

15. HALOGEN COMPOUNDS- CONTENTS

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🌟 Learning outcomes

After the completion of the chapter, learners should be able to:

1. recall the reactions (reagents and conditions) by which halogenoalkanes can be produced:
 - (a) the free-radical substitution of alkanes by Cl_2 or Br_2 in the presence of ultraviolet light, as exemplified by the reactions of ethane
 - (b) electrophilic addition of an alkene with a halogen, X_2 , or hydrogen halide, $\text{HX}(\text{g})$, at room temperature
 - (c) substitution of an alcohol, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4 ; or with PCl_3 and heat; or with PCl_5 ; or with SOCl_2
2. classify halogenoalkanes into primary, secondary and tertiary
3. describe the following nucleophilic substitution reactions:
 - (a) the reaction with $\text{NaOH}(\text{aq})$ and heat to produce an alcohol
 - (b) the reaction with KCN in ethanol and heat to produce a nitrile
 - (c) the reaction with NH_3 in ethanol heated under pressure to produce an amine
 - (d) the reaction with aqueous silver nitrate in ethanol as a method of identifying the halogen present, as exemplified by Bromoethane
4. describe the elimination reaction with NaOH in ethanol and heat to produce an alkene as exemplified by Bromoethane
5. describe the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms of nucleophilic substitution in halogenoalkanes including the inductive effects of alkyl groups
6. recall that primary halogenoalkanes tend to react via the $\text{S}_{\text{N}}2$ mechanism; tertiary halogenoalkanes via the $\text{S}_{\text{N}}1$ mechanism; and secondary halogenoalkanes by a mixture of the two, depending on the structure
7. Describe and explain the different reactivities of halogenoalkanes (with particular reference to the relative strengths of the C-X bonds as exemplified by the reactions of halogenoalkanes with aqueous silver nitrates)

Introduction

Look at the different structures of 1° , 2° and 3° haloalkanes on the [MolView](https://subarnam.com.np/) website as 3D structures.

Preparation

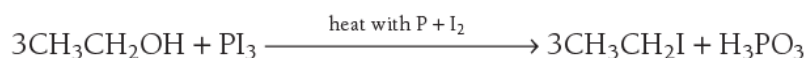
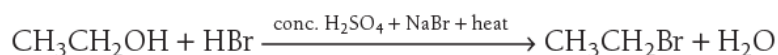
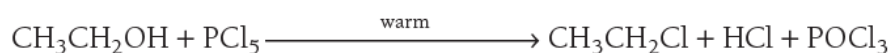
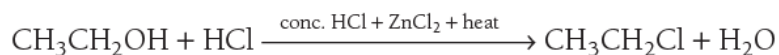
Substitution of an alcohol

by reaction with HX or KBr with H_2SO_4 or H_3PO_4

with PCl_3 and heat

with PCl_5

with SOCl_2

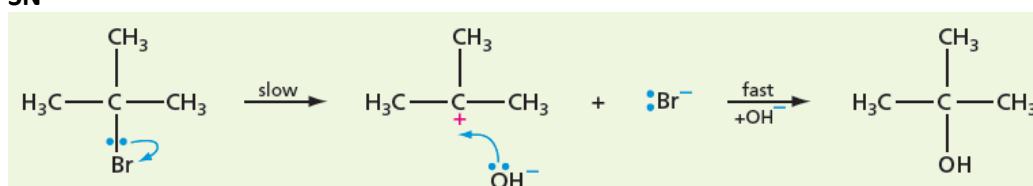


- Tertiary alcohols react easily with concentrated hydrochloric acid on shaking at room temperature. The reaction proceeds via the $\text{S}_{\text{N}}1$ mechanism.
- Secondary and primary alcohols also react with concentrated hydrochloric acid, but at a slower rate. Anhydrous zinc chloride needs to be added as a catalyst, and the mixture requires heating.
- Reaction with phosphorus(V) chloride or sulfur dichloride oxide hydrogen chloride is evolved. This fizzing with PCl_5 , and the production of misty fumes, can be used as a test for the presence of an alcohol (as long as water is absent).
- Alcohols can be converted into bromoalkanes by reaction with either concentrated hydrobromic acid or a mixture of sodium bromide, concentrated sulfuric acid and water (50%). These react to give hydrogen bromide:
 $2\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HBr}$
- Halogens react with phosphorus to give the phosphorus trihalides:
 $2\text{P} + 3\text{Br}_2 \rightarrow 2\text{PBr}_3$
 $2\text{P} + 3\text{I}_2 \rightarrow 2\text{PI}_3$
- The phosphorus trihalides, for example phosphorus triiodide, then react with alcohols to form iodoalkanes.

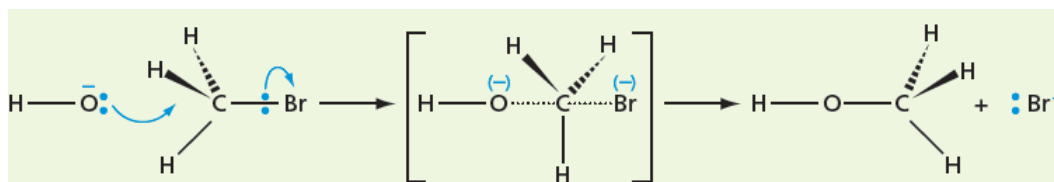
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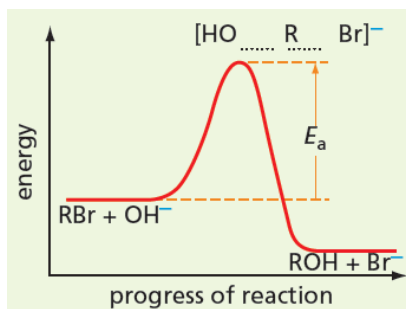
With aqueous NaOH

$\text{S}_{\text{N}}1$

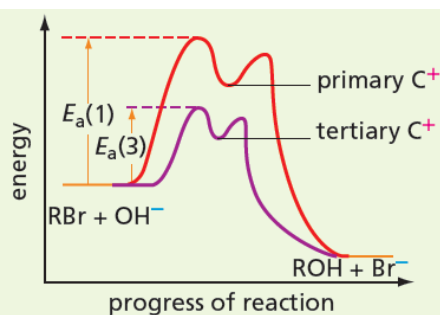


$\text{S}_{\text{N}}2$





▲ Figure 16.10 Reaction profile for the S_N2 hydrolysis of bromomethane



▲ Figure 16.11 Reaction profiles for the S_N1 hydrolysis of primary and tertiary bromoalkanes

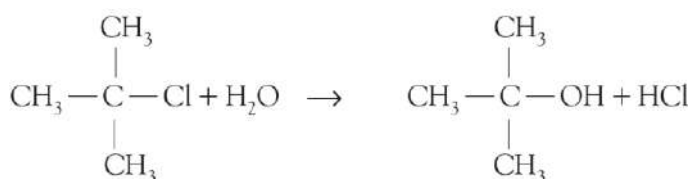
www.youtube.com/watch?v=Bg3c5c9b1BQ&t=117s
An Animated Explanation of Nucleophilic Substitution

The reaction with ethanolic KCN

The reaction with NH_3 in ethanol heated under pressure

The reaction with aqueous silver nitrate in ethanol

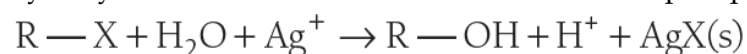
Some halogenoalkanes are reactive enough to be hydrolysed to form alcohols just by heating with water (in practice, a mixed ethanol-water solvent is used because halogenoalkanes are immiscible with water, but the ethanol is miscible with both):



The hydrolysis is quicker if it is carried out in hot aqueous sodium hydroxide:



The relative rates of hydrolysis of chloro-, bromo- and iodoalkanes can be studied by dissolving the halogenoalkane in ethanol and adding aqueous silver nitrate. As the halogenoalkane slowly hydrolyses, the halide ion is released, and forms a precipitate of silver halide:



The following table shows the results obtained.

Aqueous silver nitrate can be used to distinguish between organic chlorides, bromides and iodides.

Compound	Observation on reaction with $\text{AgNO}_3 + \text{H}_2\text{O}$ in ethanol	Colour of precipitate
$(\text{CH}_3)_2\text{CH—Cl}$	slight cloudiness after 1 hour	white
$(\text{CH}_3)_2\text{CH—Br}$	cloudiness appears after a few minutes	pale cream
$(\text{CH}_3)_2\text{CH—I}$	thick precipitate appears within a minute	pale yellow

Elimination reaction

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