ALCOHOLS : ORGANIC CHEMISTRY

R – OH

Functional group : –OH

Methanol	CH_3OH
Ethanol	CH_3CH_2OH
Propanol	$CH_3CH_2CH_2OH$
Butanol	$CH_3(CH_2)_3OH$

Alcohol Isomerism:
ie. Butan-1-ol

$CH_3CH_2CH_2CH_2OH$ $\quad$ $CH_3CH_2CH(OH)CH_3$

Positional Isomers

$CH_3CH(CH_3)CH_2OH$ $\quad$ $CH_3C(CH_3)OHCH_3$

Chain isomers

CLASSIFICATION OF ALCOHOLS

Primary (1°) $\quad$ R – CH_2 – OH

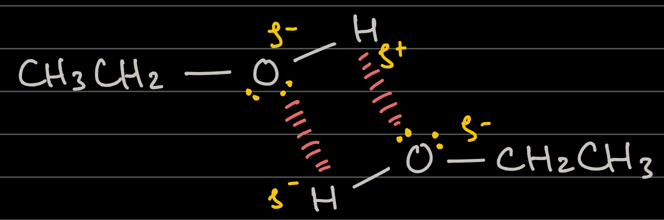
Secondary (2°) $\quad$ R – CH(R') – OH

Tertiary (3°) $\quad$ R – C(R'')(R') – OH

PHYSICAL PROPERTIES

- Main intermolecular force is hydrogen bonding
- Are polar molecules

- Their physical properties arise due to H-bonding



1. Solubility of alcohols in water

- The lower alcohols (C_1 , C_2, C_3 and some isomers of C_4 (butanol) are soluble in water as they form H- bonds with water

- As the length of the carbon chain increases, VDW become the more prominent intermolecular force, and so solubility in water decreases.

2. Boiling Points of alcohols are much higher than the corresponding alkanes due to strong intermolecular H-bonds

- As the carbon chain increases, the boiling point generally increases as the ID-ID intermolecular forces are getting stronger

- The boiling point of a tertiary alcohol is less than a secondary alcohol which is less than that of a primary alcohol
  ↳ as the strength of the H-bonding decreases
  (because in branched molecules, H-bonding is sterically hindered → difficult for other branched alcohol molecule to approach the OH group)

- In 3° alcohols, the OH group is surrounded by methyl groups, which prevent the close approach of other alcohol molecules and therefore inhibit the formation of hydrogen bonds
  (steric hindrance)

PREPARATION OF ALCOHOLS

1. Fermentation

- Source of sugar or glucose
- yeast → enzymes present in yeast help metabolize the sugar
- Optimum temperature for enzymes to work → 37 – 40°C
- water
- Anaerobic conditions (no O_2)
  ↳ so the alcohol does not get oxidised to carboxylic acids

$$C_6H_{12}O_6 \xrightarrow[\text{yeast, } H_2O \;\; 37°C]{\text{no } O_2} \underset{\sim 13\%}{2CH_3CH_2OH} + 2CO_2$$

- fermentation stops when the alcohol concentration is ~13 %, as above this concentration, the mixture denatures (destroys) the enzymes present in yeast
- Fractional distillation is used to make a more concentrated alcohol

Hydration of Alkenes

$$CH_2 = CH_2 + \underset{\text{steam}}{H_2O\,(g)} \xrightarrow[300^\circ C,\ 70atm]{H_3PO_4} \underset{\text{ethanol}}{CH_3CH_2OH}$$

Note: (Drinking) ethanol is made by fermentation of a sugar source – so as to obtain different alcohols of different aromas, tastes and colours

Hydrolysis of Alkyl Halides

$$CH_3CH_2Br + NaOH\,(aq) \longrightarrow CH_3CH_2OH + NaBr$$

Reduction of Aldehydes, Ketones, and Carboxylic Acids (separately)

↳ using a reducing agent

a) Aldehydes

$$\begin{array}{c} R-C-H \\ \| \\ O \end{array} + 2[H] \xrightarrow[rtp]{NaBH_4,\ H_2O} \begin{array}{c} H \\ | \\ R-C-H \\ | \\ OH \end{array}$$ 1° alcohol

b) Ketones

$$\begin{array}{c} R-C-R' \\ \| \\ O \end{array} + 2[H] \xrightarrow[rtp]{NaBH_4,\ H_2O} \begin{array}{c} H \\ | \\ R-C-R' \\ | \\ OH \end{array}$$ 2° alcohol

c) Carboxylic Acids

$$\begin{array}{c} O \\ \| \\ \underline{R-C-OH} \end{array} + 4[H] \xrightarrow[\text{in dry ether, rtp}]{LiAlH_4} \begin{array}{c} H \\ | \\ R-C-OH \\ | \\ H \end{array} + H_2O$$ 1° alcohol

↳ acids require stronger reducing agents

REACTIONS OF ALCOHOLS

Combustion

- lower alcohols burn readily to form CO_2 and H_2O

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Note: when balancing, do not forget the alcohols -OH group oxygen

Nucleophilic Substitution

1. Bromination of Alcohols

Reagent: HBr (g)

But HBr is very toxic, so it is made "in situ" ("in situation")

$$NaBr + \underset{\text{conc.}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2HBr$$

So, basically...

$$CH_3CH_2OH \xrightarrow{[NaBr + H_2SO_4 \text{ conc.}]} CH_3CH_2Br + H_2O$$

$CH_3CH_2 \{ OH$ → The carbon-oxygen has to be broken but the OH is a "poor leaving group" as the C-O bond is very strong

↳ Thus, we need to convert OH into a better leaving group by protonating it (H^+) and making the leaving group H_2O

Not really in our syllabus, but indirect questions are often asked

Dative

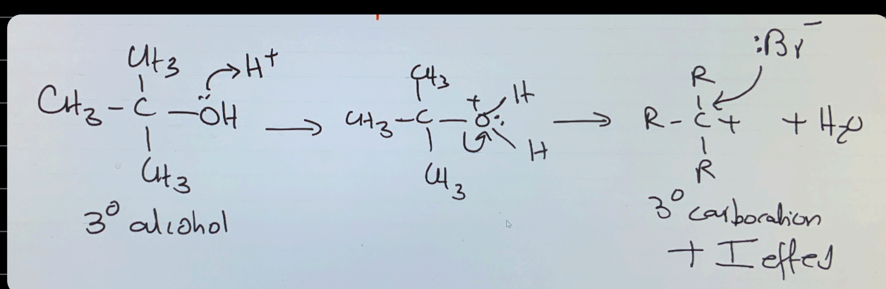
$$CH_3CH_2-\ddot{O}H \xrightarrow{H^+} CH_3CH_2-\overset{+}{O}(H)-H \rightarrow CH_3\overset{+}{C}H_2 + H_2O$$

$:Br^-$ nucleophile

OR

$$CH_3CH_2-\ddot{O}H \xrightarrow{H^+} CH_3CH_2-\overset{+}{O}(H)-H$$

$^-Br:$ nucleophile



2. Chlorination of Alcohols

HCl is NOT used to chlorinate → for explanation refer to "halogens" chapter

A chlorinating agent is used:

- PCl_3 (l) Phosphorous trichloride
- PCl_5 (s) Phosphorous pentachloride
- $SOCl_2$ (l) Thionyl Chloride

PCl_3

$$3CH_3CH_2OH + PCl_3 \xrightarrow{heat} 3CH_3CH_2Cl + \underbrace{H_3PO_3}_{\text{phosphorous acid}}$$

PCl_5

$$CH_3CH_2OH + PCl_5 \xrightarrow{rtp} CH_3CH_2Cl + \underbrace{HCl\,(g)}_{\text{white fumes}} + \underbrace{PCl_3O}_{\text{phosphorous trichloride oxide}}$$

↳ can be used as a test for alcohols, as white fumes are produced

$SOCl_2$

$$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + HCl\,(g) + SO_2\,(g)$$

Best rxn:
↳ Because HCl (g) and SO_2 (g) will escape and CH_3CH_2Cl will be the only product left

HCl → white fumes
SO_2 → is a "reducing agent"
↳ so if a paper dipped in $K_2Cr_2O_7$ / H^+ is held on top of the test tube, it turns blue / green

3. Iodination of Alcohols

Red Phosphorous + I_2 : Reagents
↳ Allotrope of Phosphorous

$$2P + 3I_2 \longrightarrow 2PI_3 \quad \text{(used in situ.)}$$

$$CH_3CH_2OH \xrightarrow{[P + I_2]} CH_3CH_2I$$

$$CH_3CH_2OH + PI_3 \longrightarrow 3CH_3CH_2I + H_3PO_3$$

SUMMARY of Reagents

Chlorination : PCl_3, PCl_5, or $SOCl_2$
Bromination : HBr → (NaBr + conc. H_2SO_4 in situ.)
Iodination : PI_3 → (Red P + I_2 in situ.)

Reactions of Alcohols with Metals

↳ Alcohols react with metals to form salt and hydrogen gas

$$CH_3CH_2OH + Na \xrightarrow{rtp} \underbrace{CH_3CH_2O}_{}Na + \frac{1}{2}H_2(g)$$

ethoxide ion

sodium ethoxide

$$R-OH + Na \xrightarrow{rtp} [RO]^- [Na]^+ + \frac{1}{2}H_2$$

Note: Alcohols do <u>not</u> react with alkalis

Ex: $2CH_3CH_2OH + Mg \longrightarrow (CH_3CH_2O)_2Mg + H_2$

Magnesium Ethoxide

Dehydration of Alcohols

↳ produces alkenes

$$CH_2CH_2 + H_2O(g) \xrightarrow[300°C,\ 70atm]{H_3PO_4} CH_3CH_2OH$$

steam

→ This was hydration of alkenes that produced an alcohol, hence going backwards in this reaction, ie dehydrating an alcohol would produce an alkene

a) Using Al_2O_3 as a catalyst

$$CH_3CH_2OH \xrightarrow[heat]{Al_2O_3} CH_2=CH_2 + H_2O$$

non-polar

↳ hence can be collected over water (downward displacement)

b) Using conc. H_2SO_4 as a dehydrating agent

$$CH_3CH_2OH \xrightarrow[180°C]{conc.\ H_2SO_4} CH_2=CH_2 + H_2O$$

Oxidation of Alcohols

↳ requires an oxidising agent

1. $K_2Cr_2O_7 / H^+(aq)$ → Acidified Potassium (VI) Dichromate

(orange)

reduced ↓

Cr^{3+} (green)

2. $KMnO_4 / H^+$ (aq) $\longrightarrow$ Acidified Potassium (VII) Manganate

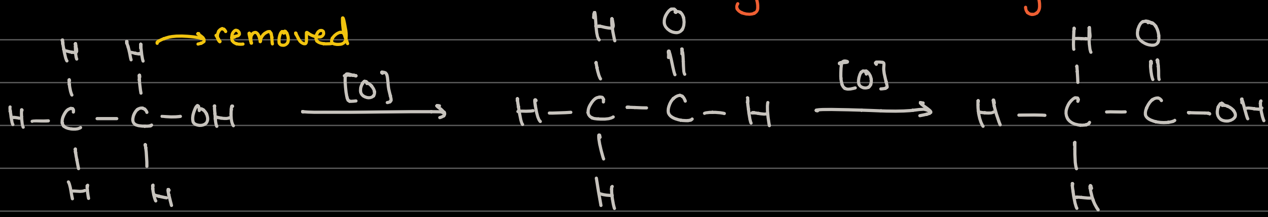
$\downarrow$ reduced (purple)

Mn^{2+} (colorless)

- Oxidation of an alcohol involves the removal of a hydrogen atom from the carbon atom bonded to the OH group

- The reaction depends on the position of the OH group

1° alcohols $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ Carboxylic Acid



1° alcohol — ethanal — ethanoic acid

$CH_3CH_2OH \xrightarrow{K_2Cr_2O_7 / H^+ \text{ heat under reflux}} CH_3COOH$ ethanoic acid

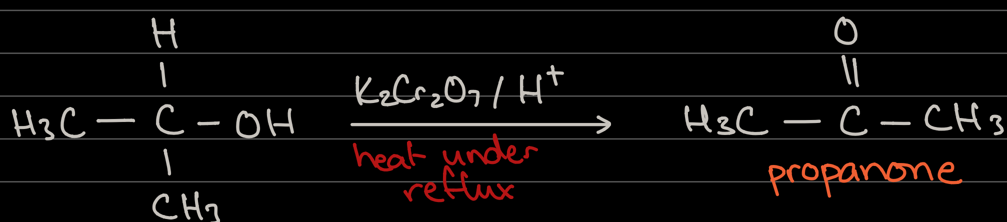
1° alcohol

warm + distill product immediately - - - -> CH_3CHO

ethanal

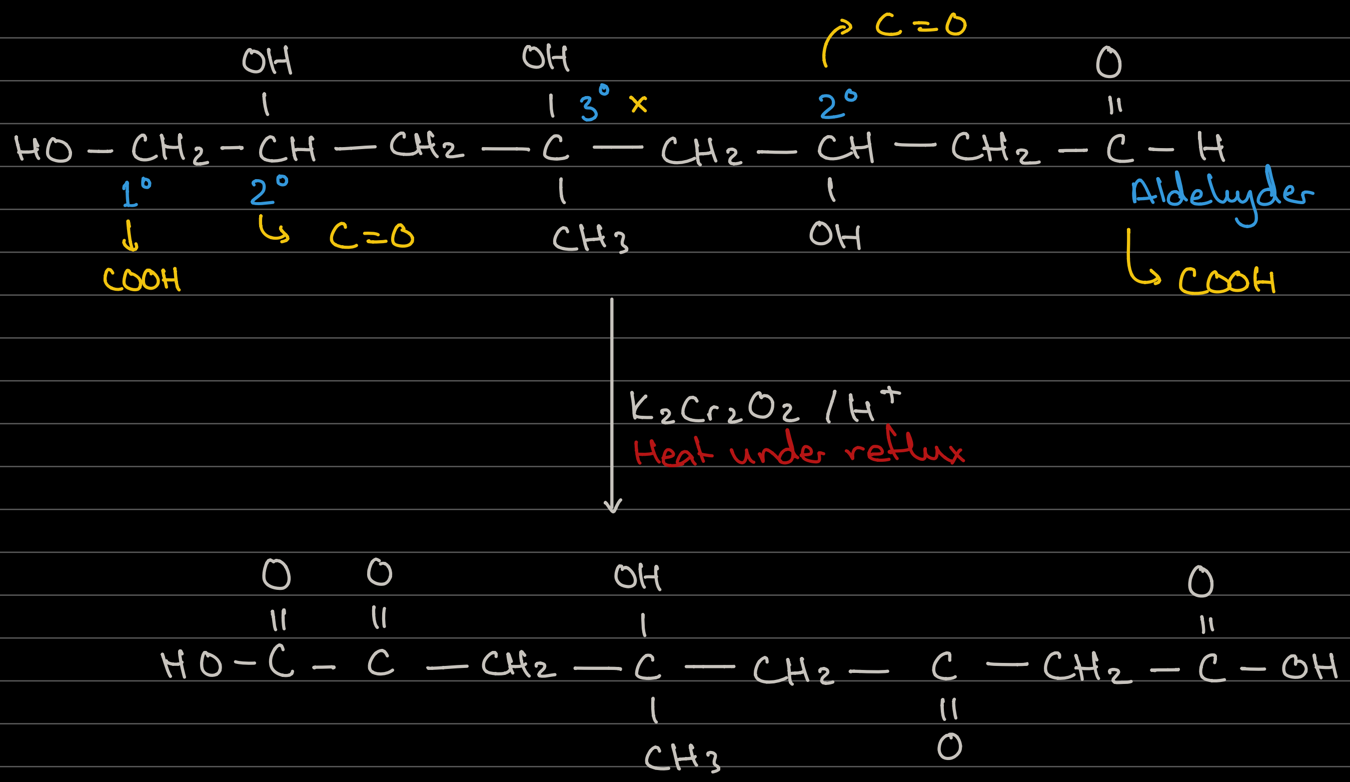
Distills first because both alcohol and carboxylic acid have H-bonds while ethanal only has PD-PD forces

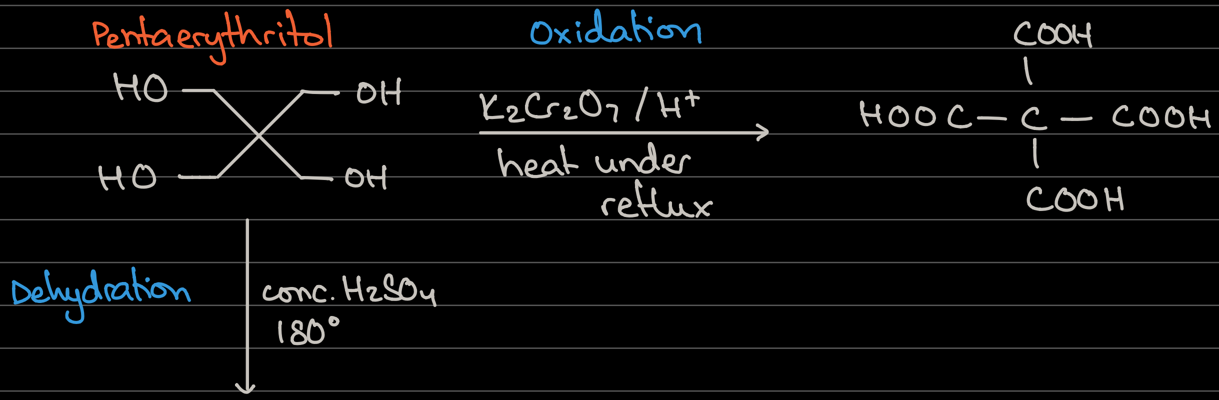
2° alcohols $\xrightarrow{[O]}$ Ketones only



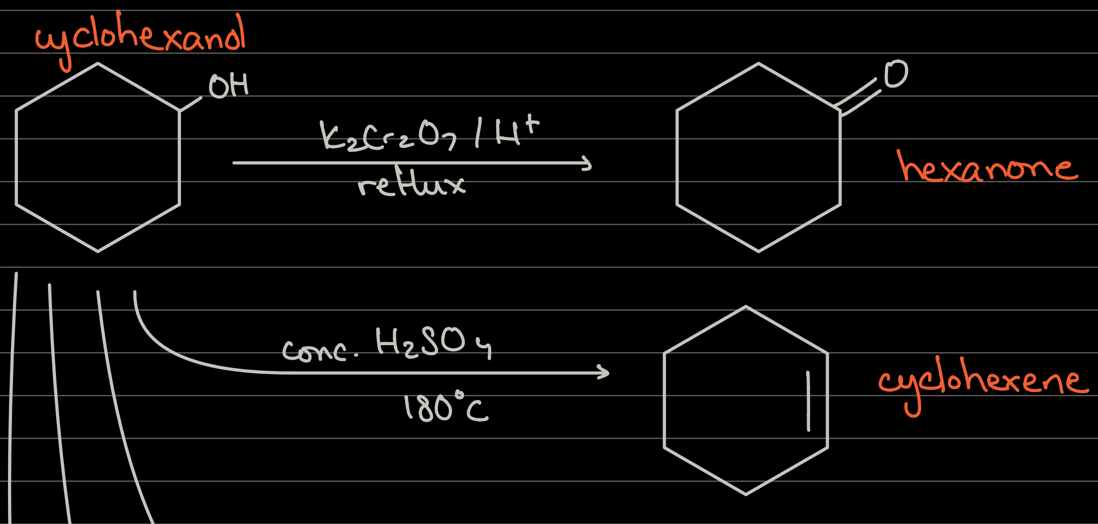
2° alcohols — propanone

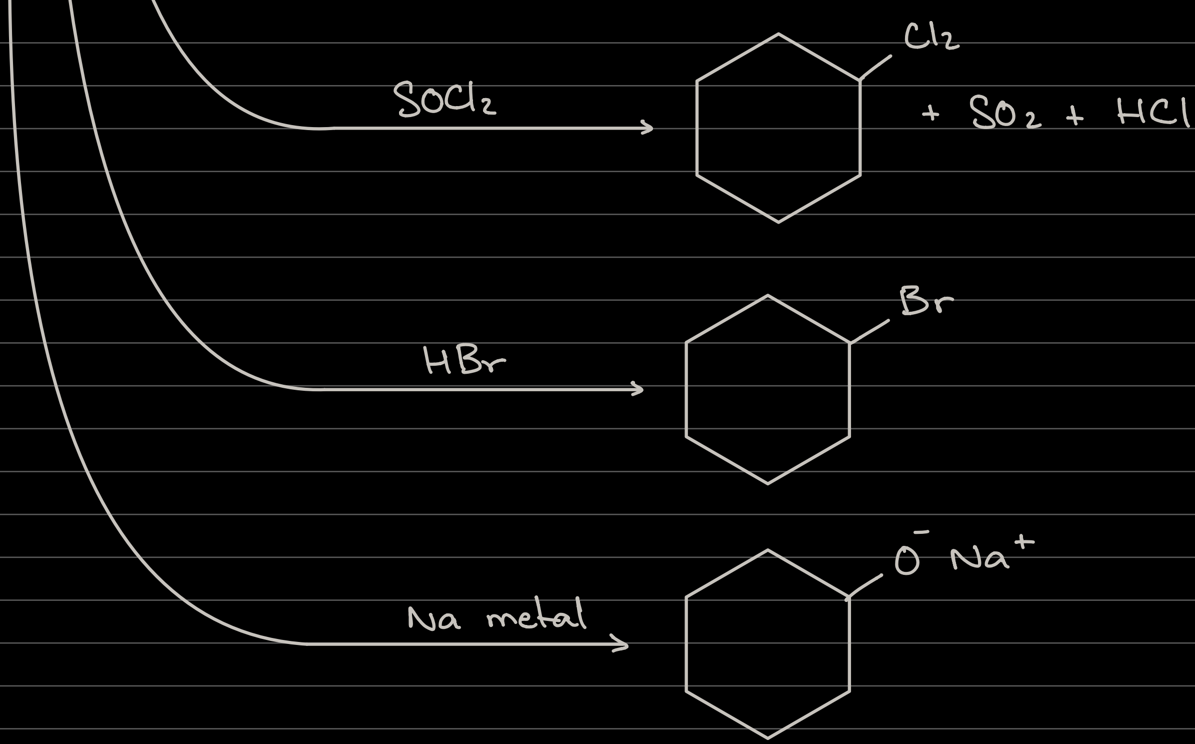
3° alcohols $\xrightarrow{[O]}$ No Rxn





No RXN
→ will not undergo dehydration
→ carbon cannot form 4 double bonds
+ Adjacent (central) carbon has no Hs to lose





with more than one OH group

POLYHYDRIC ALCOHOLS and their uses

one OH : Monohydric
two OH : Dihydric
three OH : Trihydric
>3 OH : Polyhydric

$HO-CH_2-CH_2-OH$ — ethane-1,2-diol or 1,2-ethanediol

"antifreeze"

↳ added to car coolant systems

- Also used in the manufacture of polyester fabric (Terylene)

$HO-CH_2-CH(OH)-CH_2-OH$ — propane-1,2,3-triol aka. "glycerol"

- Highly viscous
- lots of H-bonding
- found in nature as part of fats + oils

$$HO-CH_2-CH_2-OH \xrightarrow{\text{dehyd.}} HO-CH=CH_2$$

this is left like this and not oxidised further

However, if there are more carbons between the two OH groups...

$$HO-CH_2-CH_2-CH_2-CH_2-OH \xrightarrow{\text{dehyd.}} CH_2=CH-CH=CH_2$$

However...

$$HO-CH_2-CH_2-CH_2-OH \xrightarrow{\text{dehyd.}} CH_2=CH-CH_2-OH$$

we avoid forming consecutive double bonds, so we're going to leave it like this.

Iodoform test for Alcohols

Reagents : [I_2 (aq), NaOH (aq)] → together, this is known as "alkaline aqueous iodine"

- Alcohols that have a methyl group ($-CH_3$), a hydrogen atom ($-H$) on the same carbon that bears the $-OH$ group can be oxidised by alkaline aqueous iodine to the corresponding carbonyl compound ($-\overset{O}{\overset{\|}{C}}-$)

- The reaction goes through multiple substitutions + bond fissions to produce the sodium salt of a carboxylic acid and triiodomethane (CHI_3) aka. "Iodoform"

$$\boxed{CH_3}-\underset{|}{\overset{\boxed{OH}}{\boxed{CH}}}-CH_2-CH_3$$

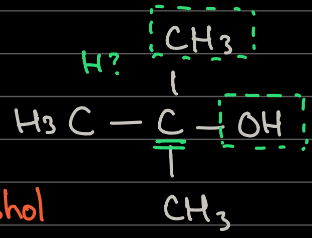
2° alcohol

Hence, fits the criteria above, and will return a positive iodoform test

$$\underbrace{CH_3-CH_2}_{\text{not methyl}}-\overset{\boxed{OH}}{\boxed{CH}}-\underbrace{CH_2-CH_3}_{\text{not methyl}}$$

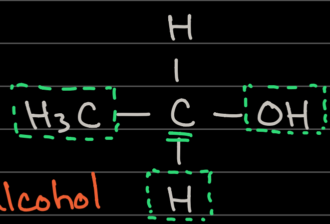
2° alcohol

→ does not have a methyl group attached and hence, fails the above criteria and will return a negative iodoform test



3° alcohol

→ does not have a hydrogen atom attached and hence fails the iodoform test.



1° alcohol

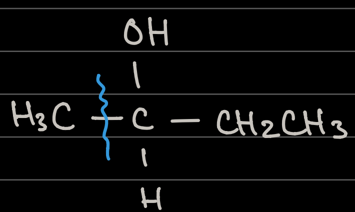
→ fulfills criteria
returns a positive iodoform test

- No 3° alcohols will give a positive iodoform test.
- Only 2° methyl alcohols will give a positive iodoform test.
- Ethanol is the only primary alcohol that gives a positive iodoform test

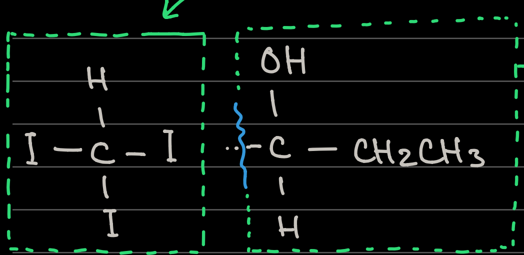
But what is a positive iodoform test ?

$CH_3CH(OH)CH_2CH_3 + 4I_2\,(aq) + 6NaOH \longrightarrow CHI_3\,(s) + CH_3CH_2COONa + 5NaI + 5H_2O$

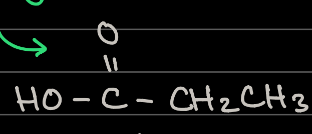
- triiodomethane
- pale yellow ppt.
- antiseptic odour



- $-CH_3$ group breaks off and gets substituted with I_2 → CHI_3

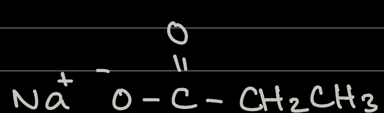


→ oxidised to carboxylic acid



propanoic acid

aq. NaOH

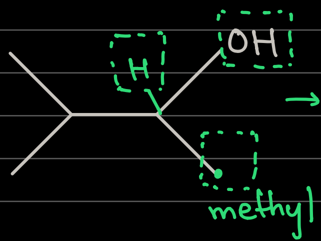


sodium propanoate salt

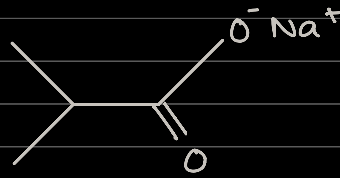
CH_3CH_2COONa

Examples.

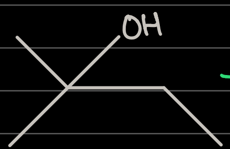
For each of the following alcohols, indicate whether or not it will give a positive iodoform test and if yes, what will be product?

i) 

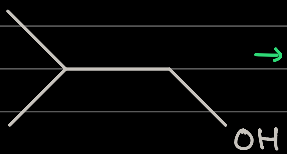
→ will give positive iodoform test

and product will be : 

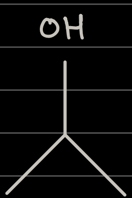
$+ CHI_3 (s)$

ii) 

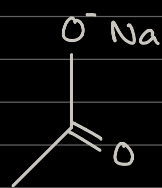
→ will not return a positive iodoform test

iii) 

→ will not return a positive iodoform test

iv) 

→ will return a positive iodoform test

and the product will be : 

$+ CHI_3 (s)$

BIOFUELS

↳ are alternatives to fossil fuels

- They are produced from plants (ie. corn)
- They are called "carbon neutral", meaning that the CO_2 that is released during the burning of this fuel is used up again in the production of more of these fuels (plants absorb CO_2 as part of photosynthesis)
- Examples of biofuels include
  - Gasohol (10% ethanol + 90% petrol)

X — END OF: ALCOHOLS — X