) + [O] \rightarrow CH_3COCH_3 + H_2O$



- → conditions : aqueous $K_2Cr_2O_7$ in dilute H_2SO_4, heat under reflux.

OXIDATION OF 1° ALCOHOL TO ALDEHYDE

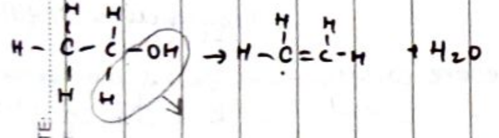


- → H_2SO_4 add to H_2O slowly to avoid acid spray (highly exothermic)
- → anti-bumping granules, prevent sudden formation of large bubbles, or else 'bumping' ⇒ spill
- → ethanal bp ⇒ 21°C, ∴ ice to reduce evaporation.
- → alcohol + dichromate add slowly to avoid ~~an~~ excess of oxi agent
- → not possible to prevent oxi to ethanoic acid 100% cuz easily oxidised.
- → in industry, use vapour phase oxidation of ethanol using air over heated silver cataly.
  - ↳ cuz sodium dichromate toxic & expensive
  - ↳ no separation needed.

Alcohols

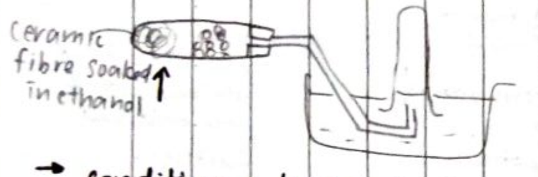
DEHYDRATION (ELIMINATION)

- → alcohols → alkones
- → $C_2H_5OH \rightarrow CH_2=CH_2 + H_2O$



$H-CH_2-CH_2-OH \rightarrow H-CH=CH-H + H_2O$

- → conditions : excess conc. H_2SO_4, 170°C
- → in lab :



liquid dehydrating agent

Solid dehydrating agent

- → conditions : Heat & aluminium oxide (pumice) catalyst
- → H must next to OH
- → OH in middle can have 2 ways of losing H_2O, but no major / minor.
- → can have cis trans.

COMBUSTION

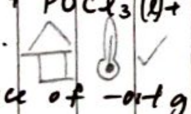
- → $C_2H_5OH + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(l)$
  - → ↑ enthalpies of combustion
  - → no sulphur ∴ less pollution
  - → from renewable resources.

ALCOHOL + SODIUM → H_2 + SALT

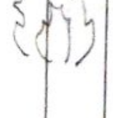
- → $2CH_3CH_2OH(l) + 2Na(s) \rightarrow 2CH_3CH_2ONa + H_2(g)$
  (alc)
  (white solid)
- → reaction slower w/ alcohol than H_2O

HALOGENATION (SUBSTITUTION)

- → alcohol → chloroalkanes
- → $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3(l) + HCl$ (steamy fumes)
- → conditions : dry, room temp.



- → PCl_5 used to test for presence of -OH group
  不然 react w/ H_2O 的 -OH
- → alcohols → iodoalkanes
- → $2P + 3I_2 \rightarrow 2PI_3$
- → $3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3(l)$
- → heat under reflux.



no other way
- selali 加进去 heat

products need to be separated ∴ to avoid this, use thionyl chloride ($SOCl_2$)

- → alcohols → bromoalkanes
  - ② → $2P + 3Br_2 \rightarrow 2PBr_3$
  - ② → $3C_2H_5OH + PBr_3 \rightarrow 3C_2H_5Br + H_3PO_3$ (RT)
  - OR ① → $C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$ (RT)

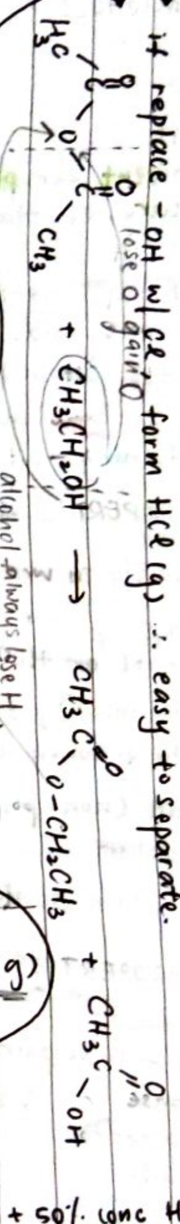
→ conditions, PBr + 50% conc H_2SO_4 (forms HBr), add alcohol at RT then heat (to distil product)

- → $C_2H_5OH(l) + SOCl_2(l) \rightarrow C_2H_5Cl(l) + SO_2(g) + HCl(g)$
  conditions : RT

Either
① - add PBr + 50% conc H_2SO_4 @ room temp, heat under reflux to alcohol (会 form HBr)
② - add alcohol + red P + bromine at room temp, then heat under reflux.

ESTERIFICATION

- → carboxylic acid + alcohol ⇌ ester + H_2O (reversible w/ acid)
- → heat under reflux with conc. H_2SO_4
- → nucleophilic addition then elimination (condensation)
- → if replace -OH w/ Cl, form HCl (g) ∴ easy to separate.
- →

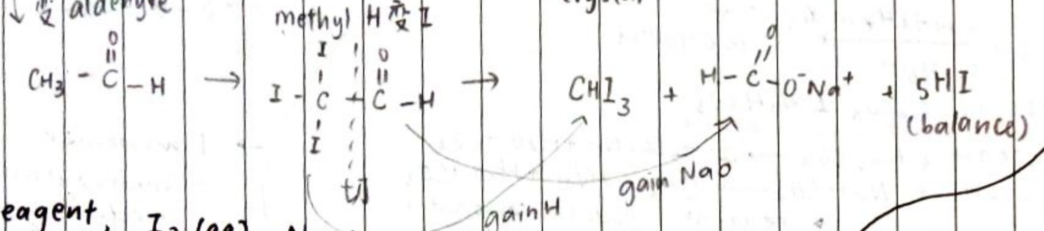


$H_3C-C(=O)-O-CH_3 + CH_3CH_2OH \rightarrow CH_3C(=O)-O-CH_2CH_3 + CH_3C(=O)-OH$

TRI-IODOMETHANE REACTION (IODOFORM)

- → test for $CH_3CH(OH)-$ group ~~(2° alcohol)~~
- → $CH_3CH_2OH + 4I_2 + NaOH \xrightarrow{warm} \underset{\text{yellow crystal}}{CHI_3} + H-C(=O)-O^-Na^+ + 5HI$

↓ 变 aldehyde



$CH_3-C(=O)-H \rightarrow I_3C-C(=O)-H \rightarrow CHI_3 + H-C(=O)-O^-Na^+ + 5HI$

- → reagent, I_2 (aq), NaOH (aq)
- → conditions: warm

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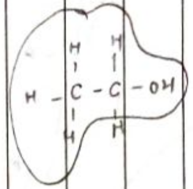

ESTERS

- → only hydrolysis ↓ takes place w/ acid (aq) or alkali (aq)
- → W/ ACID
- → $HCOOCH_2CH_2CH_3 + \overset{\text{hydrolysis add water}}{H_2O} \xrightleftharpoons{H_3O^+} HCOOH + CH_3CH_2CH_2OH$

"main" reagent 是 H_2O

"catalyst" 是 H_3O^+

- → reagent: HCl (aq), heat under reflux
  - ↑ or NaOH (aq) followed by HCl
- → W/ ALKALI
  - → NOT reversible
  - → alcohol & sodium salt of carboxylic acid produced.
  - → $CH_3COOCH_2CH_3 + H_2O \xrightarrow{NaOH} CH_3COO^-Na^+ + CH_3CH_2OH$

    ↓ to remove Na^+ add H^+
  - → reagent: NaOH (aq), heat under reflux.