

Haloalkanes and Haloarenes

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24-02-2025

Contents

| | | |
|----------|--|----------|
| 1 | Introduction | 1 |
| 1.1 | Compounds containing $sp^3 - x$ bond | 1 |
| 1.1.1 | Alkyl Halides | 2 |
| 1.1.2 | Allylic Halides | 2 |
| 1.1.3 | Benzylic Halides | 2 |
| 1.2 | Compounds containing $sp^2 - x$ bond | 2 |
| 2 | Preparation of Haloalkanes | 3 |
| 2.1 | From Alcohols | 3 |
| 2.2 | Free Radical Halogenation | 4 |
| 2.3 | From Alkenes | 5 |
| 2.3.1 | Addition of Hydrogen Halides | 5 |
| 2.3.2 | Addition of Halogens | 5 |
| 2.4 | Halogen Exchange | 5 |
| 2.4.1 | In Protic Solvents | 5 |
| 2.4.2 | In Aprotic Solvents | 5 |
| 3 | Preparation of Haloarenes | 6 |

1 Introduction

The replacement of hydrogen atoms by halogen atoms in hydrocarbons yield haloalkanes and haloarenes. Haloalkanes contain halogen atoms attached to sp^3 hybridized carbon atoms while haloarenes contain halogen atoms attached to sp^2 hybridized atoms.

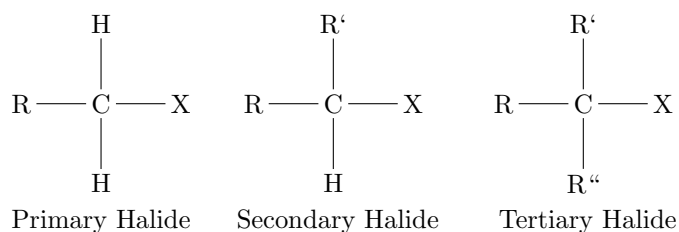
1.1 Compounds containing $sp^3 - x$ bond

These include:

1. Alkyl Halides or Haloalkanes ($R - X$)
2. Allylic Halides
3. Benzylic Halides

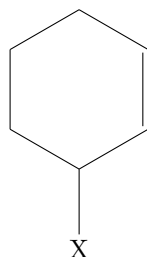
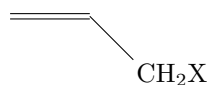
1.1.1 Alkyl Halides

Here, the halogen is bonded to an alkyl group (R). They are further classified into primary, secondary and tertiary according to the nature of carbon to which the halogen is attached.



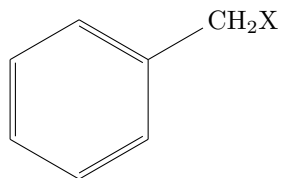
1.1.2 Allylic Halides

Here, the halogen is bonded to an sp^3 hybridized carbon adjacent to which is a carbon - carbon double bond. For example:



1.1.3 Benzylic Halides

These are compounds where the sp^3 carbon attached to the halogen is bonded to an aromatic ring.



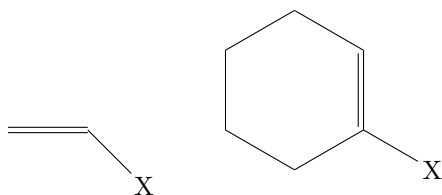
1.2 Compounds containing $sp^2 - x$ bond

These include

1. Vinylic Halides
2. Aryl Halides

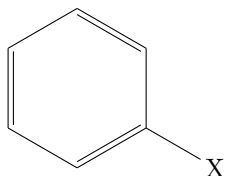
Vinylic Halides

Here, the halogen is bonded to an sp^2 hybridized atom of a carbon - carbon double bond. ($C=C$)



Aryl Halides

Here, the halogen is bonded to an sp^2 hybridized carbon which is part of an aromatic ring.

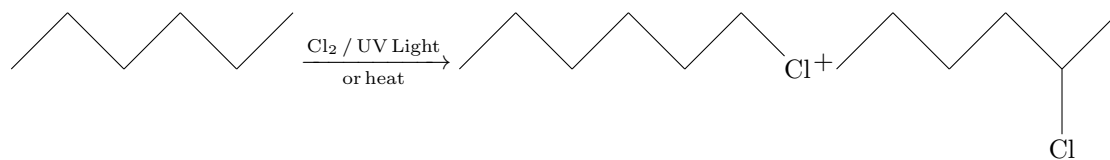


2 Preparation of Haloalkanes

2.1 From Alcohols

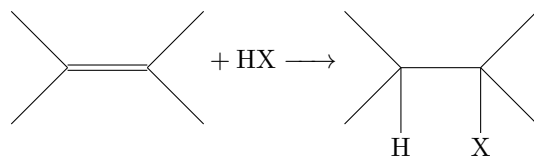
1. $R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$
2. $R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$
3. $3 R-OH + PX_3 \longrightarrow 3 R-X + H_3PO_3$
4. $3 R-OH + PCl_5 \longrightarrow 3 R-Cl + HCl + POCl_3$
5. $3 R-OH \xrightarrow[X_2 = Br_2, I_2]{red P/X_2} R-X$
6. $3 R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$

2.2 Free Radical Halogenation

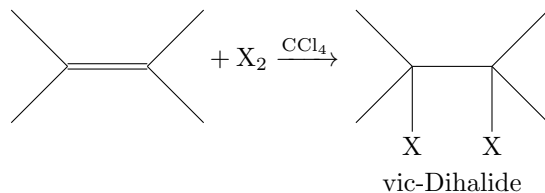


2.3 From Alkenes

2.3.1 Addition of Hydrogen Halides



2.3.2 Addition of Halogens



2.4 Halogen Exchange

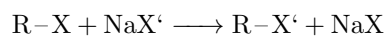
These reactions proceed by the displacement of one halogen with another. In protic solvents, halogens with smaller hydrated size displace halogens with greater hydrated size, while in aprotic solvents, halogens with smaller atomic size displace halogens with greater atomic size.

2.4.1 In Protic Solvents

$R-X + NaX' \longrightarrow R-X' + NaX$ This reaction is known as **Finkelstein Reaction**.

tion. Here halogen with bigger size displaces halogen with smaller size. Alkyl iodides are often prepared by this reaction.

2.4.2 In Aprotic Solvents



This reaction is known as **Schwartz Reaction**. Here halogen with smaller size displaces halogen with bigger size. Alkyl fluorides are often prepared by this reaction.

3 Preparation of Haloarenes