Monday, 22 January 2024

Dehydration of Alcohols

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Learning Objective

- Understand the products of dehydration of alcohols

Success Criteria

- Identify and describe other reactions of alcohols.
- Explain what is meant by *dehydration*.
- Outline and draw the mechanism for dehydration of alcohols via elimination mechanism.
- State Zaitsev's rule.
- Apply Zaitsev's rule in predicting the products of dehydration of alcohols.

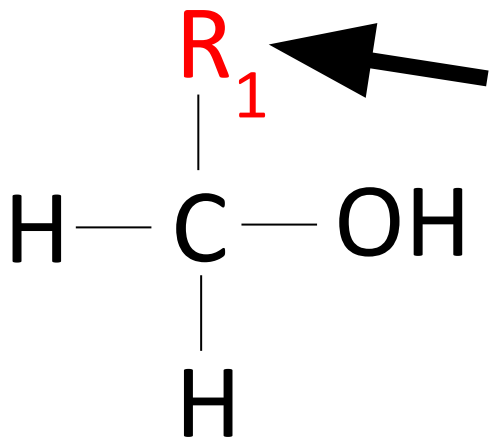
Keywords

- Primary, secondary, tertiary alcohols
- Carbocation
- Carbocation stability
- Dehydration
- Elimination mechanism
- Zaitsev’s rule

Recall: Classification of Alcohols

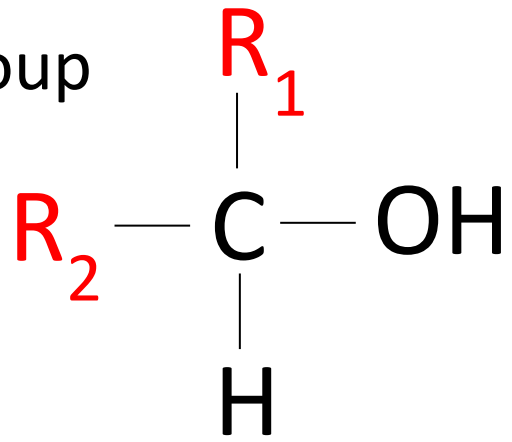
Alcohols have the functional group **–OH** (hydroxyl) in its homologous series

Primary Alcohols (1°)



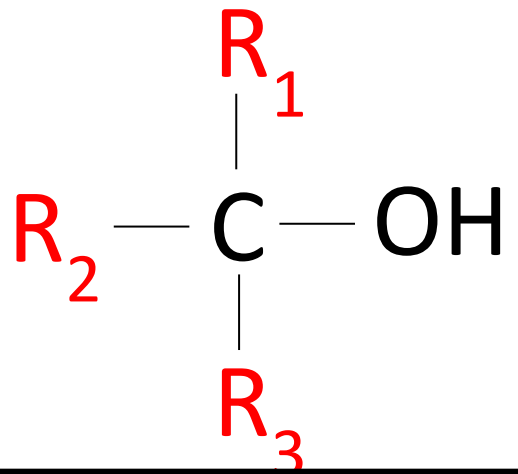
Butan-1-ol
$CH_3CH_2CH_2CH_2OH$

Secondary Alcohols (2°)



Butan-2-ol
$CH_3CH_2CH(OH)CH_3$

Tertiary Alcohols (3°)



2-methylpropan-2-ol
$CH_3C(CH_3)(OH)CH_3$

Reactions of the alcohols

1 Combustion

When ignited, the alcohols react with oxygen in the air. The products of complete combustion are carbon dioxide and water. For example, ethanol burns with a clean blue flame in a good supply of air:

$$\text{alcohol} + \text{oxygen} \longrightarrow \text{carbon dioxide} + \text{water}$$

$$\underset{\text{ethanol}}{C_2H_5OH} + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

2 Substitution to form a halogenoalkane

In this substitution reaction with a hydrogen halide, such as hydrogen chloride, the —OH group in the alcohol is replaced by a halogen atom to produce a halogenoalkane.

Sulfur dichloride oxide, $SOCl_2$

$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + HCl + SO_2$$

phosphorus(V) chloride, PCl_5:

$$C_2H_5OH + PCl_5 \xrightarrow{\text{room temperature}} C_2H_5Cl + HCl + POCl_3$$

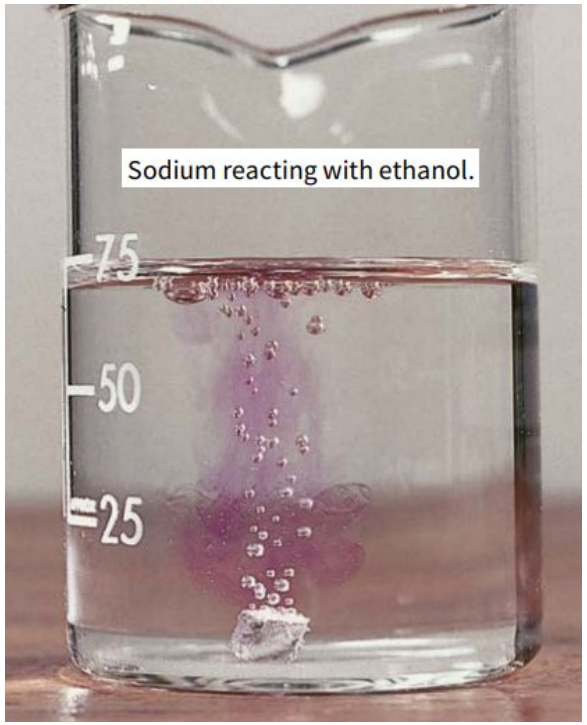
phosphorus(III) halide, PBr_3 or PI_3,

$$3C_2H_5OH + PI_3 \longrightarrow \underset{\text{iodoethane}}{3C_2H_5I} + H_3PO_3$$

3 Reaction with sodium metal

In the reaction with hydrogen halides, the C—O bond in the alcohol breaks. However, in some other reactions the O—H bond in the alcohol breaks. The reaction with sodium metal is an example:

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{sodium}}{Na} \longrightarrow \underset{\text{sodium ethoxide}}{C_2H_5O^-Na^+} + \underset{\text{hydrogen}}{H_2}$$



Sodium reacting with ethanol.

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4. Dehydration of alcohols

Alkenes can be made **sustainably** from alcohols – providing the alcohol has been made via fermentation of glucose from plants.

We can **eliminate** water from an alcohol to produce an alkene. Because we are eliminating water we call it **dehydration**.

The reaction involves the use of an **acid catalyst** either **sulfuric acid** (H_2SO_4) or **phosphoric acid** (H_3PO_4)

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

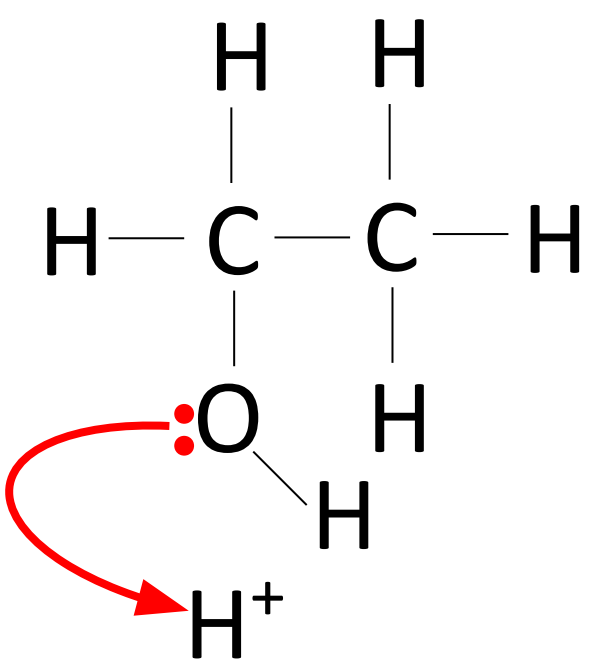
Ethanol → Ethene + Water

By using alcohol made from **fermentation** of plants we are making alkenes more sustainably. Normally alkenes are sourced from **crude oil** which is non-renewable.

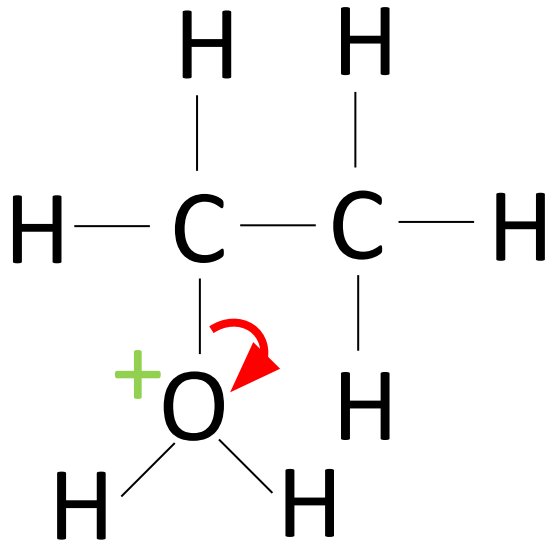
Alkenes are mainly used to make **polymers** which can be used to make **plastics**.

Elimination Reaction

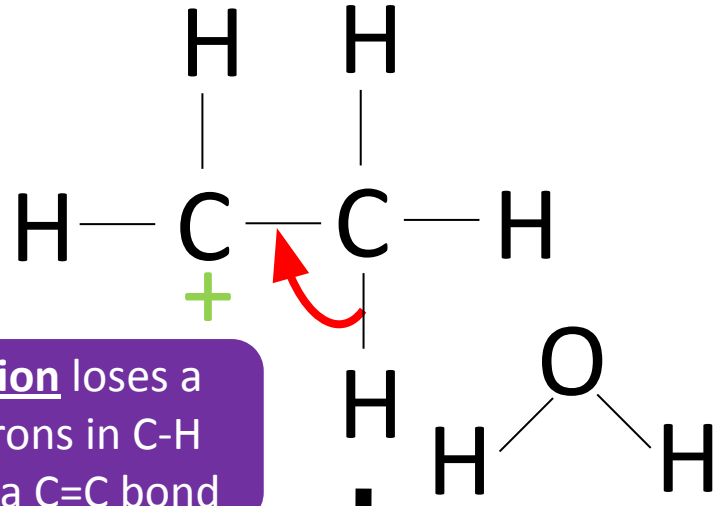
Dehydration of alcohols can be illustrated using an **elimination mechanism**



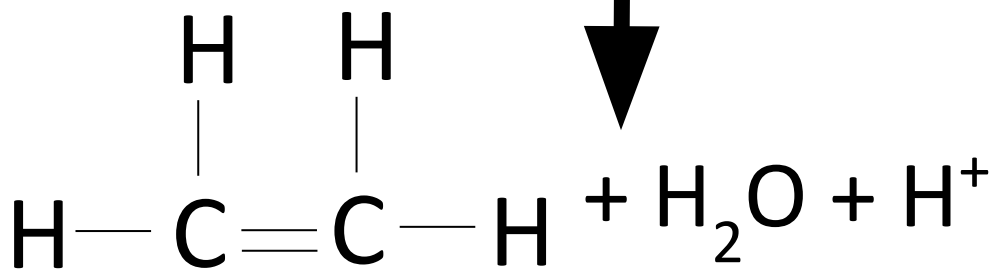
The **lone pair** on the oxygen will attach the H^+ ion which has come from the **acid catalyst**.



The intermediate formed has a **+ charge** on the oxygen. Oxygen pulls electrons in the **C-O bond** strongly to break the bond leaving an unstable **carbocation intermediate**.



The **carbocation** loses a H^+. The electrons in C-H move to form a C=C bond

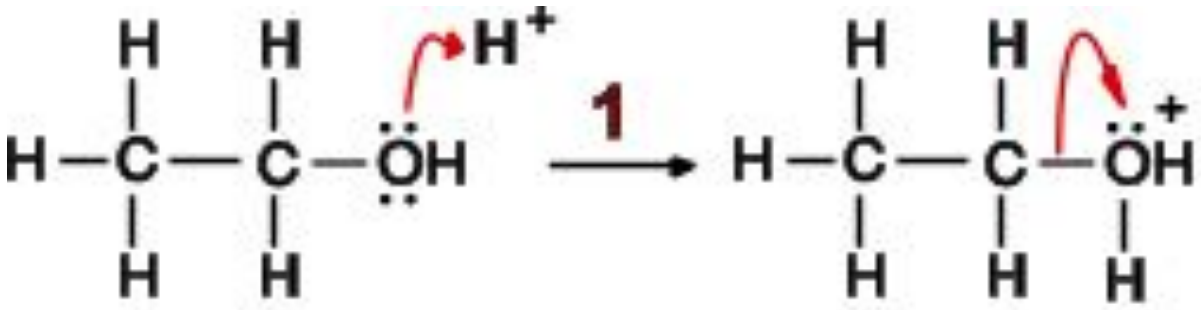


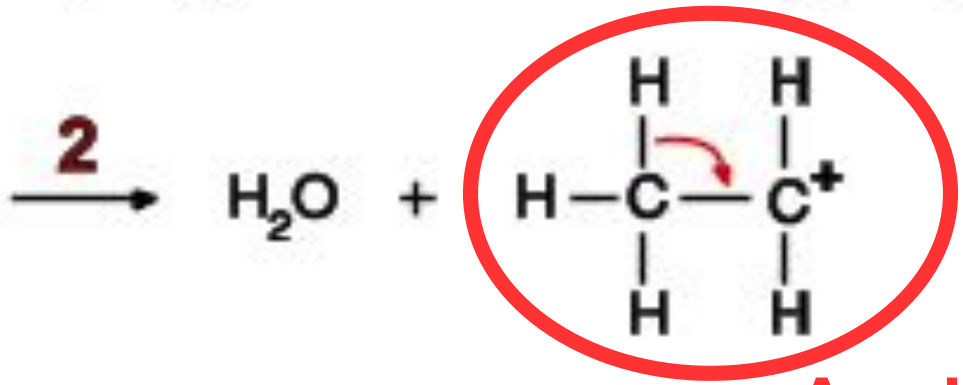
Ethene is made and the H^+ is re-formed – catalyst.

ELIMINATION OF WATER (DEHYDRATION)

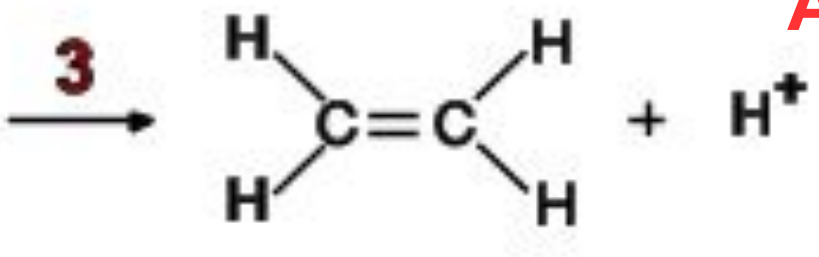
Conditions: Reflux, 180°C, conc. H_2SO_4

$$C_2H_5OH(l) \rightarrow CH_2 = CH_2(g) + H_2O(l)$$





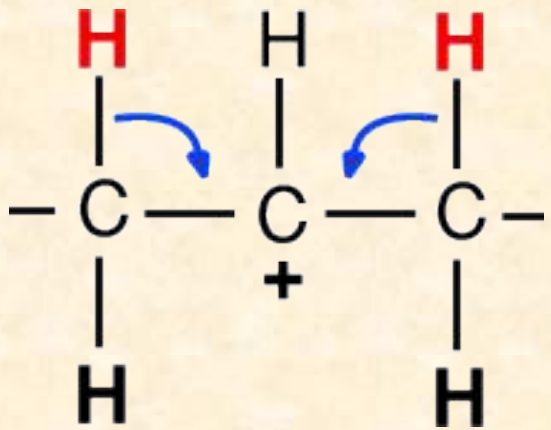
A primary carbocation



ELIMINATION OF WATER (DEHYDRATION)

There must be at least one hydrogen, where the 3 orange hydrogens are for step 2 to be possible

Alcohols with the OH in the middle of a chain can have two ways of losing water. This gives a mixture of alkenes from unsymmetrical alcohols...

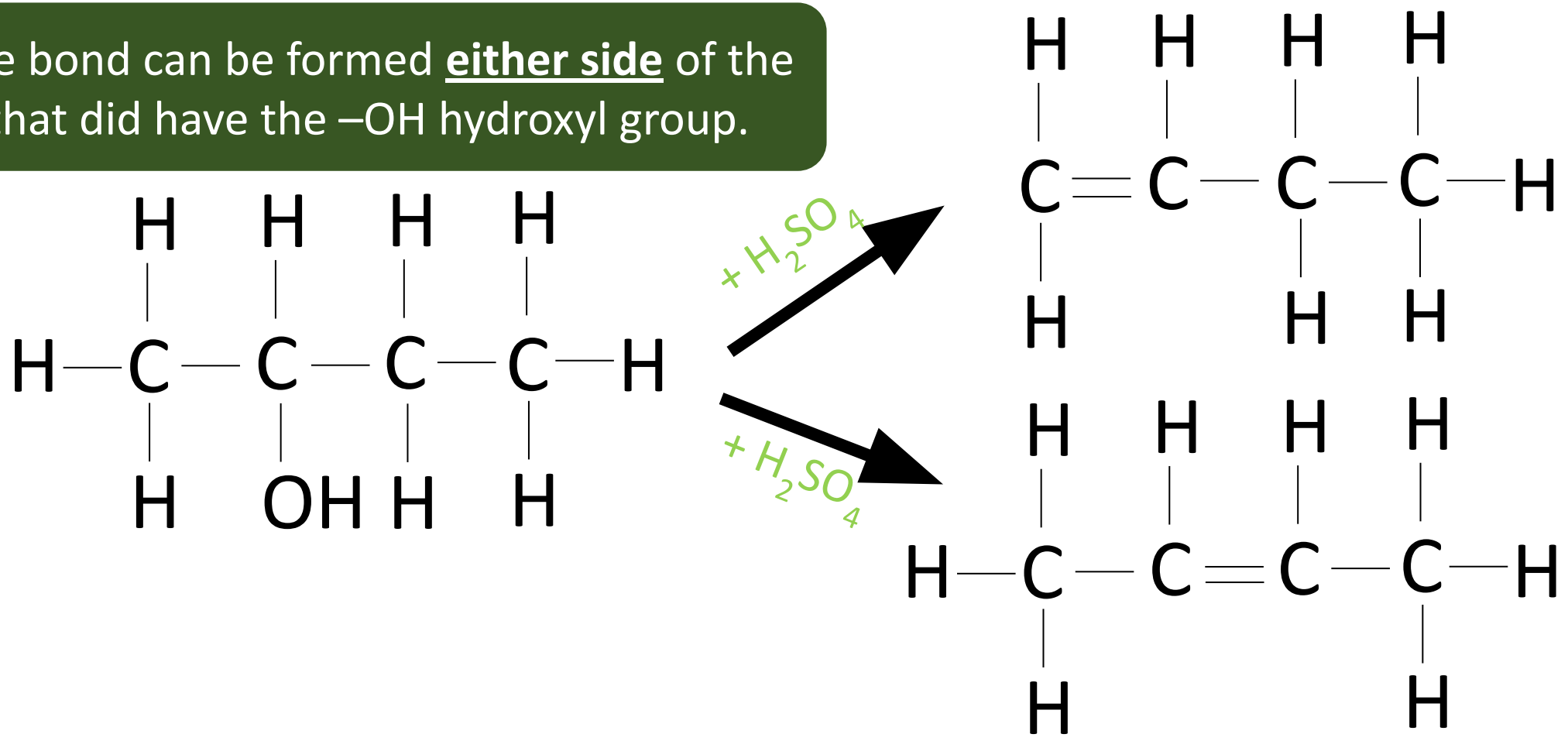


Freesciencelessons

A Level Chemistry

Dehydration of non-primary alcohols can lead to **2 different alkenes**

The double bond can be formed **either side** of the carbon that did have the –OH hydroxyl group.

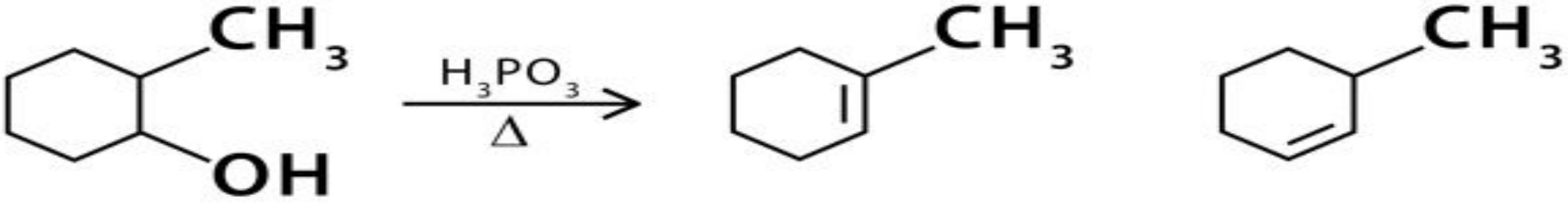


Zaitsev's Rule

states that the <u>more highly substituted alkene</u> is the more likely product (i.e., major product) of an elimination reaction.

This elimination reaction *can* give two different alkenes

But the major product is the alkene with most carbons directly attached



2-Methyl cyclohexanol

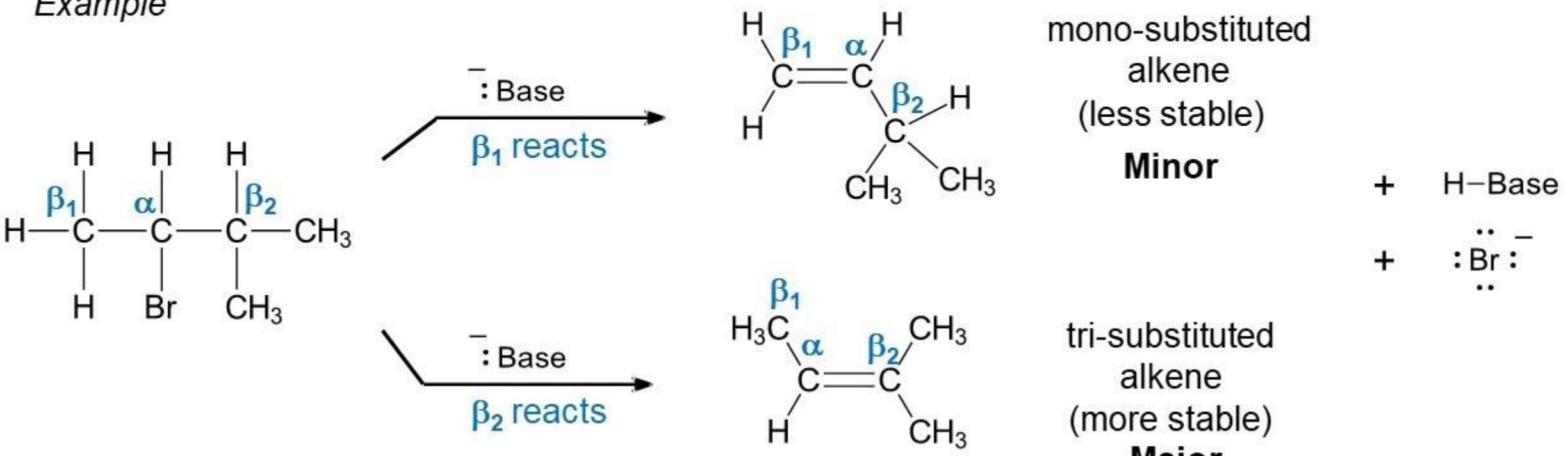
1-Methyl cyclohexene
More stable, 84%

2-Methyl cyclohexene
Less stable, 16%

8.5 Zaitsev's rule

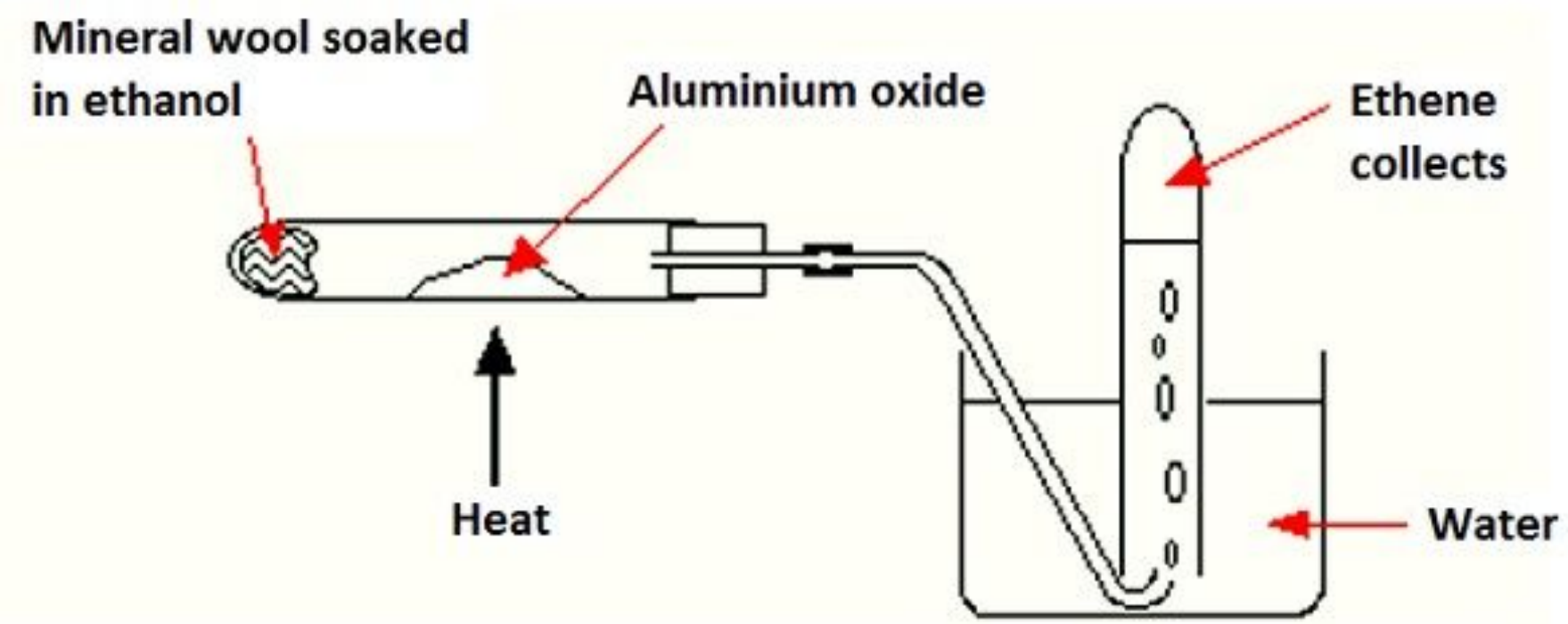
- In elimination reactions where more than one alkene is produced, the major product is the most stable alkene

Example



ELIMINATION OF WATER (DEHYDRATION)

Aside from using concentrated H_2SO_4, **dehydration** also occurs when passing alcohol vapour over aluminium oxide catalyst, Al_2O_3, at 350°C.



Dehydration using Al_2O_3 catalyst

TASK #1

Draw the structures of the alkene(s) you might get if you dehydrate the following alcohols. Identify and name the major product if there are two possible products.

a) propan-1-ol: $CH_3CH_2CH_2OH$

b) propan-2-ol: $CH_3\underset{\underset{OH}{|}}{C}HCH_3$

c) butan-1-ol: $CH_3CH_2CH_2CH_2OH$

d) butan-2-ol: $CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3$

e) pentan-3-ol: $CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3$

Reflection

- What has been learned
- What remained unclear
- What is necessary to work on