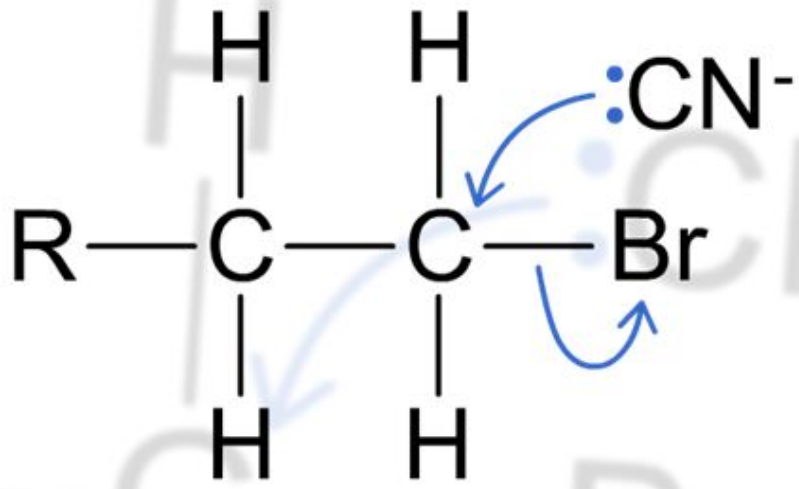
# AS Chemistry

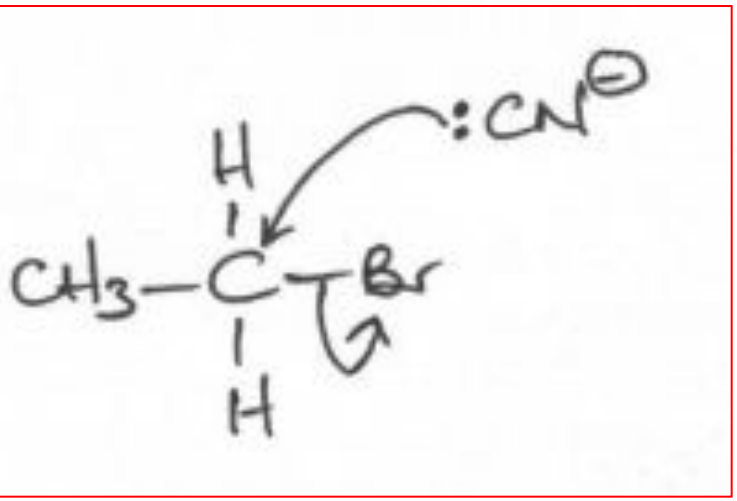
## Halogenoalkanes

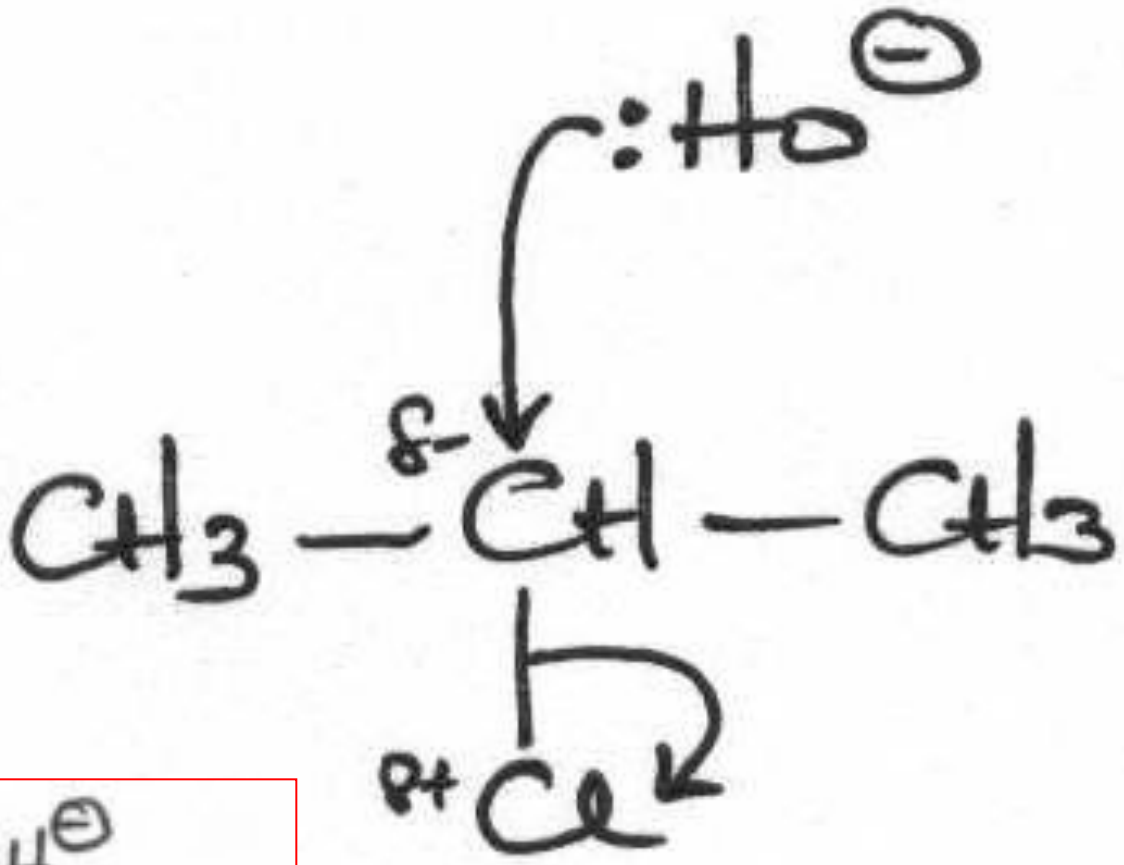


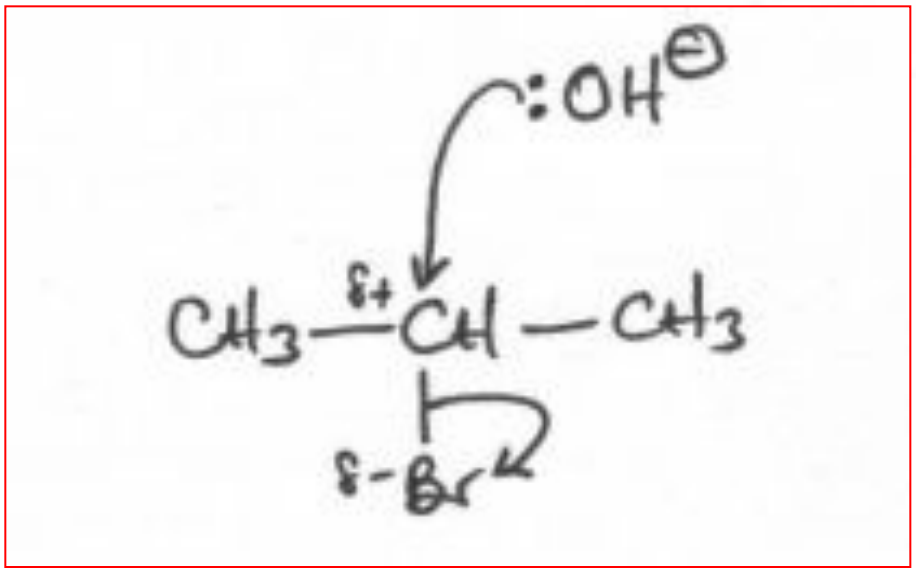

## Part 4: Elimination reactions

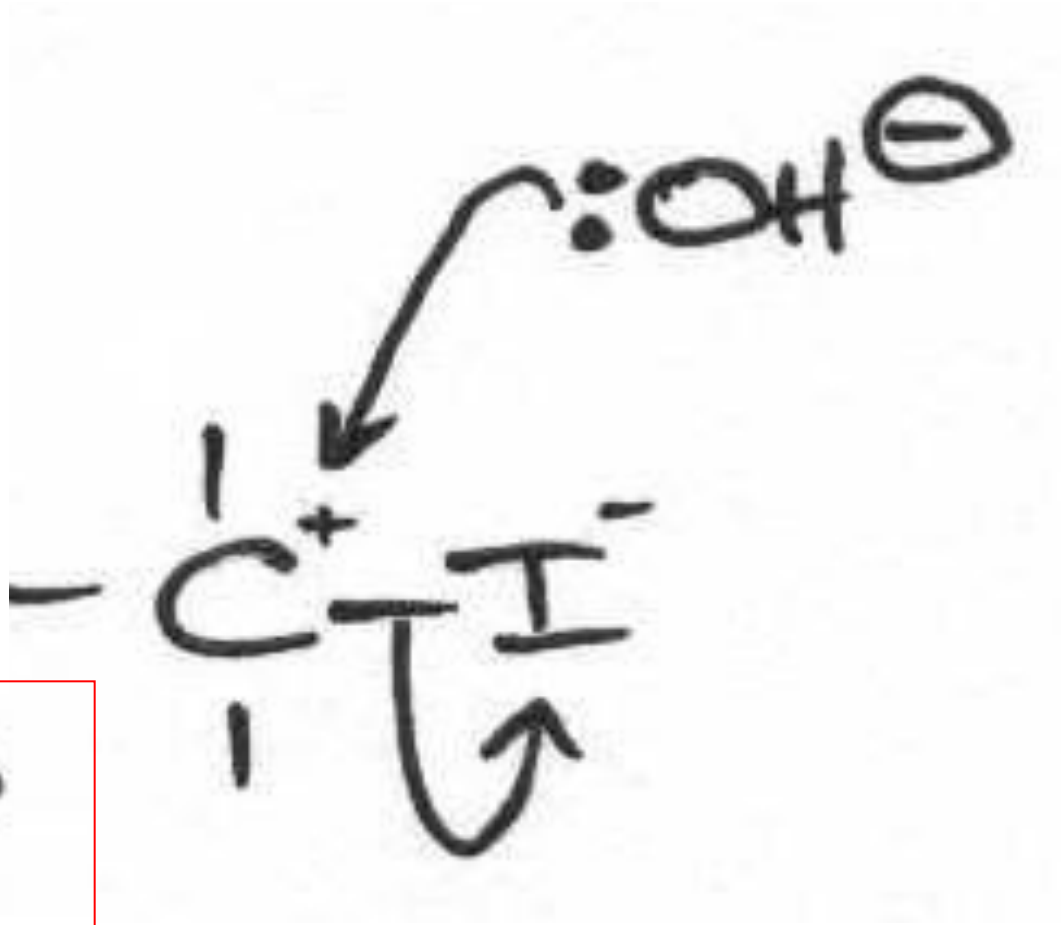
# Review on Mechanism

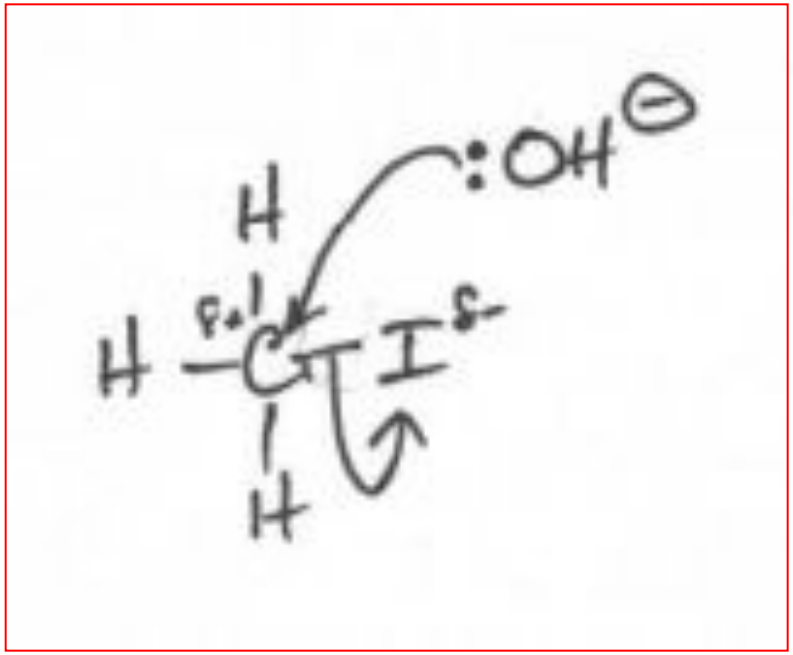
- The following mechanisms have some mistakes.
- Find out the mistake(s) and have it (them) corrected.


:CN⊖
H
CH3–C–Br
H


:HO⊖
δ-
CH3 — CH — CH3
δ+
Br


:OH⊖
δ+
CH3 — CH — CH3
δ-
Br


:OH⊖
+
−


:OH⊖
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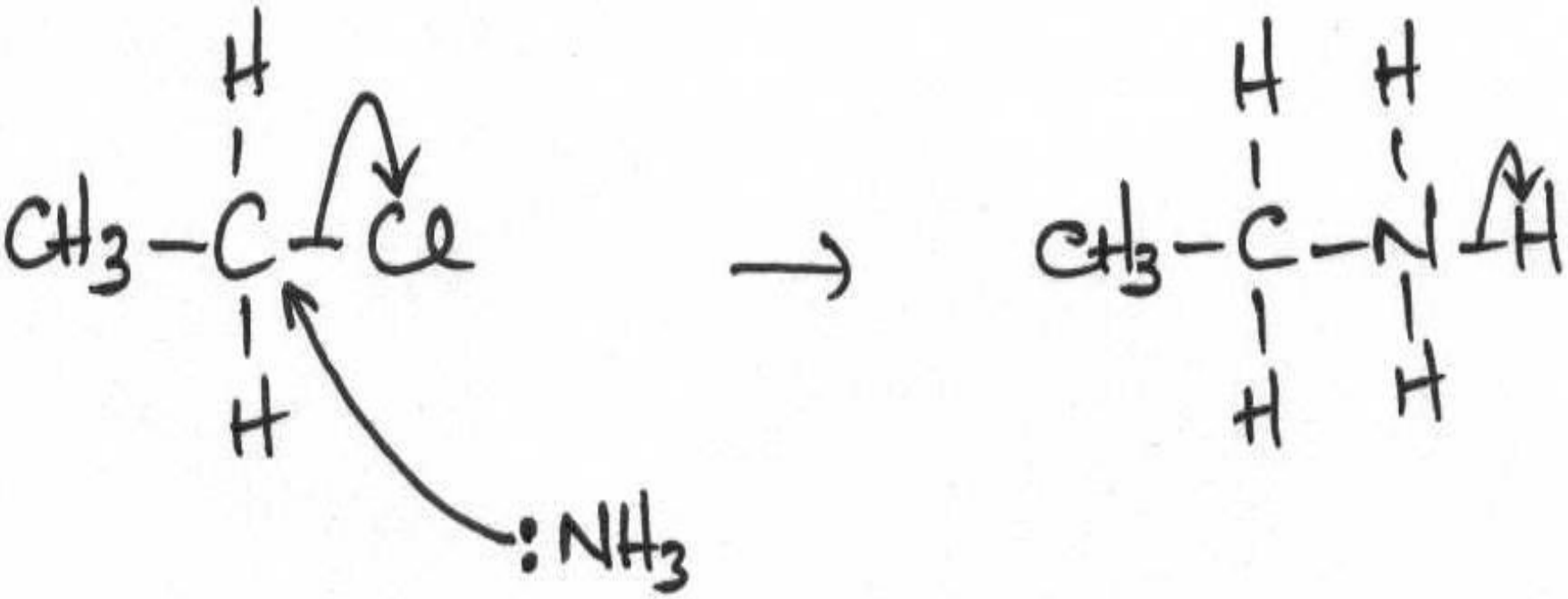
CH3
C
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:NH3
CH3
C
N
H
H
H
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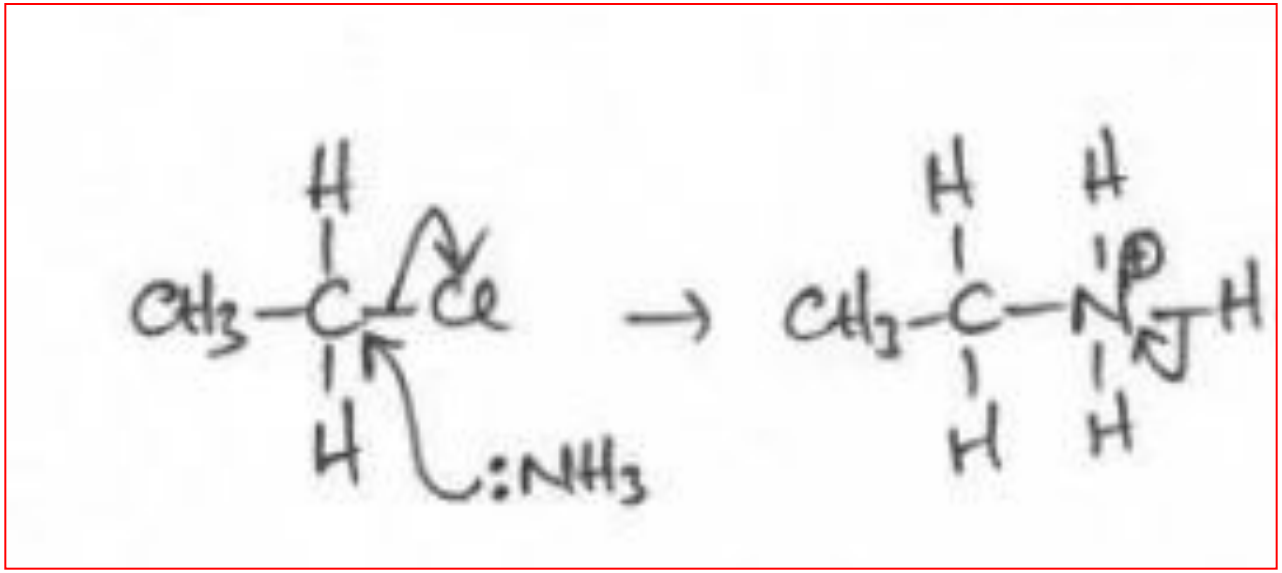
H


CH3
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:NH3
CH3
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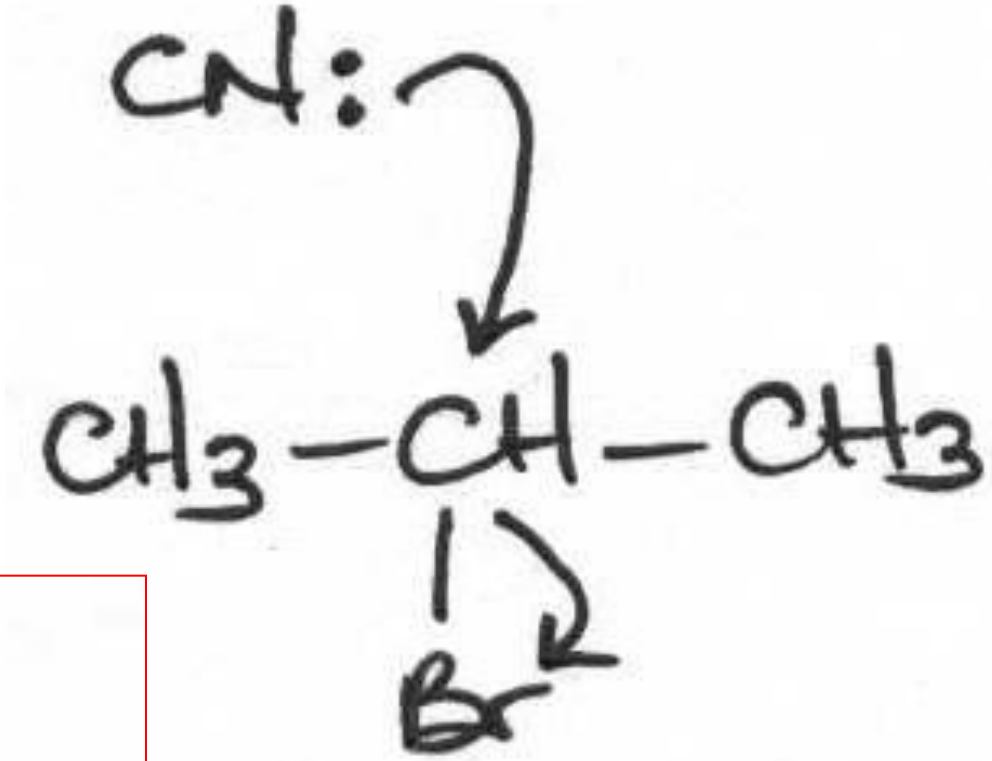
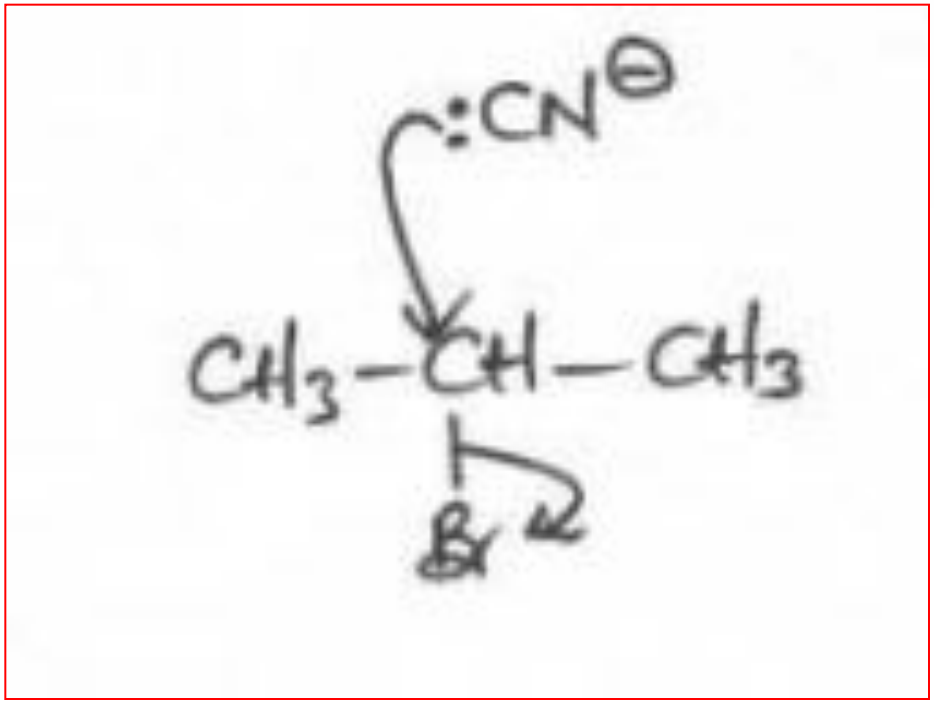

CN:
CH3 – CH – CH3
Br


:CN⊖
CH3 – CH – CH3
Br

# Learning Objectives

- Understand elimination and its mechanism
- Understand the competition between substitution and elimination
- Understand the importance of halogenoalkanes as intermediates in synthesis

# Success Criteria

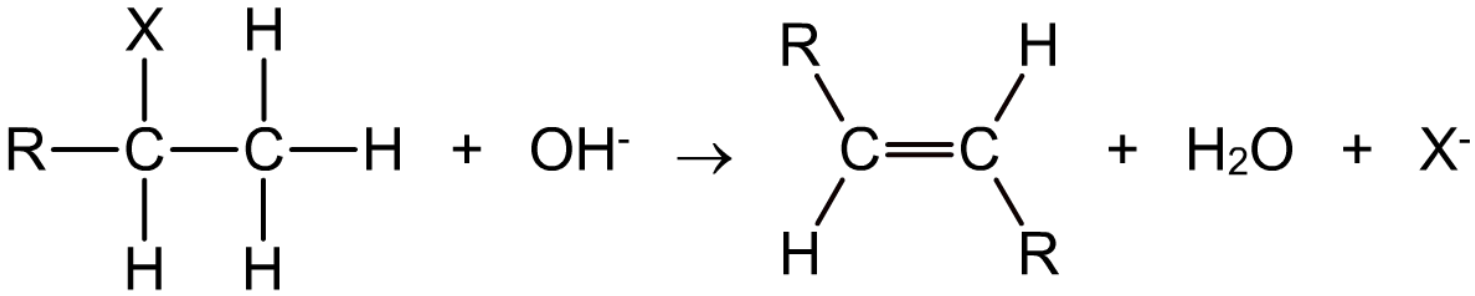
- Predict the product(s) of elimination reactions in halogenoalkanes.
- Outline the mechanism for elimination reactions in halogenoalkanes.
- Evaluate whether a given halogenoalkane undergoes elimination or substitution based on the given set of conditions.
- Compare and contrast elimination and substitution reactions in halogenoalkanes.
- Explain the importance of halogenoalkanes as intermediates in synthesis.

# Keywords

- Elimination reaction
- Nucleophilic substitution
- Nucleophile
- Base ( $H^+$ proton acceptor)
- Zaitsev's rule
- Reflux

# Elimination in halogenoalkanes

In the reaction with a strong base, halogenoalkanes will undergo not only nucleophilic substitution but also **elimination reactions**, forming alkenes and water.



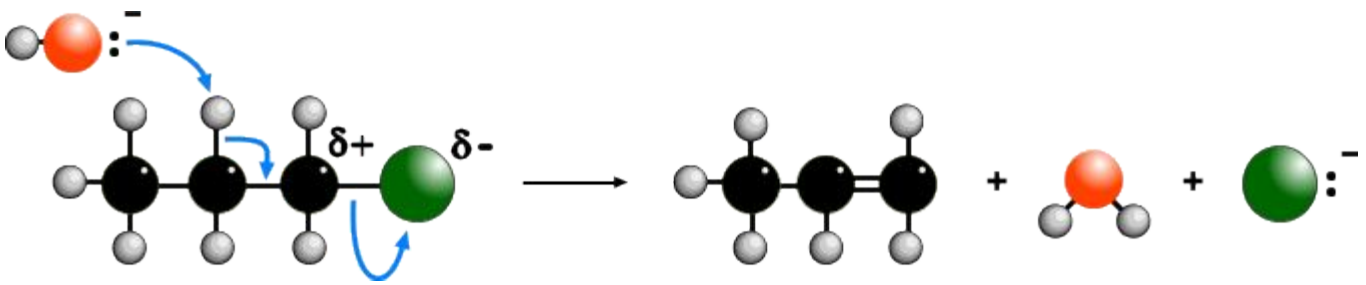

The $OH^-$ acts as both a base and a nucleophile. When acting as a base, the $OH^-$ removes $H^+$ from the halogenoalkane, which also results in the formation of a halide ion.

The reaction between a halogenoalkane and a strong base usually results in the formation of a mixture of substitution and elimination products.

# ELIMINATION

| | |
|---|---|
| **Reagent** | **Alcoholic sodium** (or potassium) **hydroxide** |
| **Conditions** | **Reflux in alcoholic solution** |
| **Product** | **Alkene** |
| **Mechanism** | **Elimination** |
| **Equation** | $C_3H_7Br + NaOH(alc) \longrightarrow C_3H_6 + H_2O + NaBr$ |

**Mechanism**




**the $OH^-$ ion acts as a base and picks up a proton**

**the proton comes from a carbon atom next to that bonded to the halogen**

**the electron pair left moves to form a second bond between the carbon atoms**

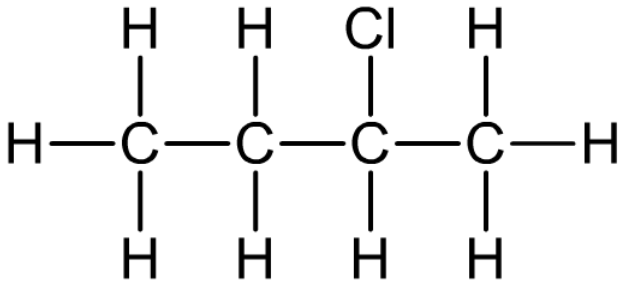
**the halogen is displaced**

**overall there is ELIMINATION of HBr.**

# Mixture of elimination products

If the carbon chain is four or more carbons in length and the halogen is not attached to a terminal carbon, a mixture of positional isomers may be formed.

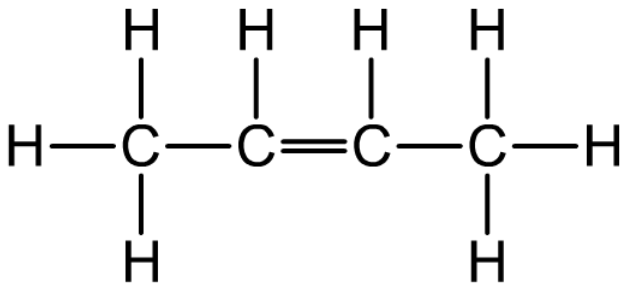
Remember the Zaitsev's Rule!



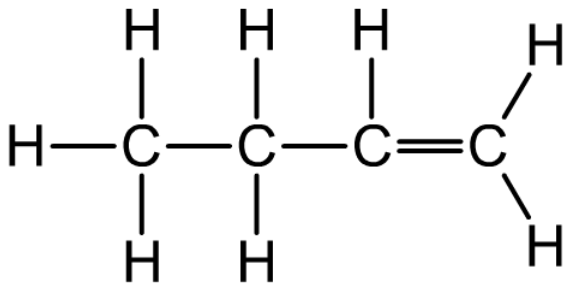

A B

attack at A

attack at B

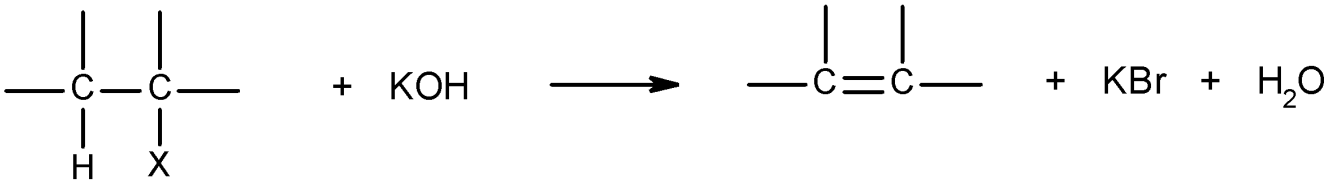


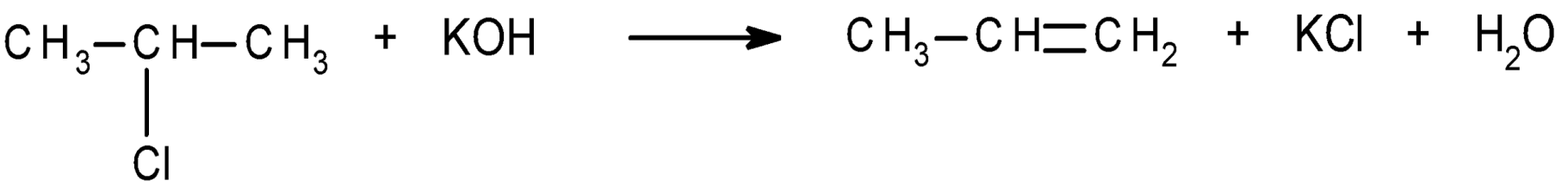

but-2-ene

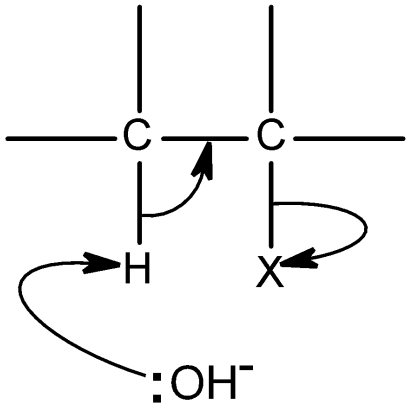


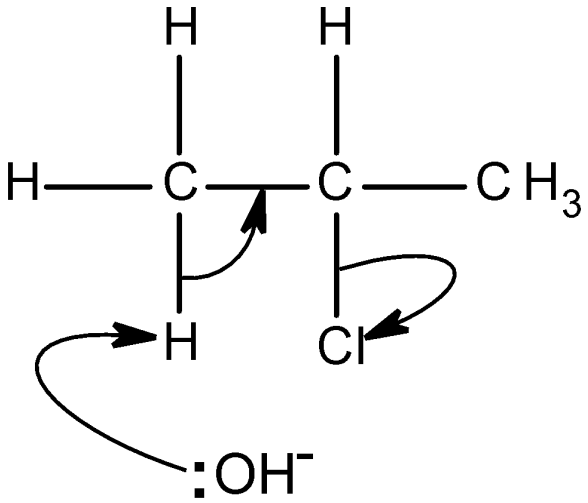

but-1-ene

# EXAMPLE 1 2-chloropropane + hot ethanolic KOH

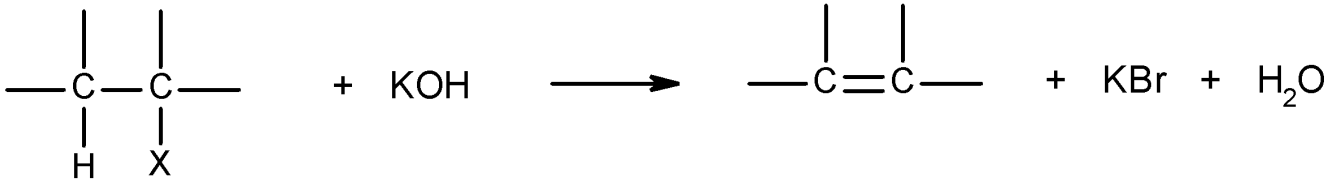


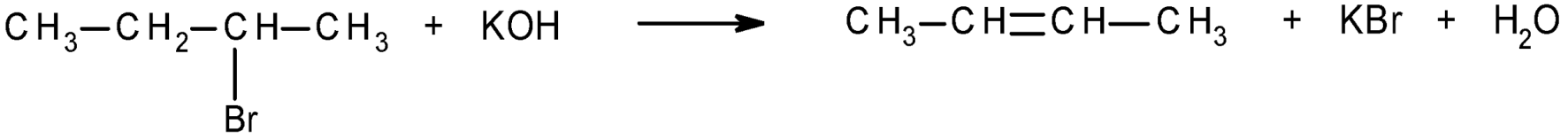



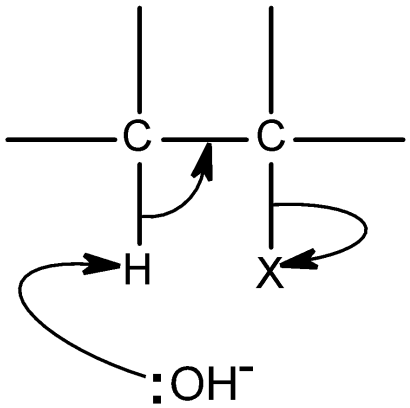



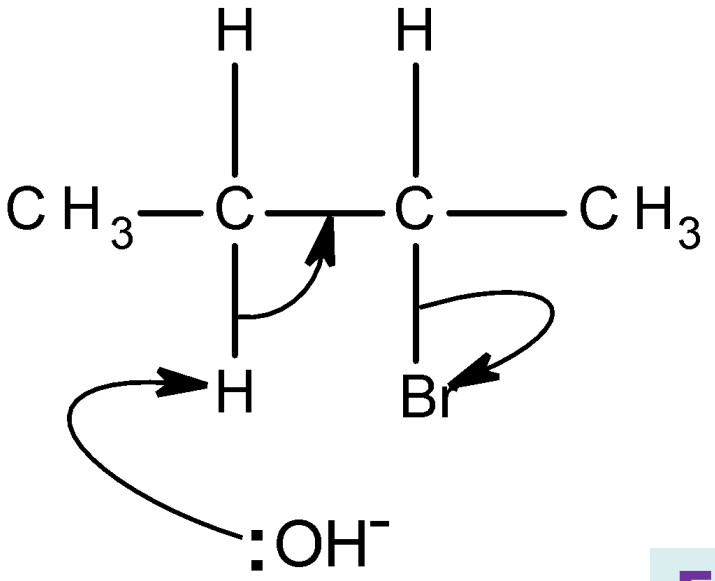
# EXAMPLE 2 2-bromobutane + hot ethanolic KOH




(major product)




Eliminat
ion

# Conditions are important

The conditions for the reaction that favour substitution or elimination are different.

- **Base strength**: the stronger the base used, the more elimination is favoured. Sodium hydroxide in aqueous solution contains $OH^-$, but when dissolved in ethanol, $CH_3CH_2O^-$ is also present, which is a stronger base.

  Therefore elimination is favoured by NaOH in ethanolic solution, and substitution is favoured by NaOH in aqueous solution.

- **Temperature**: elimination is favoured at hotter temperatures whereas substitution is favoured by warm conditions.

# ELIMINATION VS. SUBSTITUTION

**The products of reactions between haloalkanes and $OH^-$ are influenced by the solvent**

| SOLVENT | ROLE OF $OH^-$ | MECHANISM | PRODUCT |
|---|---|---|---|
| WATER | NUCLEOPHILE | SUBSTITUTION | ALCOHOL |
| ALCOHOL | BASE | ELIMINATION | ALKENE |

**Modes of attack**

**Aqueous soln** **$OH^-$ attacks the slightly positive carbon bonded to the halogen.**

**$OH^-$ acts as a nucleophile**

**Alcoholic soln** **$OH^-$ attacks one of the hydrogen atoms on a carbon atom adjacent the carbon bonded to the halogen.**

**$OH^-$ acts as a base (A BASE IS A PROTON ACCEPTOR)**

***Both reactions take place at the same time but by varying the solvent you can influence which mechanism dominates.***

# Substitution vs. Elimination

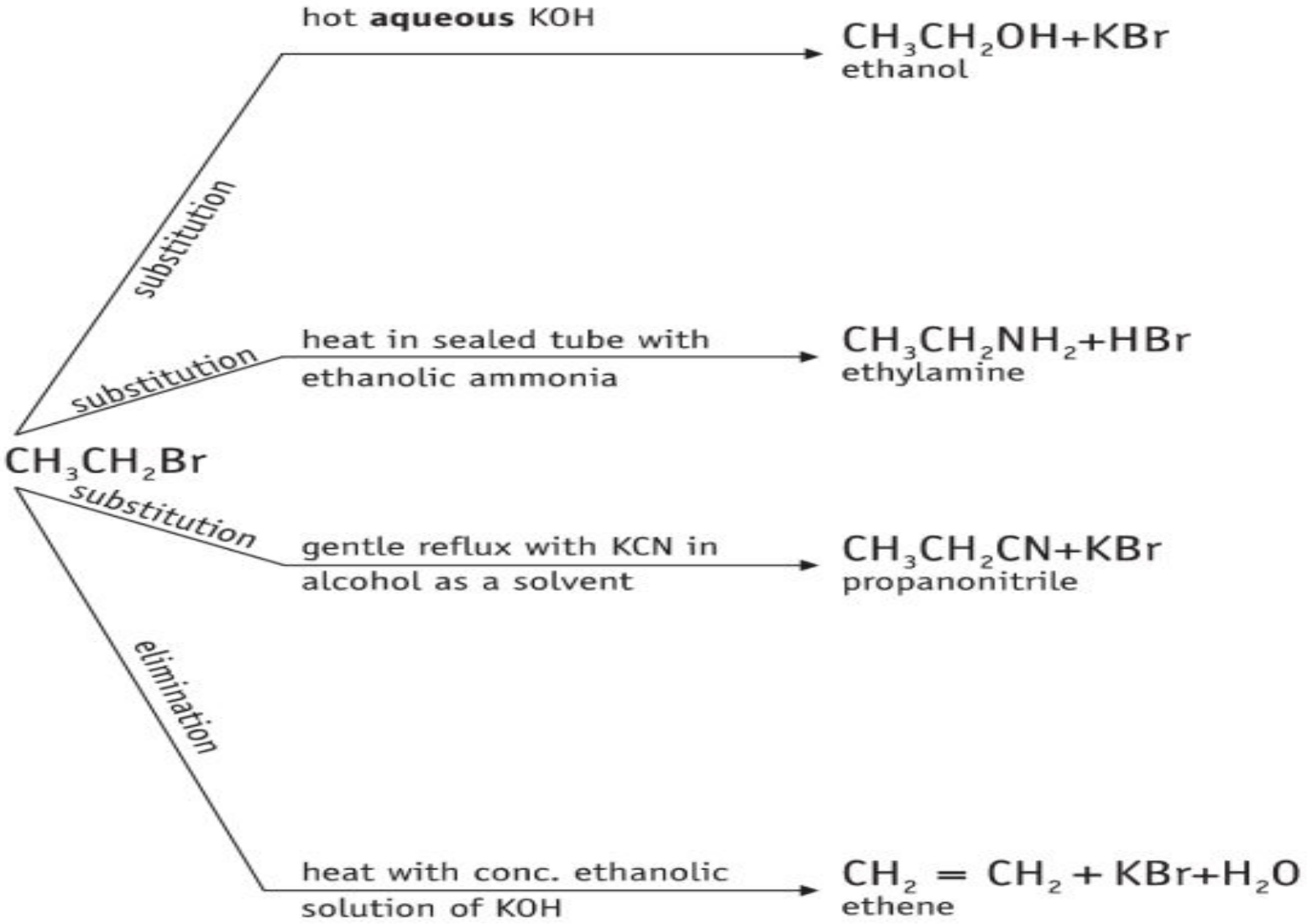
| Substitution | Elimination |
|---|---|
| $OH^-$ is a nucleophile | $OH^-$ is a base |
| Alcohol is the organic product | Alkene is the organic product |
| OH- attacks the carbon that has halogen | OH- attacks H on carbon next to carbon that has halogen |
| Mainly primary haloalkanes undergo this reactions. Some secondary halogenoalkanes, too. | Mainly tertiary halogenoalkanes undergo this reactions. Some secondary halogenoalkanes, too. |
| Water is the solvent – aqueous NaOH<br>50/50 mixture of water and ethanol is best. | Ethanol is the solvent – ethanolic KOH |
| Low temperature reflux (warm) | Higher temperature reflux (hot) |

# Halogenoalkanes as intermediates

- As well as being useful in their own right, halogenoalkanes are important **intermediates** in synthesis.
- They can be used to introduce a **reactive site** into a hydrocarbon molecule.
- The reactive halogen can then be substituted by another group which could not be introduced directly.
- This kind of synthesis is important in small-scale preparations such as those carried out in the laboratory or in the manufacture of pharmaceuticals. Many drugs have complicated organic molecules and their synthesis involves building up a complex from a simple starting compound (which involves many steps).

# Halogenoalkanes as intermediates

- Bromoalkanes are probably the most useful intermediates in synthetic pathways.



# CHECK-UP QUIZ

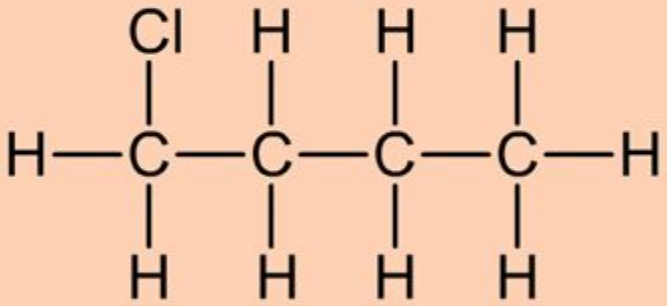
## *Learning Objectives*

- **Understand elimination and its mechanism**
- **Understand the competition between substitution and elimination**
- **Understand the importance of halogenoalkanes as intermediates in synthesis**

# Elimination or substitution?

Structure: 1

in warm aqueous sodium hydroxide



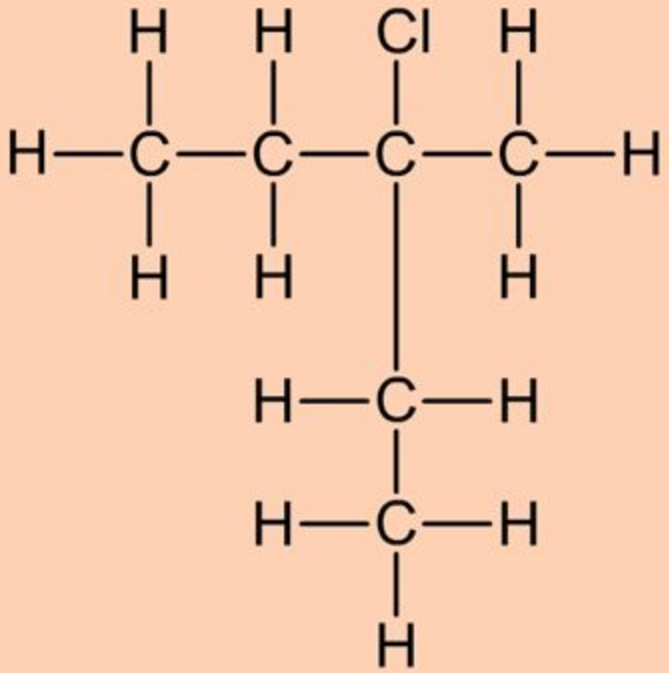

nucleophilic substitution ✓

elimination

# Elimination or substitution?

Structure: 2

in hot sodium hydroxide in ethanol



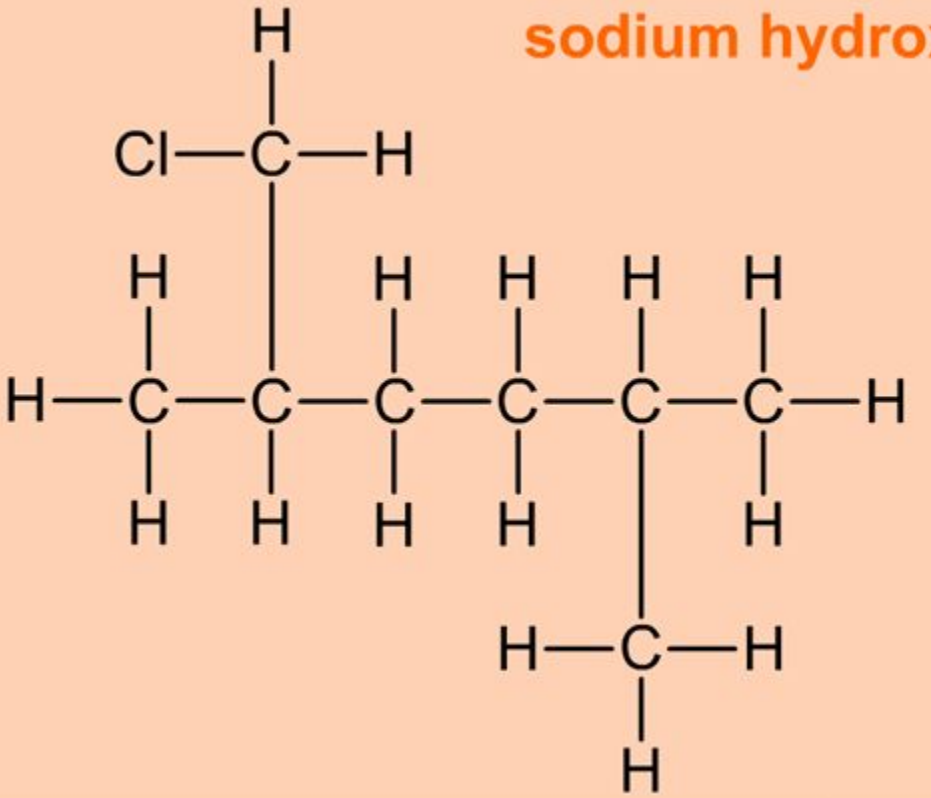
nucleophilic substitution

elimination ✓

# Elimination or substitution?

Structure: 3

in warm aqueous sodium hydroxide

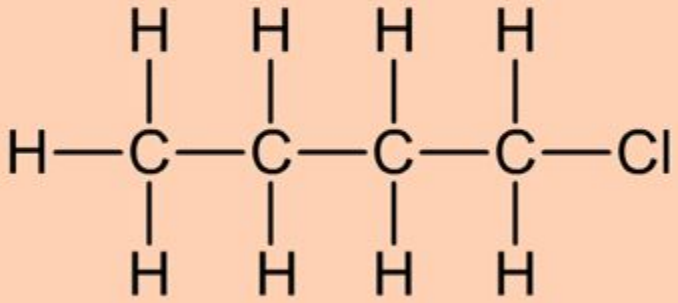


nucleophilic substitution ✓

elimination

# Elimination or substitution?

**Structure: 4** **in hot sodium hydroxide in ethanol**



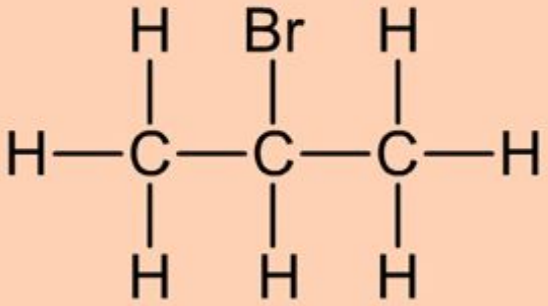

nucleophilic substitution

elimination ✓

# Elimination or substitution?

Structure: 5

in hot sodium hydroxide in ethanol




nucleophilic substitution

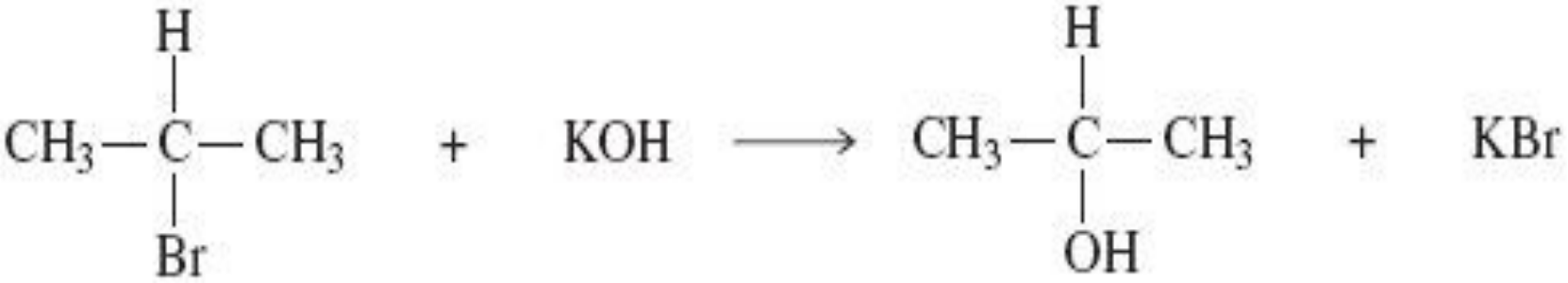
elimination ✓

# What are the differences between substitution and elimination reactions?

| Substitution | Elimination |
| --- | --- |
| OH- is nucleophile | OH- is base |
| The organic product is alcohol | The organic product is alkene |
| OH- attacks the carbon that has halogen | OH- attacks H on carbon next to carbon that has halogen |
| The solvent is water (aqueous NaOH 50/50 mixture of water and ethanol is best) | The solvent is ethanol |
| Low temperature reflux | Higher temperature reflux |

# Elimination or substitution?

## (a) Consider the following reaction.

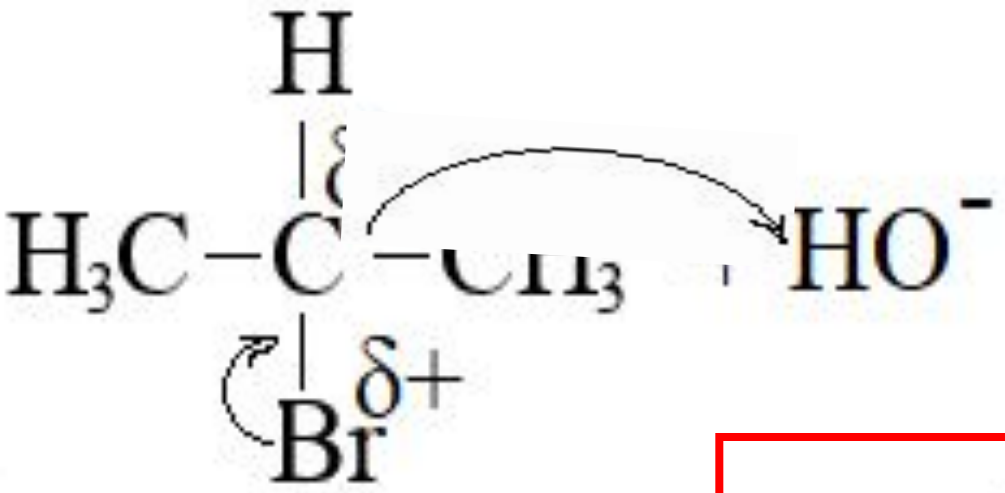


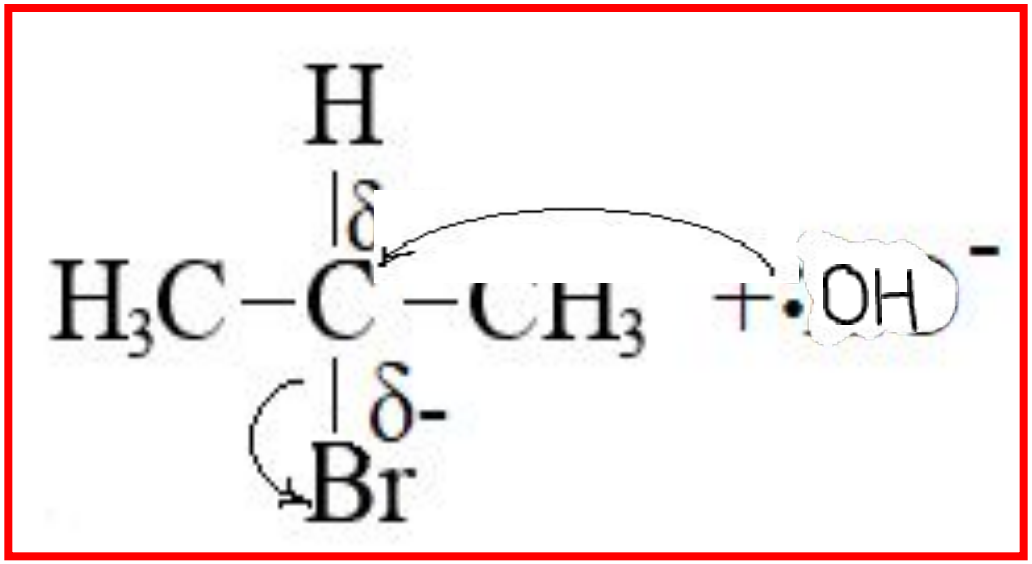

## (i) Name the mechanism for this reaction.

**Nucleophilic substitution $S_N1$ or $S_N2$**

# Elimination or substitution?

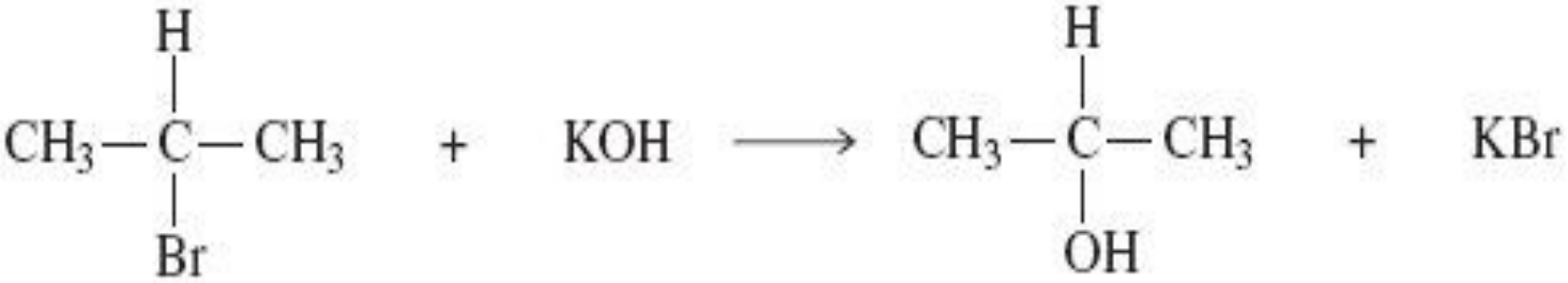
**(ii) The following mechanism has some mistakes. Find out the mistakes and correct them.**



# Elimination or substitution?

(iii) Name the halogenoalkane in this reaction.



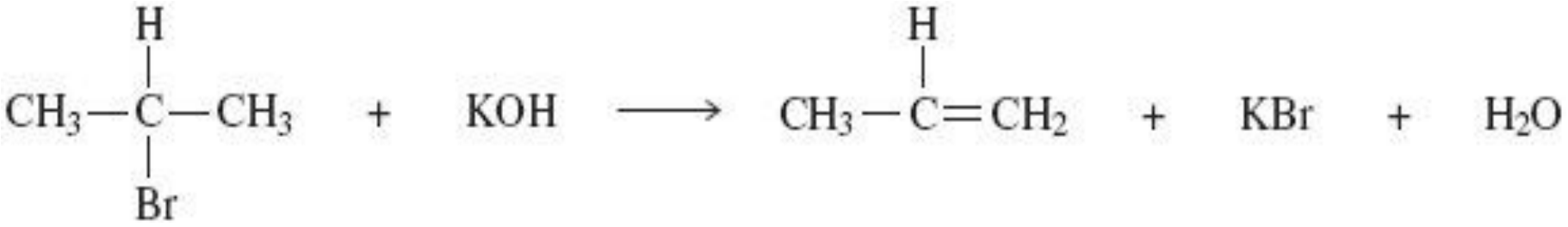

2-bromopropa
ne

(iv) Identify the characteristic of the halogenoalkane molecule that enables it to undergo this type of reaction.

Answer: Polar C–Br OR polar carbon–bromine bond OR dipole on C–Br OR δ+ (δ–)

# Elimination or substitution?

**(b) An alternative reaction can occur between this halogenoalkane and potassium hydroxide as shown by the following equation.**




**(i) Name the mechanism for this reaction.**

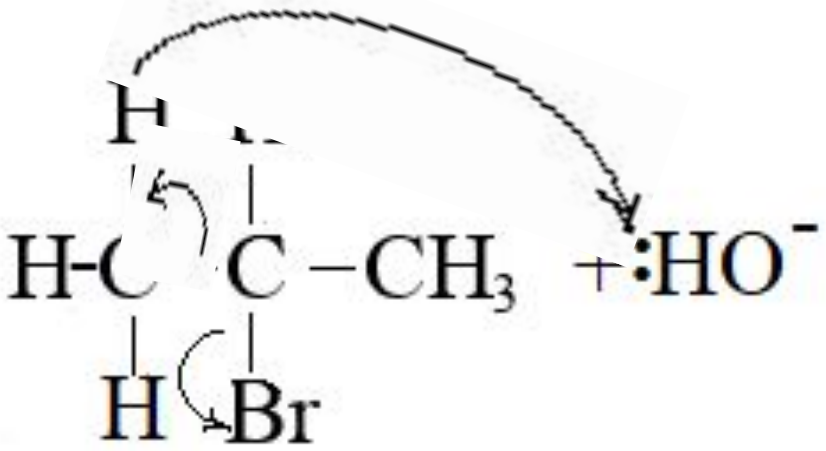
Eliminatio
n

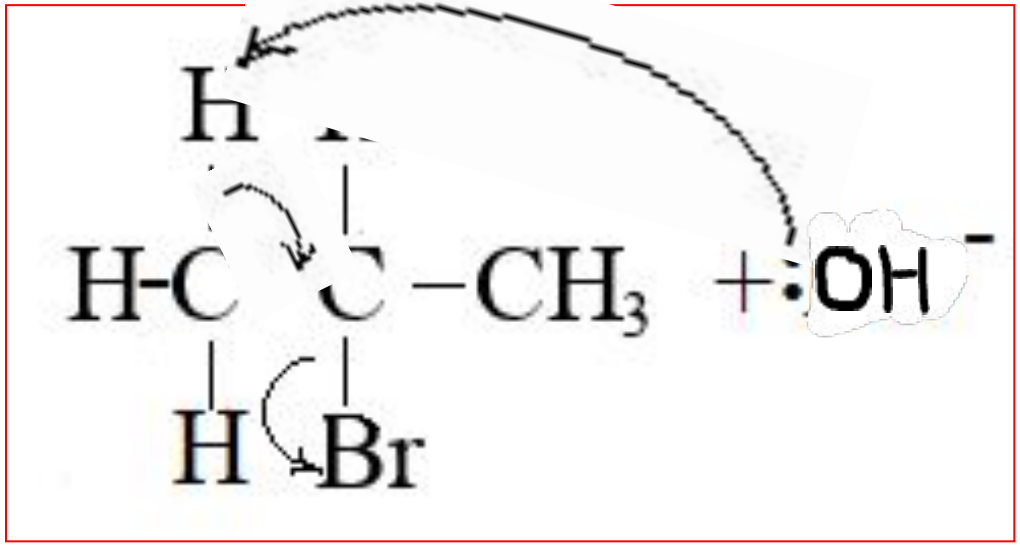
**(ii) Give the conditions for this reaction.**

Hot or higher temp. reflux AND ethanolic or alcoholic

# Elimination or substitution?

**(ii) The following mechanism has some mistakes. Find out mistakes and correct them.**



# SA Units 2 and 3

| UNIT AND SUB UNIT | LESSON OBJECTIVES |
|---|---|
| **.3B - Alcohols** | |
| Classification | - understand and be able to apply the classification of alcohols<br>- understand the oxidation of alcohols and their products |
| Reactions: substitution and elimination | - understand the products of dehydration of alcohols |
| Industrial manufacture of ethanol | - understand the two main routes for ethanol production and the advantages and disadvantages of each<br>- understand environmental issue, including those with bioethanol fuels and understand the concept of carbon neutrality<br>- be able to discuss biofuels in this context |
| **- Halogenoalkanes** | |
| Reactions: Photo chlorination (free radical) | - recall the synthesis of chloroalkanes<br>- understand environmental concerns about halogenoalkanes and understand the mechanism of ozone depletion<br>- know less environmentally damaging substitutes for haloalkanes |
| Nucleophilic substitution of halogenoalkanes | - recognise that halogenoalkanes will react with nucleophiles<br>- understand the mechanism of nucleophilic substitution reactions<br>- be able to write equations and mechanisms for a general case and some common examples |
| Elimination reaction of halogenoalkanes | - understand elimination and its mechanism<br>- understand the competition between substitution and elimination<br>- understand the importance of halogenoalkanes as intermediates in synthesis (including industrial processes) |
| Revision for unit 2-3<br>SA Unit 2-3 | |