FSc / ICS Part-II Chemistry — Punjab Board

CHAPTER 10
Alkyl Halides

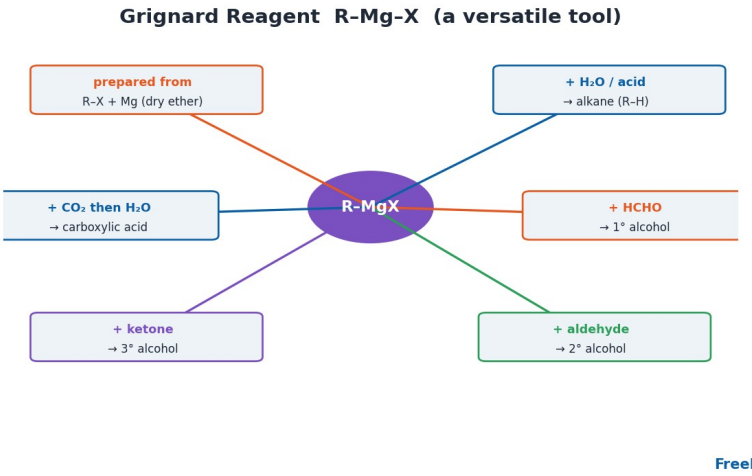

Figure 10.1 — The Grignard reagent (R–MgX), a versatile synthetic tool made from alkyl halides.

1. Chapter Overview

Alkyl halides (haloalkanes) are compounds in which one or more hydrogen atoms of an alkane have been replaced by a halogen atom, giving the general formula R–X (where X = F, Cl, Br, I). Although they are not usually found in nature, they are extremely useful in the laboratory and industry because the carbon–halogen bond is polar and reactive. This makes alkyl halides ideal starting materials for making alcohols, ethers, amines and, above all, Grignard reagents, which are among the most powerful tools for building larger organic molecules.

2. Learning Objectives

- Define alkyl halides and classify them as primary, secondary and tertiary.
- Describe methods of preparing alkyl halides.
- Explain nucleophilic substitution reactions and distinguish SN1 from SN2.
- Describe elimination (dehydrohalogenation) reactions.
- Describe the preparation and synthetic uses of the Grignard reagent.
- State the order of reactivity of alkyl halides.

3. Key Concepts

3.1 What Are Alkyl Halides?

An alkyl halide has the general formula R–X. The carbon–halogen bond is polar because the halogen is more electronegative than carbon, giving the carbon a small positive charge (δ+). This polarity is the key to the chemistry of alkyl halides: the δ+ carbon is attacked by nucleophiles (electron-rich species).

Classification

Type	Carbon bearing the halogen is joined to…	Example
Primary (1°)	one other carbon	CH_3CH_2–Cl
Secondary (2°)	two other carbons	$(CH_3)_2CH$–Cl
Tertiary (3°)	three other carbons	$(CH_3)_3C$–Cl

Memory Trick

Reactivity of C–X bond: R–I > R–Br > R–Cl > R–F (weakest bond breaks most easily → iodide most reactive).

3.2 Preparation

Alkyl halides can be prepared by several routes: from alkanes by free-radical halogenation (in sunlight), from alkenes by adding a hydrogen halide (following Markownikoff's rule), and — most usefully in the laboratory — from alcohols by replacing the –OH group using reagents such as HX, PCl_3, PCl_5 or $SOCl_2$.

3.3 Nucleophilic Substitution

The most important reactions of alkyl halides are nucleophilic substitutions, in which a nucleophile replaces the halogen (the leaving group). For example, with aqueous KOH an alkyl halide gives an alcohol, and with alcoholic KCN it gives a nitrile. There are two mechanisms:

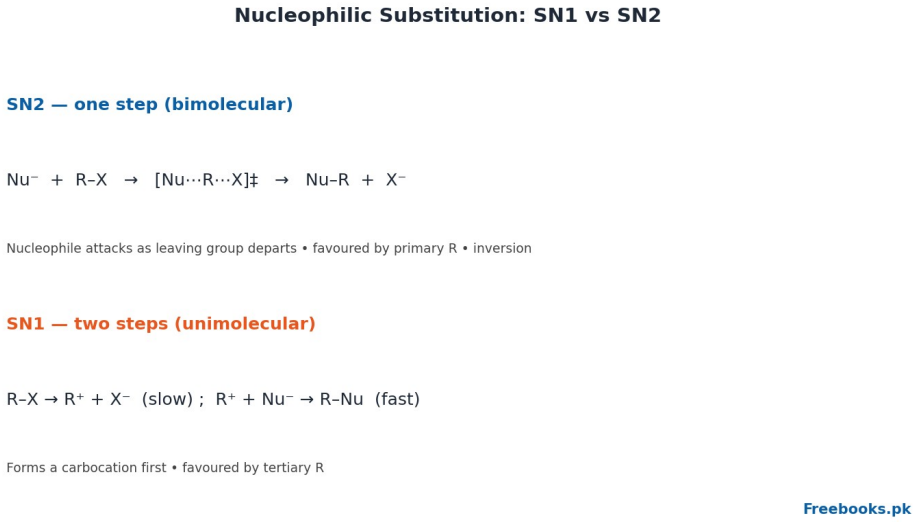

Figure 10.2 — The SN2 (one-step) and SN1 (two-step) mechanisms.

SN1 vs SN2 at a glance

SN2: one step, the nucleophile attacks as the halide leaves; rate depends on both reactants; favoured by primary halides.

SN1: two steps, the halide leaves first to form a carbocation, then the nucleophile attacks; rate depends only on the halide; favoured by tertiary halides.

3.4 Elimination (Dehydrohalogenation)

When an alkyl halide is heated with alcoholic KOH, a molecule of hydrogen halide is eliminated and a double bond forms, giving an alkene. This elimination reaction competes with substitution; strong, hot, alcoholic base favours elimination, while aqueous conditions favour substitution.

3.5 The Grignard Reagent

One of the most important reasons for studying alkyl halides is the Grignard reagent, formed when an alkyl halide reacts with magnesium in dry ether: R–X + Mg → R–Mg–X. The carbon attached to magnesium is strongly nucleophilic, so Grignard reagents react with many compounds to build larger molecules. They give alkanes with water, primary alcohols with methanal, secondary alcohols with other aldehydes, tertiary alcohols with ketones, and carboxylic acids with carbon dioxide.

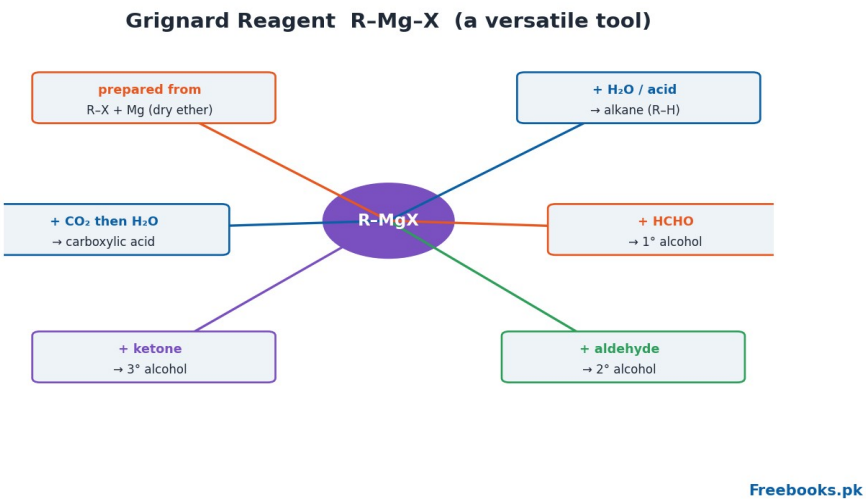

Figure 10.3 — Some reactions of the Grignard reagent.

Teacher's Note

The Grignard reagent must be made and used in perfectly dry conditions, because even a trace of water destroys it (turning it into an alkane). This 'moisture-sensitivity' is a favourite exam point.

4. Important Definitions

Term	Definition
Alkyl halide	A compound R–X in which a halogen replaces a hydrogen of an alkane.
Nucleophile	An electron-rich species that attacks a positive (δ+) carbon centre.
Nucleophilic substitution	Replacement of a leaving group by a nucleophile.
SN1 / SN2	Two mechanisms of nucleophilic substitution (unimolecular / bimolecular).
Elimination	Removal of HX from an alkyl halide to form an alkene.
Grignard reagent	An organomagnesium compound R–Mg–X used to build larger molecules.

5. Formulas / Rules

Must-Know Facts

General formula: R–X; classify as 1°, 2°, 3°.

Reactivity: R–I > R–Br > R–Cl > R–F.

SN2 → primary; SN1 → tertiary (via carbocation).

Alc. KOH → elimination (alkene); aq. KOH → substitution (alcohol).

Grignard: R–X + Mg (dry ether) → R–MgX; + CO_2 → carboxylic acid.

6. Diagrams / Illustrations

Key diagrams for revision:

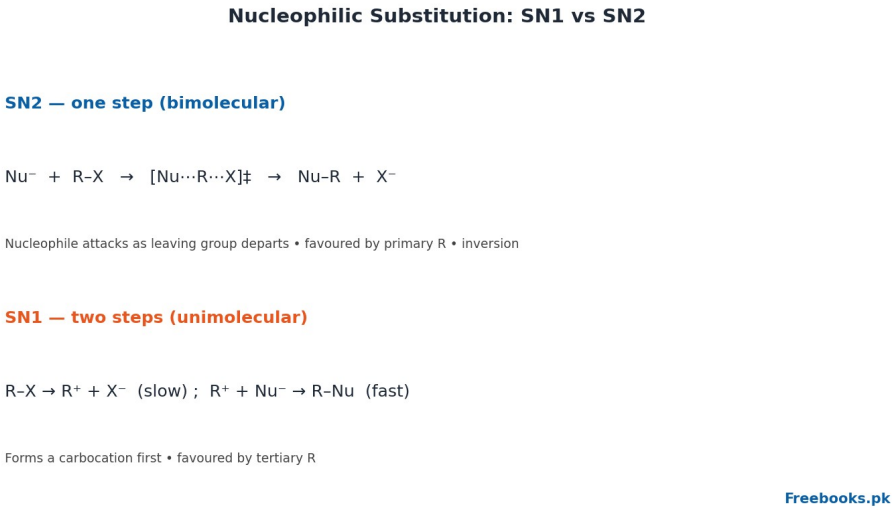

Diagram 1 — SN1 vs SN2 mechanisms.

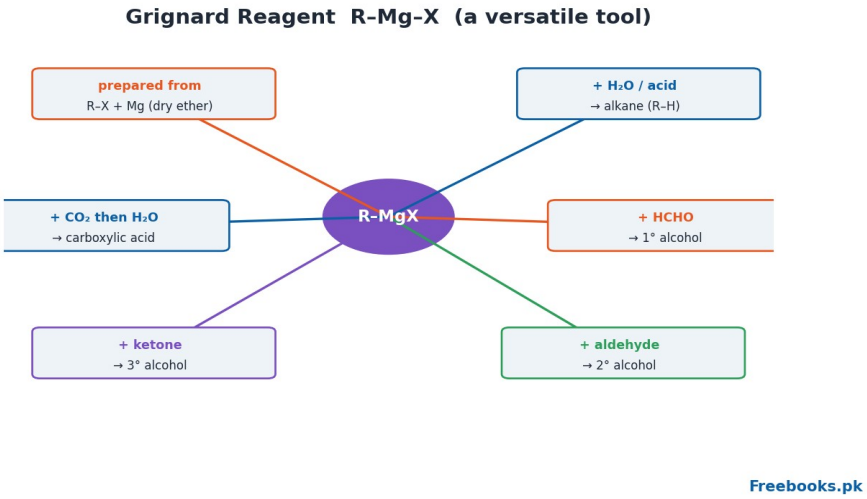

Diagram 2 — Reactions of the Grignard reagent.

7. Solved Examples

Example 1 — Substitution product

Q: What is formed when ethyl bromide is heated with aqueous KOH?

Solution: Nucleophilic substitution occurs: the OH^- replaces Br^-, giving ethanol (C_2H_5OH) and KBr.

Example 2 — Substitution vs elimination

Q: How can ethyl bromide be converted to ethene?

Solution: Heat it with alcoholic KOH. This causes elimination of HBr (dehydrohalogenation) and forms ethene.

Example 3 — Grignard synthesis

Q: How would you make a carboxylic acid using a Grignard reagent?

Solution: React the Grignard reagent (R–MgX) with carbon dioxide, then hydrolyse with dilute acid: R–MgX + CO_2 → R–COO–MgX → R–COOH. The product has one more carbon than R.

8. Short Questions

Q1. What is an alkyl halide?
Ans. A compound R–X formed when a halogen replaces a hydrogen atom of an alkane.

Q2. Why is the C–X bond reactive?
Ans. It is polar; the carbon is δ+ and is attacked by nucleophiles, while X^- is a good leaving group.

Q3. Arrange R–F, R–Cl, R–Br, R–I in order of reactivity.
Ans. R–I > R–Br > R–Cl > R–F (weaker bond, easier to break).

Q4. Differentiate SN1 and SN2.
Ans. SN2 is a one-step bimolecular reaction (primary halides); SN1 is a two-step unimolecular reaction via a carbocation (tertiary halides).

Q5. How is an alkene obtained from an alkyl halide?
Ans. By heating it with alcoholic KOH, which eliminates HX (dehydrohalogenation).

Q6. How is a Grignard reagent prepared?
Ans. By reacting an alkyl halide with magnesium in dry ether: R–X + Mg → R–MgX.

Q7. Why must Grignard reagents be kept dry?
Ans. Water destroys them, converting them into alkanes.

Q8. What does a Grignard reagent give with CO_2?
Ans. A carboxylic acid (after hydrolysis).

9. Long Questions

Q1. Describe the nucleophilic substitution reactions of alkyl halides (SN1 and SN2).

Because the carbon–halogen bond is polar, the carbon carries a partial positive charge and is attacked by nucleophiles, which replace the halogen (the leaving group). This replacement can happen by two mechanisms. In the SN2 (bimolecular) mechanism the reaction occurs in a single step: the nucleophile approaches the carbon from the side opposite the halogen and forms a bond at the same time as the carbon–halogen bond breaks, passing through a transition state and giving inversion of configuration. Its rate depends on both the alkyl halide and the nucleophile, and it is favoured by primary halides, which have little steric hindrance. In the SN1 (unimolecular) mechanism the reaction occurs in two steps: first the halide leaves to give a carbocation (the slow, rate-determining step), and then the nucleophile attacks the carbocation. Its rate depends only on the alkyl halide, and it is favoured by tertiary halides, which form the most stable carbocations. Typical products are alcohols (with aqueous KOH) and nitriles (with alcoholic KCN).

Q2. Explain the preparation and synthetic importance of the Grignard reagent.

The Grignard reagent is an organomagnesium compound of the form R–Mg–X, prepared by adding an alkyl halide to magnesium turnings in dry ether, where it forms R–X + Mg → R–Mg–X. In this reagent the carbon attached to magnesium is strongly nucleophilic, which makes the Grignard reagent one of the most useful tools in organic synthesis. With water or dilute acid it gives an alkane; with methanal (formaldehyde) it gives a primary alcohol; with other aldehydes it gives secondary alcohols; with ketones it gives tertiary alcohols; and with carbon dioxide, followed by hydrolysis, it gives a carboxylic acid with one more carbon atom than the original halide. Because these reactions form new carbon–carbon bonds, the Grignard reagent allows chemists to build larger and more complex molecules from simple alkyl halides. It must, however, be prepared and used in completely dry conditions, since even a trace of water destroys it.

Q3. Distinguish between substitution and elimination reactions of alkyl halides.

Alkyl halides can react in two competing ways, and the conditions decide which one dominates. In a substitution reaction a nucleophile replaces the halogen while the carbon skeleton stays the same; for example, ethyl bromide with aqueous KOH gives ethanol. In an elimination reaction a molecule of hydrogen halide is removed from two adjacent carbons to create a carbon–carbon double bond; for example, ethyl bromide with hot alcoholic KOH gives ethene. Thus the same reagent (KOH) can give different products depending on the solvent: aqueous conditions favour substitution (forming an alcohol), while hot, concentrated, alcoholic conditions favour elimination (forming an alkene). Tertiary halides and strong, bulky bases also favour elimination, whereas primary halides favour substitution.

10. Multiple Choice Questions (MCQs)

1. The general formula of alkyl halides is:
(A) R–OH (B) R–X (C) R–CHO (D) R–COOH

2. Which alkyl halide is most reactive?
(A) R–F (B) R–Cl (C) R–Br (D) R–I

3. SN2 reactions are favoured by ___ halides:
(A) primary (B) secondary (C) tertiary (D) aromatic

4. SN1 reactions proceed through a:
(A) free radical (B) carbocation (C) carbanion (D) transition metal

5. Alkyl halide + aqueous KOH gives:
(A) alkene (B) alcohol (C) alkane (D) ether

6. Alkyl halide + alcoholic KOH gives:
(A) alcohol (B) alkene (C) acid (D) amine

7. A Grignard reagent is:
(A) R–OH (B) R–MgX (C) R–ONa (D) $R–NH_2$

8. Grignard reagent + CO_2 (then H_2O) gives:
(A) alkane (B) alcohol (C) carboxylic acid (D) ketone

9. Grignard reagents are prepared in:
(A) water (B) dry ether (C) dilute acid (D) alcohol

10. Grignard reagent + ketone gives a:
(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) carboxylic acid

MCQ Answer Key

1-B 2-D 3-A 4-B 5-B 6-B 7-B 8-C 9-B 10-C

11. Quick Revision / Summary

- Alkyl halide R–X; classify 1°, 2°, 3°; C–X bond polar and reactive.
- Reactivity: R–I > R–Br > R–Cl > R–F.
- Nucleophilic substitution: SN2 (one step, primary) and SN1 (carbocation, tertiary).
- Aq. KOH → substitution (alcohol); alc. KOH → elimination (alkene).
- Grignard R–MgX from R–X + Mg (dry ether); builds C–C bonds.
- Grignard + CO_2 → carboxylic acid; + aldehyde/ketone → alcohols.

12. Exam Tips

Teacher's Note

Contrast SN1 and SN2 in a small table: steps, molecularity, which halide is favoured.
Remember: aqueous KOH → alcohol (substitution), alcoholic KOH → alkene (elimination).
Learn the full set of Grignard reactions — a very common long question.
Always mention that Grignard reagents need dry conditions.
Reactivity order R–I > R–Br > R–Cl > R–F is a frequent MCQ.