

# ALCOHOLS : ORGANIC CHEMISTRY

R - OH

Functional group : - OH

|          |  |
|----------|--|
| Methanol | CH <sub>3</sub> OH                                 |
| Ethanol  | CH <sub>3</sub> CH <sub>2</sub> OH                 |
| Propanol | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH |
| Butanol  | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH |

Alcohol Isomerism :

i.e. Butan-1-ol



↳ Positional Isomers ↳



↳ Chain Isomers ↳

## CLASSIFICATION OF ALCOHOLS

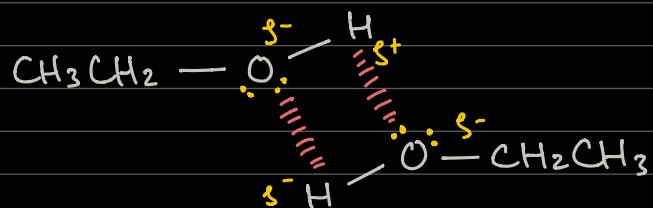
Primary ( $1^\circ$ )      R - CH<sub>2</sub> - OH

Secondary ( $2^\circ$ )      R -  $\begin{matrix} \text{CH} \\ | \\ \text{R''} \end{matrix}$  - OH

Tertiary ( $3^\circ$ )      R -  $\begin{matrix} \text{C} \\ | \\ \text{R''} \\ | \\ \text{R'} \end{matrix}$  - 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.

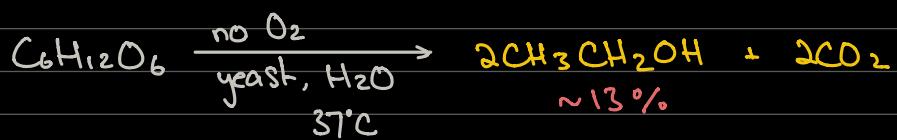
## 2. Boiling Points of alcohols are much higher than the corresponding alkanes due to strong intermolecular H-bonds

- 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  $3^\circ$  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

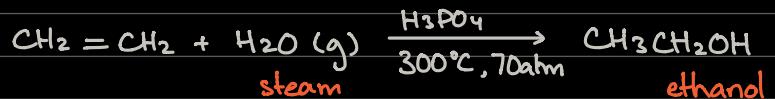
### 1. Fermentation

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



- 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



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

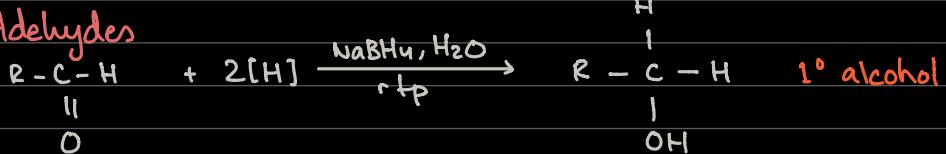
### Hydrolysis of Alkyl Halides



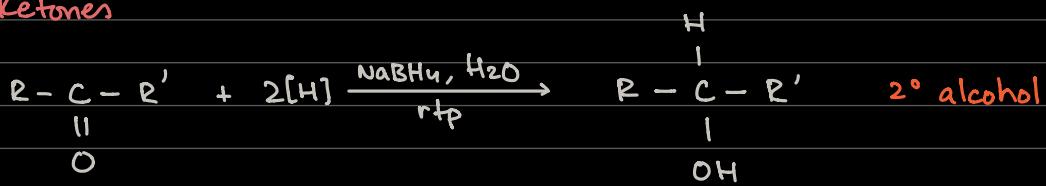
### Reduction of Aldehydes, Ketones, and Carboxylic Acids (separately)

↳ using a reducing agent

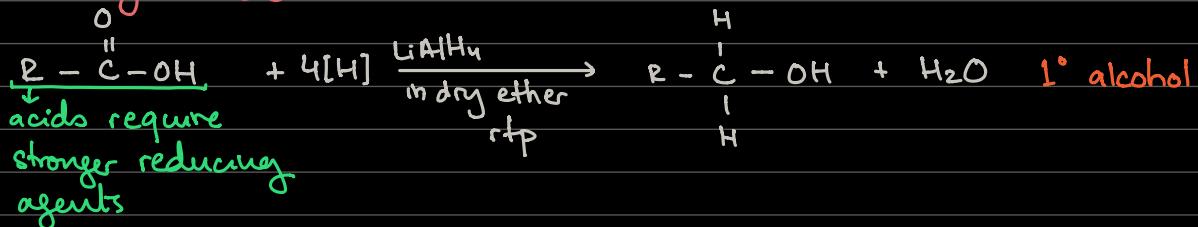
#### a) Aldehydes



#### b) Ketones



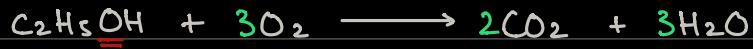
#### c) Carboxylic Acids



# REACTIONS OF ALCOHOLS

## Combustion

- lower alcohols burn readily to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$



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

## Nucleophilic Substitution

### 1. Bromination of Alcohols

Reagent:  $\text{HBr}$  (g)

But  $\text{HBr}$  is very toxic, so it is made "in situ" ("in situation")



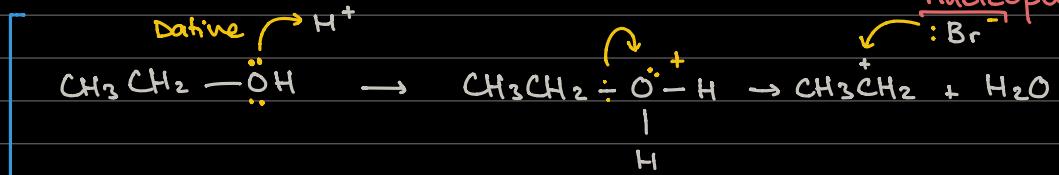
So, basically...



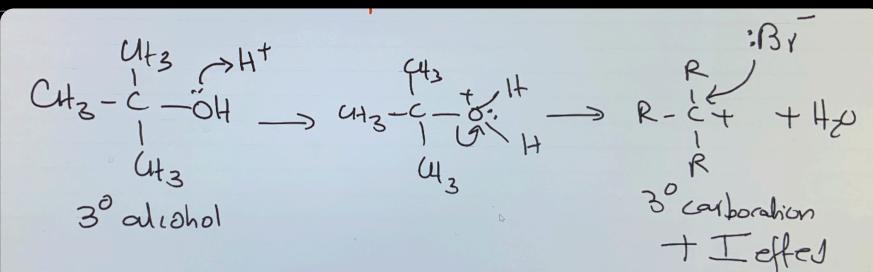
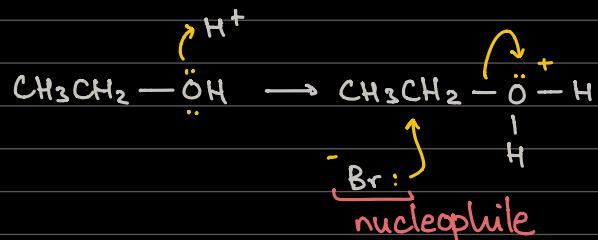
$\text{CH}_3\text{CH}_2-\ddot{\text{O}}\text{H} \rightarrow$  The carbon-oxygen has to be broken but the OH is a "poor leaving group" as the C-O bond is very strong

↳ Thus, we need to convert OH into a better leaving group by protonating it ( $\text{H}^+$ ) and making the leaving group  $\text{H}_2\text{O}$  nucleophile

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



OR



## 2. Chlorination of Alcohols

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

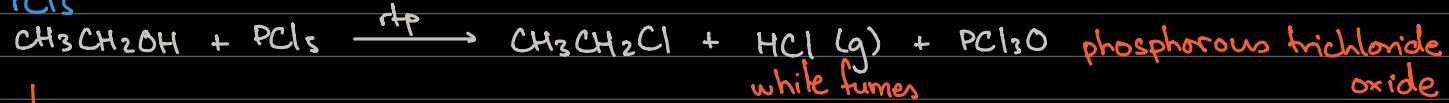
A chlorinating agent is used:

- $\text{PCl}_3$  (l) Phosphorous trichloride
- $\text{PCl}_5$  (s) Phosphorous pentachloride
- $\text{SOCl}_2$  (l) Thionyl Chloride

$\text{PCl}_3$



$\text{PCl}_5$



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

$\text{SOCl}_2$



Best rxn:

↳ Because  $\text{HCl(g)}$  and  $\text{SO}_2\text{(g)}$  will escape and  $\text{CH}_3\text{CH}_2\text{Cl}$  will be the only product left

$\text{HCl} \rightarrow$  white fumes

$\text{SO}_2 \rightarrow$  is a "reducing agent"

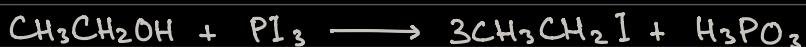
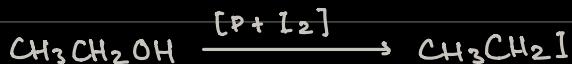
↳ so if a paper dipped in  $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$  is held on top of the test tube, it turns blue/green

## 3. Iodination of Alcohols

Red Phosphorous +  $\text{I}_2$  : Reagents

↳ Allotrope of

Phosphorous



## SUMMARY of Reagents

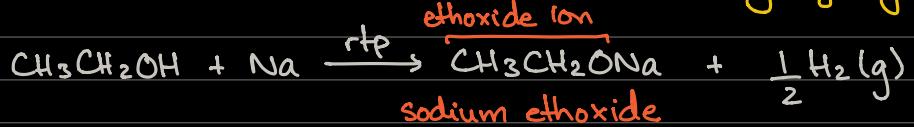
Chlorination :  $\text{PCl}_3$ ,  $\text{PCl}_5$ , or  $\text{SOCl}_2$

Bromination :  $\text{HBr} \rightarrow (\text{NaBr} + \text{conc. H}_2\text{SO}_4 \text{ in situ.})$

Iodination :  $\text{PI}_3 \rightarrow (\text{Red P} + \text{I}_2 \text{ in situ.})$

## Reactions of Alcohols with Metals

↳ Alcohols react with metals to form salt and hydrogen gas

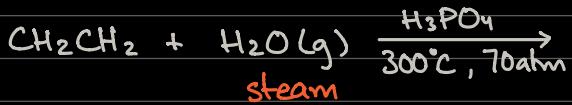


Note: Alcohols do not react with alkalis



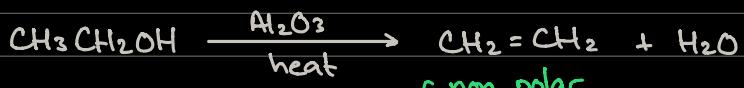
## Dehydration of Alcohols

↳ produces alkenes



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  $\text{Al}_2\text{O}_3$  as a catalyst



(non-polar)

↳ hence can be collected over water (downward displacement)

b) Using conc.  $\text{H}_2\text{SO}_4$  as a dehydrating agent

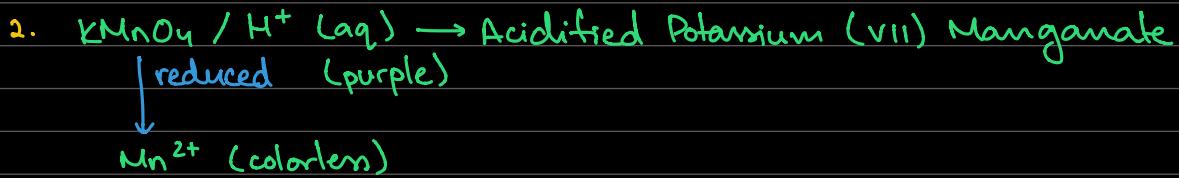


## Oxidation of Alcohols

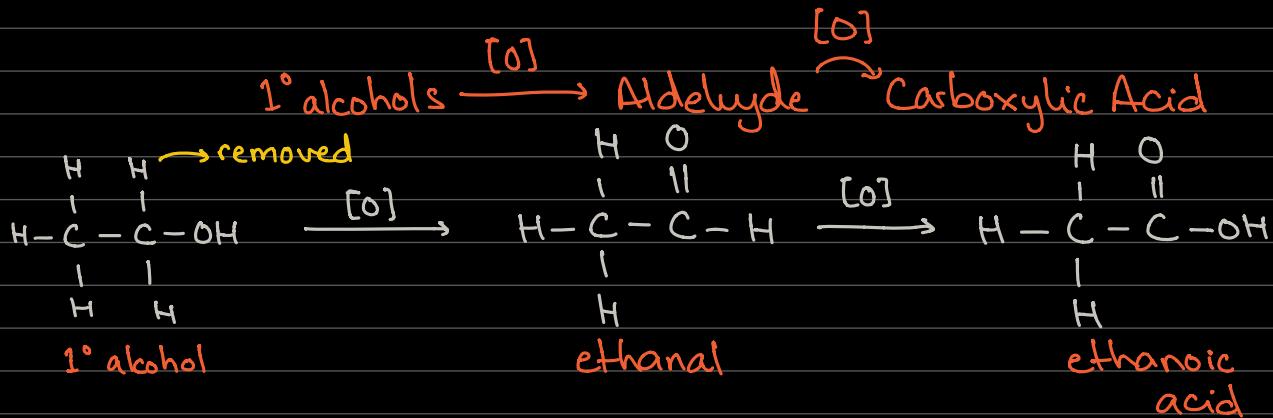
↳ requires an oxidising agent

1.  $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+(\text{aq}) \rightarrow$  Acidified Potassium (VI) Dichromate

$\downarrow$   
reduced (orange)  
 $\text{Cr}^{3+}$  (green)

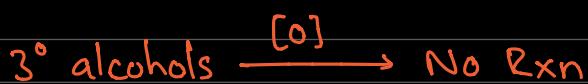
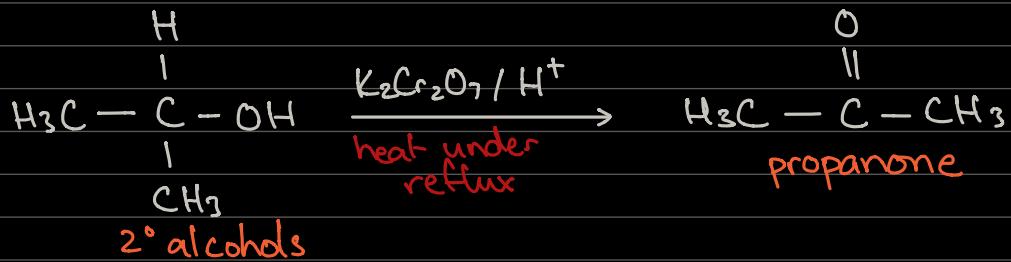


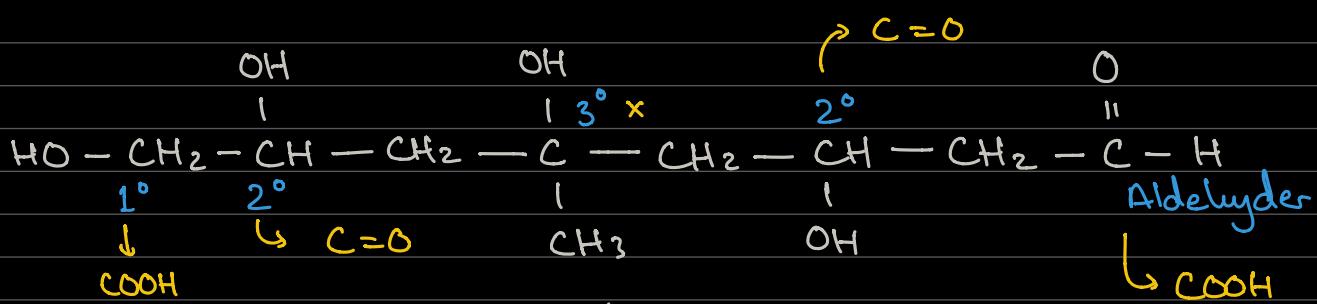
- Oxidation of an alcohol involves the removal of a hydrogen atom from the carbon atom bonded to the OH group
- The reaction depends on the position of the OH group



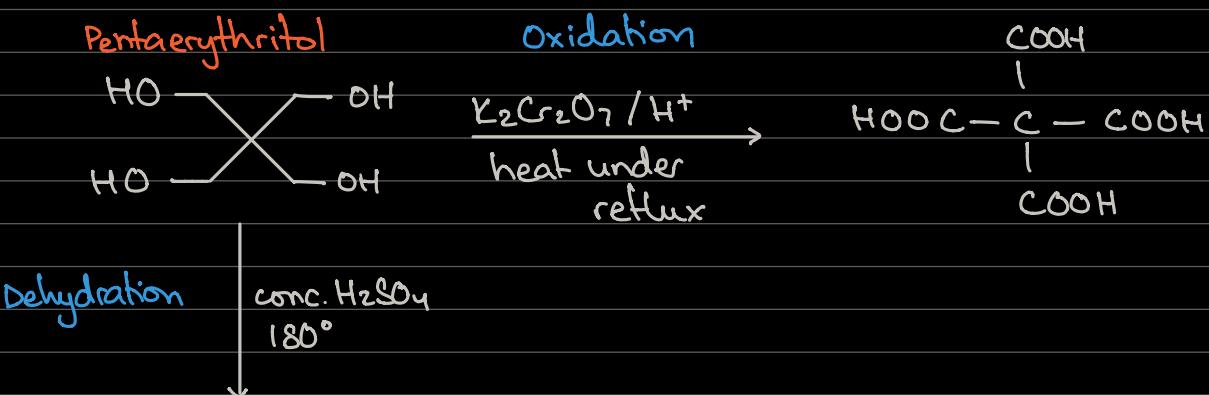
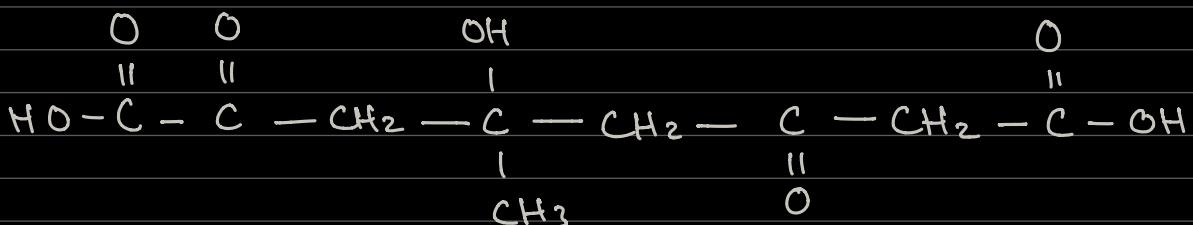
warm +  
distill product ----->  $\text{CH}_3\text{CHO}$   
 immediately                              ethanal

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

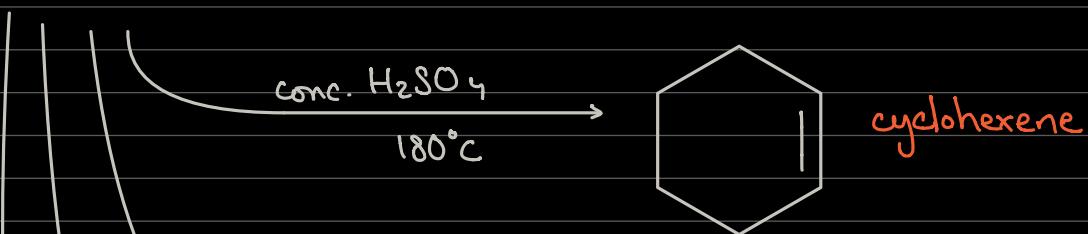
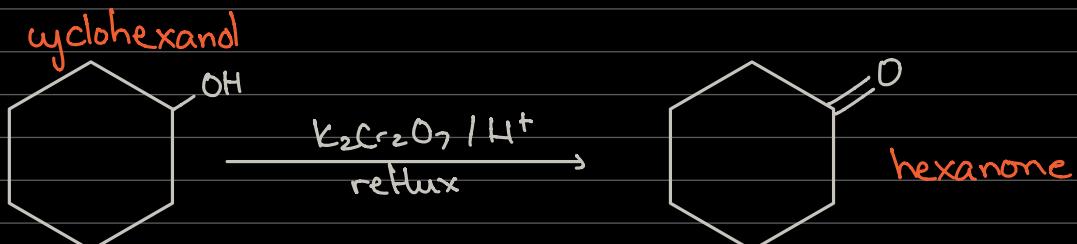


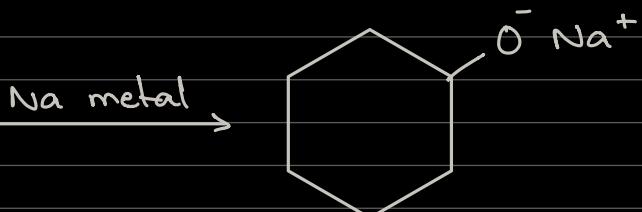


$K_2Cr_2O_7 / H^+$   
Heat under reflux



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





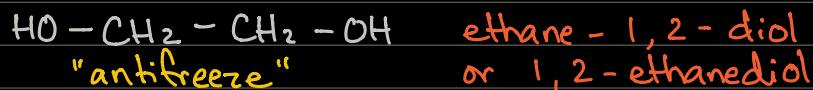
→ with more than one OH group  
**POLYHYDRIC ALCOHOLS** and their uses

one OH : Monohydric

two OH : Dihydric

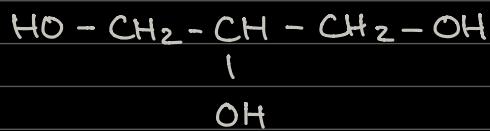
three OH : Trihydric

>3 OH : Polyhydric



↳ added to car coolant systems

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



propane - 1, 2, 3 - triol  
aka. "glycerol"

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



this is left like this  
and not oxidised further

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



However...

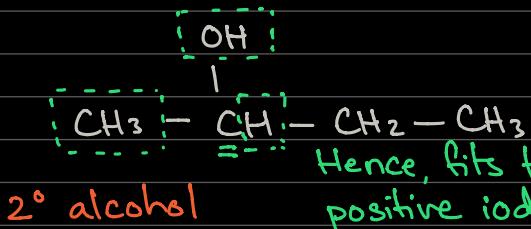


we avoid forming  
consecutive double bonds,  
so we're going to leave it  
like this.

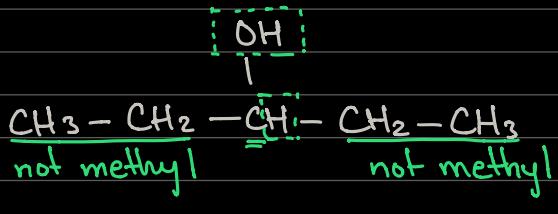
### Iodoform test for Alcohols

Reagents:  $[\text{I}_2 \text{ (aq)}, \text{NaOH (aq)}]$  together, this is known as  
"alkaline aqueous iodine"

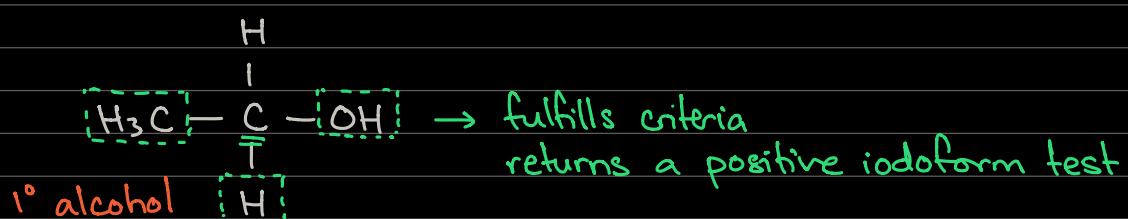
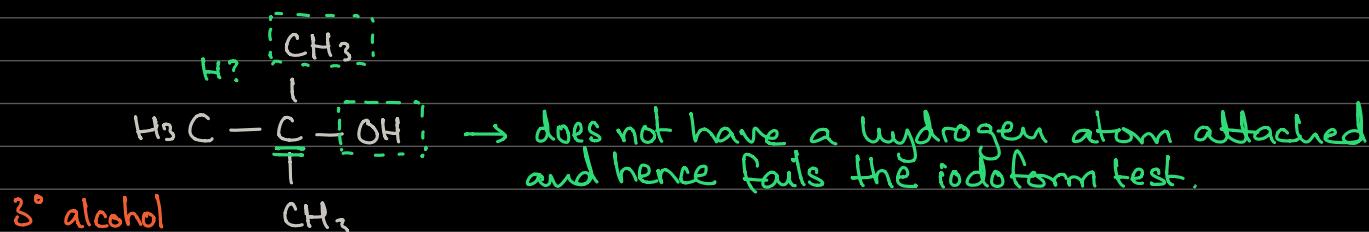
- Alcohols that have a methyl group ( $-\text{CH}_3$ ), a hydrogen atom ( $-\text{H}$ ) on the same carbon that bears the  $-\text{OH}$  group can be oxidised by alkaline aqueous iodine to the corresponding carbonyl compound ( $-\text{C}-$ )
- The reaction goes through multiple substitutions + bond fissions to produce the sodium salt of a carboxylic acid and triiodomethane ( $\text{CHI}_3$ ) aka. "iodoform"



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

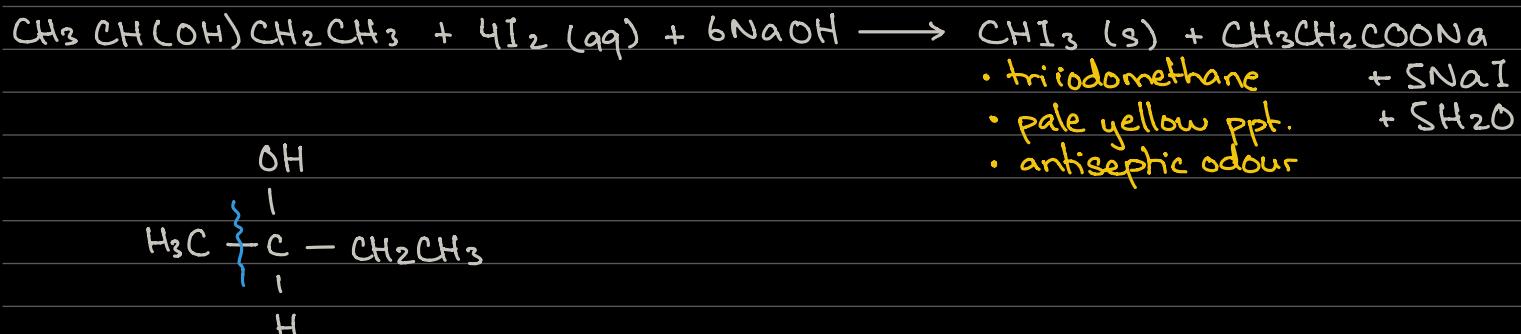


→ does not have a methyl group attached and hence, fails the above criteria and will return a negative iodoform test

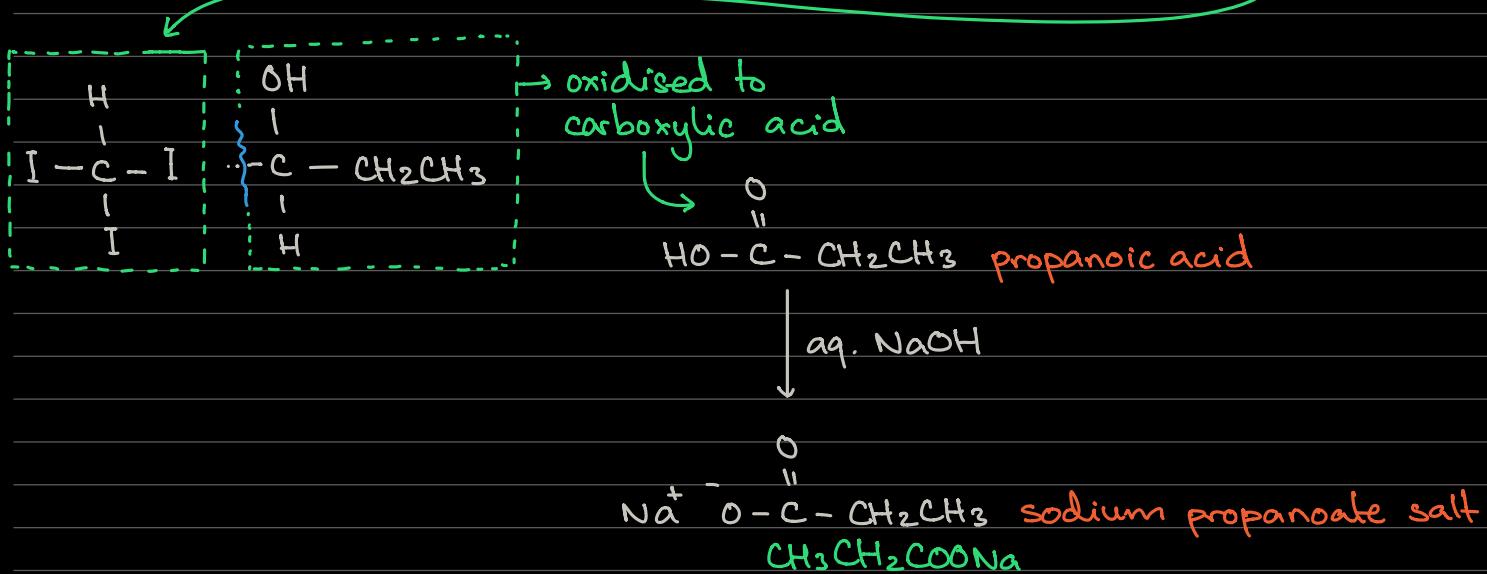


- No 3° alcohols will give a positive iodoform test.
- Only 2° methyl alcohols will give a positive iodoform test.
- Ethanol is the only primary alcohol that gives a positive iodoform test

But what is a positive iodoform test?

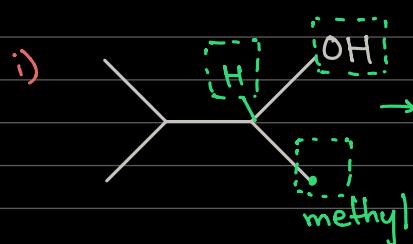


-  $\text{CH}_3$  group breaks off and gets substituted with  $\text{I}_2 \rightarrow \underline{\text{CHI}_3}$



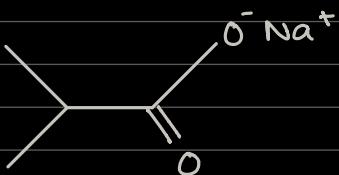
Examples.

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

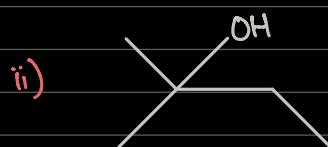


→ will give positive iodoform test

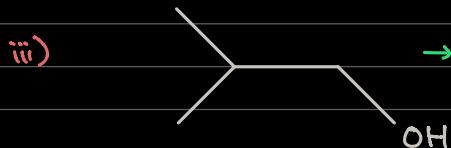
and product will be :



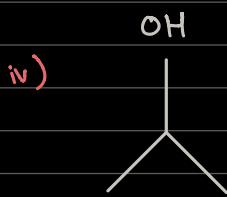
+  $\text{CHI}_3(s)$



→ will not return a positive iodoform test

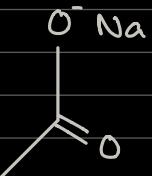


→ will not return a positive iodoform test



→ will return a positive iodoform test

and the product will be :



+  $\text{CHI}_3(s)$

## BIOFUELS

↳ are alternatives to fossil fuels

- They are produced from plants (i.e. corn)
- They are called "carbon neutral", meaning that the  $\text{CO}_2$  that is released during the burning of this fuel is used up again in the production of more of these fuels (plants absorb  $\text{CO}_2$  as part of photosynthesis)
- Examples of biofuels include
  - Gasohol (10% ethanol + 90% petrol)