Class: 12th

Subject: Chemistry

Chapter 10: ALKYL HALIDES

🩸 Important Keypoints MCQs

1. Monohalo derivatives of alkanes are called:

(a) Haloarenes

(b) Alkyl halides ✅

(c) Aryl halides

(d) Polyhalides

2. The general formula of alkyl halides is:

(a) C_nH_{2n}

(b) C_nH_{2n+2}

(c) $C_nH_{2n+1}X$ ✅

(d) $C_nH_{2n}X_2$

3. The best method for preparing alkyl halides from alcoho uses:

(a) H_2SO_4

(b) Organic acids

(c) $SOCl_2$, PX_3 or PX_5 (inorganic halides) ✅

(d) H_2O_2

4. Alkyl halides generally undergo:

(a) Only oxidation

(b) Only addition reactions

(c) Nucleophilic substitution and elimination reactions ✅

(d) Polymerization

5. A one-step nucleophilic substitution mechanism is called:

(a) SN1

(b) SN2 ✅

(c) E1

(d) E2

6. The mechanism that follows first-order kinetics is:

(a) SN2

(b) SN1 ✅

(c) E2

(d) Free radical substitution

7. Elimination of two atoms or groups from adjacent carbons is called:

(a) Substitution

(b) Addition

(c) Elimination reaction (β-elimination) ✅

(d) Rearrangement

8. Grignard reagent is prepared by reacting alkyl halide with magnesium in:

(a) Water

(b) Concentrated HCl

(c) Dry diethyl ether ✅

(d) Alcoholic solution

9. The carbon atom in a Grignard reagent behaves as:

(a) Electrophilic

(b) Neutral

(c) Proton donor

(d) Nucleophilic and highly reactive toward electrophiles ✅

10. Reacting Grignard reagent with ketones produces:

(a) Primary alcohols

(b) Secondary alcohols

(c) Tertiary alcohols ✅

(d) Aldehydes

🩸 Important MCQs:

1. Halogen derivatives of alkanes are called:

(a) Alkenes

(b) Alcohols

(c) Haloalkanes ✅

(d) Aldehydes

2. The general formula of monohaloalkanes (alkyl halides) is:

(a) RH

(b) RX ✅

(c) R–OH

(d) R–COOH

3. In alkyl halides, X represents:

(a) N, O, S, P

(b) F, Cl, Br, I ✅

(c) Only Cl

(d) C, H, O

4. In a primary alkyl halide, the halogen-bearing carbon is attached to:

(a) One or no carbon atom ✅

(b) Two carbon atoms

(c) Three carbon atoms

(d) Four carbon atoms

5. Chloromethane (CH_3Cl) is an example of:

(a) Secondary alkyl halide

(b) Primary alkyl halide ✅

(c) Tertiary alkyl halide

(d) Aromatic halide

6. 2-Chloropropane is a:

(a) Primary alkyl halide

(b) Secondary alkyl halide ✅

(c) Tertiary alkyl halide

(d) Vinyl halide

7. 2-Chloro-2-methylpropane is a:

(a) Primary alkyl halide

(b) Secondary alkyl halide

(c) Tertiary alkyl halide ✅

(d) None of these

8. In IUPAC nomenclature, longest carbon chain is selected to name the:

(a) Halogen

(b) Parent hydrocarbon ✅

(c) Substituent

(d) Functional group only

9. In naming haloalkanes, the halogen must get the:

(a) Highest possible number

(b) Lowest possible number ✅

(c) Middle number

(d) Odd number only

10. If a substituent occurs more than once, prefixes used are:

(a) Mono, neo, iso

(b) Di, tri, tetra ✅

(c) Cis, trans

(d) Sec, tert

11. Positions of substituents are separated by:

(a) Hyphens

(b) Brackets

(c) Commas ✅

(d) Semicolons

12. $CH_3–CH_2–CH_2–Cl$ is named as:

(a) 2-Chloropropane

(b) Propyl chloride

(c) 1-Chloropropane ✅

(d) Chloromethane

13. $CH_3–CH(Cl)–CH_2–CH_3$ is named as:

(a) 1-Chlorobutane

(b) 2-Chlorobutane ✅

(c) 3-Chlorobutane

(d) Butyl chloride

14. 2-Bromo-3-methylbutane follows IUPAC rules because:

(a) Longest chain is selected

(b) Correct numbering is done

(c) Correct substituent position is used

(d) All of these ✅

15. $(CH_3)_2CH–CH_2Cl$ (Isobutyl chloride) in IUPAC is named as:

(a) 1-Chlorobutane

(b) 1-Chloro-2-methylpropane ✅

(c) 2-Chlorobutane

(d) 3-Chloro-2-methylpropane

16. Alkyl halides are best prepared from:

(a) Alkanes

(b) Alkenes

(c) Alcohols ✅

(d) Aldehydes

17. Alcohols react with halogen acids to form alkyl halides in the presence of:

(a) $FeCl_3$

(b) $ZnCl_2$ ✅

(c) $CuSO_4$

(d) H_2SO_4

18. In the reaction of alcohol with HX in the presence of $ZnCl_2$, the by-product formed is:

(a) CO_2

(b) H_2O ✅

(c) SO_2

(d) HCl

19. Thionyl chloride ($SOCl_2$) converts alcohols into alkyl chlorides in the presence of:

(a) Water

(b) Pyridine ✅

(c) Ether

(d) Sulfuric acid

20. A major advantage of the $SOCl_2$–pyridine method is that its by-products are:

(a) Solids

(b) Liquids

(c) Gases and easily removed ✅

(d) Non-reactive solids

21. Phosphorus trihalides or pentahalides convert alcohols into alkyl halides by replacing:

(a) Hydrogen atom

(b) Alkyl group

(c) –OH group with halogen atom ✅

(d) Carbonyl group

22. Alkyl iodides cannot be prepared by direct iodination because iodine:

(a) Is too reactive

(b) Is unstable

(c) Is oxidizing

(d) Is weakly reactive toward alkanes ✅

23. Simple alkyl iodides are prepared from alkyl chlorides or bromides by using:

(a) NaBr

(b) NaCl

(c) NaI ✅

(d) KI

24. According to C–X bond energies, the most reactive alkyl halide is:

(a) Alkyl fluoride

(b) Alkyl chloride

(c) Alkyl bromide

(d) Alkyl iodide ✅

25. The correct overall reactivity order of alkyl halides is:

(a) F > Cl > Br > I

(b) Cl > Br > F > I

(c) I > Br > Cl > F ✅

(d) Br > I > Cl > F

26. Reactions in which halogen is replaced by another group are called:

(a) Addition reactions

(b) Nucleophilic substitution reactions (SN) ✅

(c) Oxidation reactions

(d) Polymerization reactions

27. Reactions involving the removal of HX from alkyl halides are called:

(a) Substitution reactions

(b) Addition reactions

(c) Elimination reactions (E) ✅

(d) Reduction reactions

28. A nucleophile is a species that is:

(a) Proton-loving

(b) Electron-loving

(c) Nucleus-loving with a lone pair of electrons ✅

(d) Positively charged only

29. Which of the following is a nucleophile?

(a) H^+

(b) NO_2^+

(c) OH^- ✅

(d) Mg^{2+}

30. The carbon attached to halogen in alkyl halides behaves as:

(a) Nucleophile

(b) Electrophile ✅

(c) Oxidizing center

(d) Reducing center

31. A good leaving group among the following is:

(a) OH^-

(b) NH_2^-

(c) OR^-

(d) Br^- ✅

32. In an SN2 mechanism, the nucleophile attacks from the:

(a) Same side as leaving group

(b) Front side

(c) Opposite side of the leaving group (backside attack) ✅

(d) Any random direction

33. SN2 mechanism occurs in:

(a) Two steps

(b) One step (single step) ✅

(c) Three steps

(d) Four steps

34. Primary alkyl halides generally follow:

(a) SN1 mechanism

(b) SN2 mechanism ✅

(c) E1 mechanism

(d) Free-radical mechanism

35. The rate of an SN2 reaction depends on:

(a) Alkyl halide only

(b) Nucleophile only

(c) Both alkyl halide and nucleophile (second-order) ✅

(d) Solvent only

36. SN1 mechanism involves formation of:

(a) Free radical

(b) Carbocation intermediate ✅

(c) Carbanion

(d) Carbonyl group

37. In SN1 reactions, configuration of product shows:

(a) 100% inversion

(b) 100% retention

(c) 50% inversion and 50% retention (racemization) ✅

(d) No change

38. Tertiary alkyl halides mostly follow:

(a) SN2 mechanism

(b) SN1 mechanism ✅

(c) E2 mechanism only

(d) None of these

39. In E2 mechanism, the leaving group departure and nucleophile attack occur:

(a) Independently

(b) Stepwise

(c) Simultaneously (single step) ✅

(d) After carbocation formation

40. Primary alkyl halides usually undergo elimination via:

(a) E1 mechanism

(b) E2 mechanism ✅

(c) SN1 mechanism

(d) Radical mechanism

41. Grignard reagents belong to which class of compounds?

(a) Carboxylic acids

(b) Organo-metallic compounds ✅

(c) Aromatic hydrocarbons

(d) Alkynes

42. Grignard reagent RMgX is prepared by the reaction of alkyl halide with:

(a) Sodium metal

(b) Magnesium metal in dry ether ✅

(c) Zinc metal in wet ether

(d) Aluminium metal

43. For the preparation of Grignard reagent, the reaction must be carried out in:

(a) Moist ether

(b) Water

(c) Absolutely dry ether (moisture-free) ✅

(d) Alcohol solution

44. Reactivity of alkyl halides with magnesium follows the order:

(a) Alkyl chloride > Alkyl bromide > Alkyl iodide

(b) Alkyl iodide > Alkyl bromide > Alkyl chloride ✅

(c) Alkyl bromide > Alkyl iodide > Alkyl chloride

(d) Alkyl chloride > Alkyl iodide > Alkyl bromide

45. The high reactivity of Grignard reagent is due to:

(a) Strong C–H bond

(b) Ionic Mg–X bond

(c) Highly polar C–Mg bond giving carbon a partial negative charge ✅

(d) Presence of double bond in RMgX

🩸 Important Keypoints Short Questions:

1. Define alkyl halides.

Answer:

👉 Monohalo derivatives of alkanes in which one hydrogen atom is replaced by a halogen atom are called alkyl halides.

2. Write the general formula of alkyl halides.

Answer:

👉 CnH2n+1X (X = F, Cl, Br, I)

3. Name any two inorganic halides used to convert alcohols into alkyl halides.

Answer:

👉 $SOCl_2$ (thionyl chloride) and PBr_3 (phosphorus tribromide).

4. Why are alkyl halides considered a very reactive class of organic compounds?

Answer:

👉 Because the carbon–halogen bond is polar, making the carbon atom electrophilic and allowing alkyl halides to undergo nucleophilic substitution and elimination reactions easily.

5. What is meant by nucleophilic substitution reaction?

Answer:

👉 It is a reaction in which a nucleophile replaces the halogen atom in an alkyl halide.

6. Give one major difference between SN1 and SN2 mechanisms.

Answer:

👉 SN1 is a two-step reaction with first-order kinetics (rate depends on alkyl halide only), while SN2 is a one-step reaction with second-order kinetics (rate depends on both alkyl halide and nucleophile).

7. Define elimination reaction.

Answer:

👉 An elimination reaction is the removal of two atoms or groups from adjacent carbon atoms of an alkyl halide, usually forming an alkene.

8. What is the role of dry ether in the preparation of Grignard reagent?

Answer:

👉 Dry ether acts as a solvent and stabilizes the Grignard reagent, preventing reaction with moisture.

9. Why is the carbon attached to magnesium in Grignard reagent nucleophilic?

Answer:

👉 Because the C–Mg bond is highly polar, making the carbon atom partially negative and able to attack electrophilic centers.

10. Which alcohol is formed when Grignard reagent reacts with ketones?

Answer:

👉 Secondary alcohols are formed when Grignard reagent reacts with ketones.

🩸 Important Short Questions:

1. What are halogen derivatives of alkanes called?

Answer:

👉 Halogen derivatives of alkanes are called haloalkanes.

2. What are monohaloalkanes also called?

Answer:

👉 Monohaloalkanes are also called alkyl halides.

3. Write the general formula of alkyl halides.

Answer:

👉 The general formula of alkyl halides is RX, where R = alkyl group and X = halogen (F, Cl, Br, I).

4. How are alkyl halides classified based on the type of carbon atom attached to halogen?

Answer:

👉 Alkyl halides are classified as:

- **Primary (1°)** – halogen attached to carbon bonded to 1 or no other carbon.
- **Secondary (2°)** – halogen attached to carbon bonded to 2 other carbons.
- **Tertiary (3°)** – halogen attached to carbon bonded to 3 other carbons.

5. Give an example of a primary alkyl halide.

Answer:

👉 Chloromethane (CH_3Cl) or Chloroethane (CH_3CH_2Cl).

6. Give an example of a secondary alkyl halide.

Answer:

👉 2-Chloropropane ($CH_3CHClCH_3$).

7. Give an example of a tertiary alkyl halide.

Answer:

👉 2-Chloro-2-methylpropane ($C(CH_3)_3Cl$).

8. What is the basic rule for naming alkyl halides using the IUPAC system?

Answer:

👉 Select the longest continuous carbon chain, number it so that the carbon bearing the halogen gets the lowest possible number, and indicate substituents with proper prefixes (di, tri, etc.) and numbers.

9. How are multiple identical substituents indicated in IUPAC nomenclature?

Answer:

👉 By using prefixes such as di, tri, tetra, and repeating the position number for substituents on the same carbon.

10. Give an example of a named alkyl halide following IUPAC rules.

Answer:

👉 2-Bromo-3-methylbutane or 2-Chloro-4-methylpentane.

11. Name two methods to prepare alkyl halides.

Answer:

👉 Alkyl halides can be prepared by:

1. Halogenation of alkanes.

2. Addition of halogen acids to alkenes.

12. What is the best method for preparing alkyl halides?

Answer:

👉 The best method is the reaction of alcohols with halogen acids or inorganic halides like $SOCl_2$, PBr_3, and PCl_5.

13. How are alcohols converted into alkyl halides using halogen acids?

Answer:

👉 Alcohol reacts with halogen acid (HX) in the presence of $ZnCl_2$ catalyst to give alkyl halide and water:

$$CH_3CH_2OH + HX \longrightarrow CH_3CH_2X + H_2O$$

14. Which reagent is used to prepare alkyl chlorides from alcohols leaving no liquid by-products?

Answer:

👉 Thionyl chloride ($SOCl_2$) in pyridine is used, producing HCl and SO_2 gases as by-products that escape.

15. Arrange alkyl halides in order of reactivity and explain why.

Answer:

👉 Iodide > Bromide > Chloride > Fluoride.

- **Reactivity** depends mainly on C–X bond strength.
- **C–I bond is weakest,** making alkyl iodides most reactive; C–F bond is strongest, making alkyl fluorides least reactive.

16. Name the two main types of reactions of alkyl halides.

Answer:

👉 1. Nucleophilic substitution reactions (S reactions)

👉 2. Elimination reactions (E reactions)

17. What is a nucleophile? Give two examples.

Answer:

👉 A nucleophile is a species that has an unshared pair of electrons and can donate it to form a bond with an electrophile.

Examples: OH^- (hydroxide ion), CN^- (cyanide ion)

18. What is meant by a leaving group in nucleophilic substitution?

Answer:

👉 A leaving group is a nucleophile that departs with an electron pair during a substitution reaction.

- **Good leaving** groups: Cl^-, Br^-, HSO_4^-
- **Poor leaving** groups: OH^-, OR^-, NH_2^-

19. What is the main difference between SN1 and SN2 mechanisms?

Answer:

👉 **SN1:** Two-step, first-order kinetics, forms a planar carbocation intermediate, can attack from both sides.

👉 **SN2:** One-step, second-order kinetics, nucleophile attacks opposite to leaving group, inversion of configuration occurs.

20. Which alkyl halides usually follow SN2 mechanism?

Answer:

👉 Primary alkyl halides always follow SN2 mechanism when attacked by nucleophiles.

21. Which alkyl halides usually follow SN1 mechanism?

Answer:

👉 Tertiary alkyl halides always follow SN1 mechanism. Secondary alkyl halides may follow both SN1 and SN2.

22. Define elimination reaction.

Answer:

👉 An elimination reaction is the removal of two atoms or groups from adjacent carbon atoms of an alkyl halide, usually forming an alkene.

23. What is the difference between E1 and E2 elimination mechanisms?

Answer:

👉 **E1:** Unimolecular, two-step, rate depends only on alkyl halide, forms carbocation intermediate.

👉 **E2:** Bimolecular, single-step, rate depends on both alkyl halide and base/nucleophile, forms double bond directly.

24. Give one example of the synthetic usefulness of alkyl halides.

Answer:

Alkyl halides react with nucleophiles to produce various organic compounds:

👉 $CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH$ (ethyl alcohol)

👉 $CH_3CH_2Br + CN^- \longrightarrow CH_3CH_2CN$ (propane nitrile)

25. What is Wurtz synthesis?

Answer:

👉 Reaction of alkyl halides with sodium in dry ether to form alkanes, particularly useful for preparing symmetrical alkanes:

$$CH_3CH_2Cl + 2Na + ClCH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_3 + 2NaCl$$

26. What is a Grignard reagent?

Answer:

👉 Grignard reagents (RMgX) are organometallic compounds derived from alkyl halides, where R is an alkyl group and X is a halogen (F, Cl, Br, I). They are highly reactive and widely used in organic synthesis.

27. Who discovered the Grignard reagent and when?

Answer:

👉 Victor Grignard discovered the Grignard reagent in 1900, and he received the Nobel Prize in Chemistry for its importance.

28. How is a Grignard reagent prepared?

Answer:

👉 By reacting a dry alkyl halide (R–X) with magnesium metal in dry ether (alcohol- and moisture-free):

$$R–X + Mg \longrightarrow R–Mg–X$$

29. Why must Grignard reagents be prepared under dry conditions?

Answer:

👉 Because Grignard reagents are highly reactive and react with water or moisture to produce alkanes, which destroys the reagent:

$$R–Mg–X + H_2O \longrightarrow R–H + Mg(OH)X$$

30. Name the type of alcohol formed when Grignard reagents react with: (i) formaldehyde, (ii) other aldehydes, (iii) ketones.

Answer:

👉 (i) Primary alcohols – with formaldehyde

👉 (ii) Secondary alcohols – with other aldehydes

👉 (iii) Tertiary alcohols – with ketones

🩸 EXERCISE

Q1. Fill in the blanks:

(i) Alkali metals are _____ reactive than alkaline-earth metals.

Answer: more ✅

(ii) In tertiary alkyl halides, the halogen atom is attached to _____ a carbon which is further attached to three carbon atoms directly.

Answer: a ✅

(iii) The best method for the preparation of alkyl halides is the reaction of _____ with inorganic reagents.

Answer: alcohols ✅

(iv) An alkyl group with a partial positive charge on the carbon atom is called _____ centre.

Answer: electrophilic ✅

(v) The mechanism is called _____ if it involves one molecule in the rate-determining step.

Answer: unimolecular (S□1 or E1) ✅

(vi) Molecularity of a reaction is defined as the number of molecules taking part in the _____.

Answer: rate-determining step ✅

(vii) The molecularity of E2 reactions is always two and the reactions show _____ order kinetics.

Answer: second ✅

(viii) Wurtz synthesis is useful for the preparation _____ of alkanes.

Answer: of symmetrical ✅

(ix) Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of _____.

Answer: dry ether ✅

(x) Nucleophilic substitution reactions in which the nucleophile attacks from the side opposite to the leaving group is called _____ mechanism.

Answer: S□2 ✅

Q2. Indicate True or False:

(i) In secondary alkyl halides, the halogen atom is attached to a carbon which is further attached to two carbon atoms directly.

Answer: True ✅

(ii) Alcohols react with thionyl chloride in ether as solvent to give alkyl halides.

Answer: False ❌ (Correct solvent: pyridine)

(iii) Order of reactivity of alkyl halides for a particular alkyl group is: Iodide > Bromide > Chloride > Fluoride.

Answer: True ✅

(iv) In Sn2 reactions the attacking nucleophile always attacks from the side in which the leaving group is attached.

Answer: False ❌ (It attacks from the opposite side, inversion of configuration)

(v) Methyl magnesium iodide on hydrolysis yields ethyl alcohol.

Answer: False ❌ (It gives primary alcohol, CH_3OH)

(vi) Primary, secondary and tertiary amines react with Grignard reagents in the same way.

Answer: False ❌

(vii) The reactions of secondary alkyl halides may follow both Sn1 and Sn2 mechanisms.

Answer: True ✅

(viii) Sn1 mechanism is a one-stage process involving a simultaneous bond breakage and bond formation.

Answer: False ❌ (It is two-step, forming a carbocation intermediate)

(ix) In β-elimination reactions, the two atoms or groups attached to two adjacent carbon atoms are lost under the influence of an electrophile.

Answer: False ❌ (They are lost under the influence of a base/nucleophile, forming an alkene)

(x) The reactivity order of alkyl halides is determined by the strength of the carbon-halogen bond.

Answer: True ✅

Q3. Multiple Choice Questions. Encircle the correct answer:

i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms?

(a) Two

(b) Three

(c) One ✅

(d) Four

ii) The reactivity order of alkyl halides for a particular alkyl group is:

(a) Fluoride > Chloride > Bromide > Iodide

(b) Chloride > Bromide > Fluoride > Iodide

(c) Iodide > Bromide > Chloride > Fluoride ✅

(d) Bromide > Iodide > Chloride > Fluoride

iii) When CO_2 reacts with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is:

(a) Propane

(b) Propanoic acid ✅

(c) Propanal

(d) Propanol

iv) Grignard reagent is reactive due to:

(a) the presence of halogen atom

(b) the presence of Mg atom

(c) the polarity of C–Mg bond ✅

(d) none of the above

v) SN2 reactions can be best carried out with:

(a) Primary alkyl halides ✅

(b) Secondary alkyl halides

(c) Tertiary alkyl halides

(d) All the three

vi) Elimination bimolecular reactions involve:

(a) first order kinetics

(b) second order kinetics ✅

(c) third order kinetics

(d) zero order kinetics

vii) For which mechanisms, the first step involved is the same:

(a) E1 and E2

(b) E2 and SN2

(c) SN1 and E2

(d) E1 and SN1 ✅

viii) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:

(a) they have an electrophilic carbon

(b) they have an electrophilic carbon and a good leaving group ✅

(c) they have an electrophilic carbon and a bad leaving group

(d) they have a nucleophilic carbon and a good leaving group

ix) The rate of E1 reaction depends upon:

(a) the concentration of substrate ✅

(b) the concentration of nucleophile

(c) the concentration of substrate as well as nucleophile

(d) None of the above

x) Which one of the following is not a nucleophile:

(a) H_2O

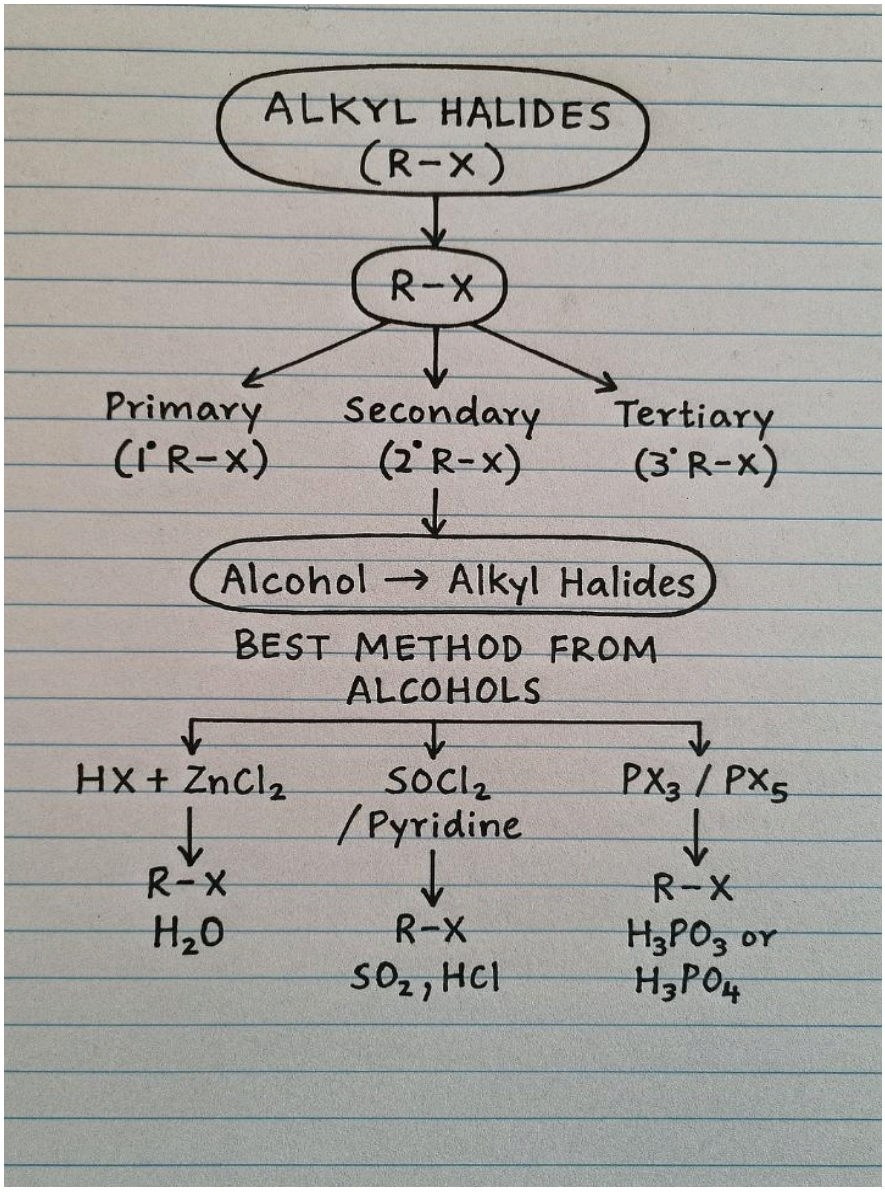
(b) H_2S

(c) BF_3 ✅

(d) NH_3

🌟 Q.4. Define Alkyl Halide. Which is the Best Method of Preparing Alkyl Halides?

✦ **Digram:**



❖ **Definition of Alkyl Halide**

👉 **Alkyl halides,** also called haloalkanes, are organic compounds in which one or more hydrogen atoms in an alkane are replaced by halogen atoms (F, Cl, Br, I).

👉 **Monohaloalkanes (Alkyl Halides):** Only one hydrogen atom is replaced by a halogen.

General Formula: R-X

- **R** = alkyl group (methyl, ethyl, propyl, etc.)
- **X** = halogen atom (F, Cl, Br, I)

✦ **Classification based on carbon attached to halogen:**

1. Primary (1°): Halogen attached to carbon connected to 1 other carbon or none.

Example: CH3CH2Cl (Chloroethane)

2. Secondary (2°): Halogen attached to carbon connected to 2 other carbons.

Example: CH3CHClCH3 (2-Chloropropane)

3. Tertiary (3°): Halogen attached to carbon connected to 3 other carbons.

Example: (CH3)3CCl (Tert-butyl chloride)

🔹 Best Method of Preparing Alkyl Halides

Alkyl halides can be prepared by several methods:

1. Halogenation of Alkanes

Example: CH4 + Cl2 ⟶ CH3Cl + HCl

2. Addition of Hydrogen Halides to Alkenes

Example: CH2=CH2 + HBr ⟶ CH3CH2Br

3. From Alcohols (Best Method)

(a) Reaction with Halogen Acids (HX + ZnCl2)

Example: CH3CH2OH + HCl ⟶ CH3CH2Cl + H2O

(b) Reaction with Thionyl Chloride (SOCl2 / Pyridine)

Example: CH3CH2OH + SOCl2 ⟶ CH3CH2Cl + SO2 + HCl

(c) Reaction with Phosphorus Halides (PX3 or PX5)

Example: $3CH_3CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2Br + H_3PO_3$

Example: $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

(d) Conversion to Alkyl Iodides

Example: $R\text{-}Cl + NaI \longrightarrow R\text{-}I + NaCl$

Example: $R\text{-}Br + NaI \longrightarrow R\text{-}I + NaBr$

Reason this is Best:

- **High yield** and purity
- **Easy** control of reaction conditions
- **Suitable for primary,** secondary, and tertiary alcohols

✦ **Summary:**

Alkyl Halides: Halo derivatives of alkanes (R−X), classified as primary, secondary, tertiary.

Best Preparation: From alcohols using halogen acids, $SOCl_2$, or phosphorus halides.

Advantages: High yield, pure products, controlled reactions.

🌟 **Q.5. Write down a method for the preparation of ethyl magnesium bromide in the laboratory.**

❖ **Answer:**

Ethyl magnesium bromide is a Grignard reagent of the formula C_2H_5MgBr. It is an organo-metallic compound and can be prepared in the laboratory using magnesium metal and ethyl bromide in dry ether.

Materials Required:

- **Magnesium** ribbon or turnings
- **Ethyl** bromide (C_2H_5Br)
- **Dry diethyl** ether (solvent, moisture-free)
- **Iodine** (optional, as an activator)

Procedure:

1. Setup:

- **Take a dry,** clean flask and add magnesium metal turnings.
- Add dry diethyl ether to the flask.

2. Activation of Magnesium (Optional):

- A small crystal of iodine may be added to remove any oxide layer on magnesium.

3. Addition of Alkyl Halide:

- **Slowly add** ethyl bromide dropwise to the flask containing magnesium in ether.
- **Stir** the mixture continuously.

4. Formation of Grignard Reagent:

The reaction proceeds as:

$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$

- (Ethyl bromide) (Magnesium) (Ethyl magnesium bromide)
- This is an exothermic reaction. Effervescence may be observed.

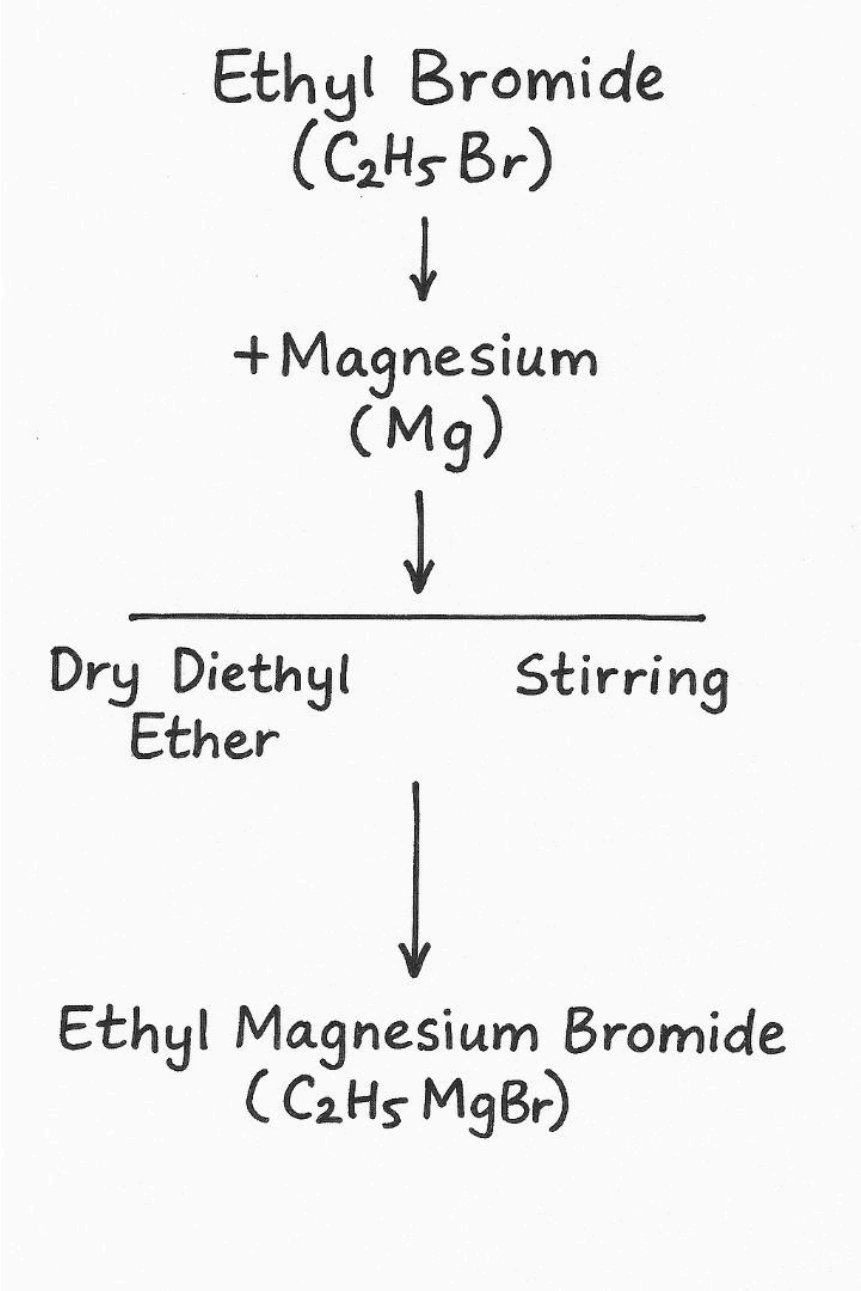
5. Observation:

- **The solution** becomes slightly turbid due to the formation of ethyl magnesium bromide.
- **The reagent** must be kept moisture-free, as it reacts violently with water.

Precautions:

- **All apparatus** must be absolutely dry; water destroys Grignard reagent.
- **Diethyl ether** must be anhydrous.
- **Reaction should** be carried out under dry, inert conditions if possible.

✦ **Digram:**



✦ **Summary:**

- **Reagents:** Ethyl bromide + Magnesium + Dry ether
- **Product:** Ethyl magnesium bromide (C2H5MgBr)

- **Reaction Type:** Formation of Grignard reagent (organometallic compound)

Key Points: Moisture-free conditions, exothermic reaction, highly reactive nucleophilic carbon atom

🌟 **Q.6 Give IUPAC names to the following compounds.**

❖ **Answer:**

1. CH_3-CH(CH_3)-CH_2-CHCl-CH_3

✅ 2-chloro-4-methylpentane

2. CH_3-CHCl-CH-C_2H_5

✅ 3-chloro-4-methylhexane

3. $(CH_3)_2$CH-CH-CH_2-CH_3

Cl

✅ 3-chloro-4-ethylhexane

4. $(CH_3)_3C\text{-}CH_2\text{-}Cl$

✅ 1-chloro-2-methylpropane

5. $(CH_3)_2CH\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2Br$

✅ 2-bromopropane

6. 1-chloro-2-ethyl-4-methylpentane

(Structure not given, name provided as per the text)

7. $H_2CBr\text{-}CHBr$

✅ 1,2-dibromoethane

8. $CHCl_2$

✅ Dichloromethane (Methylene dichloride)

9. $(CH_3)C\text{-}CH_2\text{-}CH_2Br$

✅ 1-bromo-3,3-dimethylbutane

10. $(CH_3)_2CH\text{-}CH_2\text{-}C(CH_3)_3Cl$

✅ 3-chloro-2,2,4-trimethylpentane

11. $(CH_3)_2C\text{-}C(CH_3)_2Cl_2$

✅ 2,3-dichloro-2,3-dimethylbutane

12. $(CH_3CH_2)CBr$

✅ 3-bromo-3-ethylpentane

🌟 **Q.7 Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$. Classify each as primary, secondary, or tertiary chloride and give their IUPAC names.**

Step 1: Determine the type of compounds

- **Molecular formula:** $C_6H_{13}Cl$ ⟶ This is a monohaloalkane (alkyl chloride).
- **The carbon skeleton** can be a straight chain or branched chain.

- **The halogen can be** attached to a primary (1°), secondary (2°), or tertiary (3°) carbon.

Step 2: Straight-chain hexyl chlorides ($C_6H_{13}Cl$)

1. 1-chlorohexane

- Halogen attached to primary carbon (1°)

Structure: CH_3-CH_2-CH_2-CH_2-CH_2-CH_2Cl

Classification: Primary (1°)

2. 2-chlorohexane

- Halogen attached to secondary carbon (2°)

Structure: CH_3-$CHCl$-CH_2-CH_2-CH_2-CH_3

Classification: Secondary (2°)

3. 3-chlorohexane

- Halogen attached to secondary carbon (2°)

Structure: CH_3-CH_2-CHCl-CH_2-CH_2-CH_3

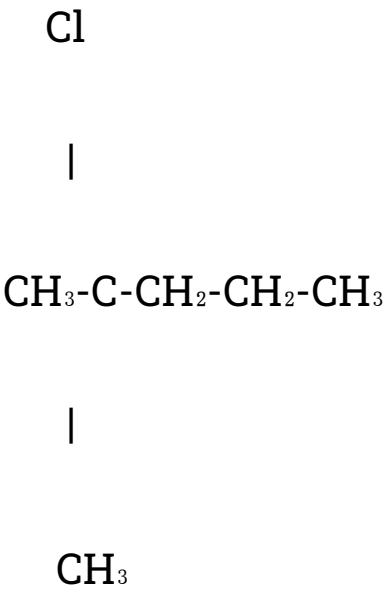
Classification: Secondary (2°)

Step 3: Branched-chain hexyl chlorides

4. 2-chloro-2-methylpentane

- Carbon skeleton branched, halogen attached to tertiary carbon (3°)

Structure:



Classification: Tertiary (3°)

5. 3-chloro-2-methylpentane

- Halogen attached to secondary carbon (2°)

Structure: CH_3-CH(Cl)-CH_2-CH(CH_3)-CH_3

Classification: Secondary (2°)

6. 2-chloro-3-methylpentane

- Halogen attached to secondary carbon (2°)

Structure: CH_3-CH(Cl)-CH(CH_3)-CH_2-CH_3

Classification: Secondary (2°)

7. 1-chloro-2-methylpentane

- Halogen attached to primary carbon (1°)

Structure: CH_3-C(Cl)-CH_2-CH_2-CH_3 (branch at C2)

Classification: Primary (1°)

8. 1-chloro-3-methylpentane

- Halogen attached to primary carbon (1°)

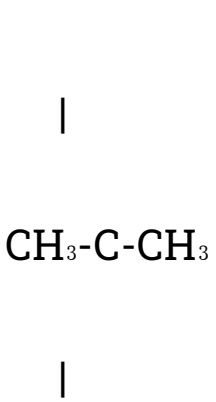
Structure: CH_3-CH_2-C(Cl)-CH_2-CH_3 (branch at C3)

Classification: Primary (1°)

9. 2-chloro-2,3-dimethylbutane

- Halogen attached to tertiary carbon (3°)

Structure:



CH_2CH_3

Classification: Tertiary (3°)

Compound Name	Type	Structure Notes
1-chlorohexane	Primary	Halogen on terminal carbon
2-chlorohexane	Secondary	Halogen on C2
3-chlorohexane	Secondary	Halogen on C3
2-chloro-2-methylpentane	Tertiary	Halogen on C2 with branch
3-chloro-2-methylpentane	Secondary	Halogen on C3
2-chloro-3-methylpentane	Secondary	Halogen on C2
1-chloro-2-methylpentane	Primary	Halogen on terminal carbon
1-chloro-3-methylpentane	Primary	Halogen on terminal carbon
2-chloro-2,3-dimethylbutane	Primary	Halogen on C2 with two branches

🌟 Q.8. Using ethyl bromide as a starting material, prepare the following compounds. Give inorganic reagents and conditions.

Starting Material: C_2H_5Br (Ethyl bromide)

(a) n-Butane (C_4H_{10})

Reaction: Wurtz reaction

Equation:

$2\ C_2H_5Br + 2\ Na \longrightarrow C_4H_{10} + 2\ NaBr$

Reagents & Conditions: Sodium metal in dry ether

Explanation: Two ethyl bromide molecules react in the presence of sodium in dry ether to form n-butane (symmetrical alkane).

(b) Ethyl alcohol (C_2H_5OH)

Reaction: Nucleophilic substitution

Equation:

$C_2H_5Br + NaOH \longrightarrow C_2H_5OH + NaBr$

Reagents & Conditions: Aqueous NaOH, heat

Explanation: Hydroxide ion replaces bromine in ethyl bromide to form ethanol.

(c) Ethyl cyanide (C_2H_5CN)

Reaction: Nucleophilic substitution with cyanide ion

Equation:

$$C_2H_5Br + KCN \longrightarrow C_2H_5CN + KBr$$

Reagents & Conditions: Potassium cyanide in ethanol, reflux

Explanation: Cyanide ion replaces bromine to form nitrile (ethyl cyanide).

(d) Ethane (C_2H_6)

Reaction: Reduction

Equation:

$$C_2H_5Br + Zn + H_2O \longrightarrow C_2H_6 + ZnBr_2$$

Reagents & Conditions: Zinc metal in aqueous acid or water

Explanation: Bromine is replaced by hydrogen to form ethane.

(e) Ethene (C_2H_4)

Reaction: Dehydrohalogenation (Elimination)

Equation:

$C_2H_5Br + KOH \longrightarrow C_2H_4 + HBr$

Reagents & Conditions: Alcoholic KOH, heat

Explanation: Bromine and a β-hydrogen are eliminated to form an alkene.

(f) Propanoic acid (C_2H_5COOH)

Reaction: Grignard reaction with CO_2

Equation:

$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$ (dry ether)

$C_2H_5MgBr + CO_2 \longrightarrow C_2H_5COOMgBr \rightarrow[H^+/H_2O]\rightarrow C_2H_5COOH$

Reagents & Conditions: Dry ether, CO_2, followed by dilute acid

Explanation: Ethyl bromide is converted to ethyl magnesium bromide, which reacts with carbon dioxide to yield propanoic acid.

(g) Propane (C_3H_8)

Reaction: Wurtz reaction with methyl bromide

Equation:

$C_2H_5Br + CH_3Br + 2\ Na \longrightarrow C_3H_8 + 2\ NaBr$

Reagents & Conditions: Sodium metal in dry ether

Explanation: Ethyl bromide reacts with methyl bromide in the presence of sodium to produce propane.

🌟 Q.9. Write a detailed note on the mechanism of nucleophilic substitution reactions.

❖ Introduction:

Nucleophilic substitution reactions are those in which a nucleophile (electron-rich species) replaces a leaving group in an organic molecule, usually an alkyl halide (RX).

General Reaction:

$Nu^- + R\text{-}L \longrightarrow R\text{-}Nu + L^-$

- **Nu^- (Nucleophile):** Electron-rich species that attacks an electrophilic carbon. Examples: OH^-, CN^-, NH_3, H_2O.
- **R-L (Substrate/Alkyl Halide):** Carbon attached to the leaving group (halogen).
- **L^- (Leaving group):** Halogen or group that leaves with electron pair. Good leaving groups: Cl^-, Br^-, I^-.

1. Types of Nucleophilic Substitution

A) Bimolecular Nucleophilic Substitution (S_N2)

Features:

- Single-step mechanism. Bond formation and breakage occur simultaneously.
- Favored by primary alkyl halides.

Rate equation:

Rate = k [R-L][Nu^-]

- Nucleophile attacks opposite side of leaving group → inversion of configuration.
- **Carbon hybridization changes:** sp^3 → sp^2 (transition state) → sp^3.

S_N2 Mechanism (Conceptual):

👉 S_N2 (Substitution Nucleophilic Bimolecular) is a one-step reaction.

👉 The nucleophile (Nu^-) attacks the carbon atom from the opposite side (backside) of the leaving group (L).

👉 The attack and removal of the leaving group occur simultaneously (concerted mechanism).

👉 No carbocation intermediate is formed.

👉 It results in inversion of configuration (Walden inversion).

👉 The reaction rate depends on both reactants:

Rate = k [R–L][Nu^-]

Structure:

Nu^-

|

↓

H --- C – L

/ \

R H

Transition state: C partially bonded to Nu and L

Product: R-Nu + L^-

B) Unimolecular Nucleophilic Substitution (S_N1)

Features:

Two-step mechanism:

1. Formation of carbocation:

R-L ⟶ R^+ + L^-

2. Attack by nucleophile:

$R^+ + Nu^- \longrightarrow R\text{-}Nu$

- Favored by tertiary alkyl halides.

Rate equation:

Rate = k [R-L]

Carbocation is planar ⟶ attack from both sides ⟶ racemic mixture.

2. Factors Affecting Mechanism Choice

Factor	SN2	SN1
Substrate	Primary > Secondary	Tertiary > Secondary
Nucleophile	Strong, negative	Weak or neutral
Solvent	Polar aprotic	Polar protic
Stereochemistry	Inversion	Racemic

✦ **Summary:**

Nucleophilic substitution = nucleophile replaces leaving group.

SN2: single-step, bimolecular, inversion, primary halides.

SN1: two-step, carbocation intermediate, racemic, tertiary halides.

Mechanism depends on substrate, nucleophile, and solvent

🌟 **Q.10. What do you understand by the term β-elimination reaction? Explain briefly the two possible mechanisms of β-elimination reactions.**

❖ **Definition:**

A β-elimination reaction is a reaction in which two atoms or groups are removed from two adjacent carbon atoms of an alkyl halide (or alcohol derivative) in the presence of a base or nucleophile, leading to the formation of a carbon–carbon double bond (alkene).

General Reaction:

R-CH2-CHX-R' + Base ⟶ R-CH=CH-R' + HX

- **The α**-carbon is the one bearing the leaving group (X).
- **The β**-carbon is the adjacent carbon from which a proton (H) is removed.

Mechanisms of β-Elimination Reactions:

1. Bimolecular Elimination (E2) Mechanism

Features:

- Single-step reaction (concerted mechanism).
- **Base abstracts** β-hydrogen while the leaving group (X^-) departs simultaneously.
- **Favored by primary** alkyl halides and strong bases.
- **Shows second-order kinetics**: rate depends on both alkyl halide and base.

Equation:

$CH_3\text{-}CH_2\text{-}CH_2\text{-}Br + OH^- \longrightarrow CH_3\text{-}CH{=}CH_2 + H_2O + Br^-$

Diagram (Conceptual):

Base abstracts β-H Leaving group leaves

```
    H       Br
    |       |
CH3-C-C-H  ⟶  CH3-C=C + H2O + Br⁻
    |
    R
```

Key Points:

One step ⟶ bond-breaking and bond-forming occur simultaneously.

Molecularity = 2 (bimolecular).

2. Unimolecular Elimination (E1) Mechanism

Features:

Two-step reaction.

1. Leaving group departs ⟶ formation of carbocation (slow, rate-determining step).

2. Base abstracts β-hydrogen ⟶ formation of alkene (fast).

- **Favored** by tertiary alkyl halides and weak bases.
- **Shows first**-order kinetics: rate depends only on alkyl halide concentration.

Equation:

$(CH3)3C\text{-}Br \longrightarrow (CH3)3C^{+} + Br^{-}$ (slow)

$(CH3)3C^{+} + OH^{-} \longrightarrow (CH3)2C{=}CH2 + H2O$ (fast)

Structure:

Step 1: Formation of carbocation

CH3

|

CH3-C-Br ⟶ CH3-C⁺ + Br⁻

|

CH3

Step 2: Abstraction of β-H by base

CH3-C⁺-CH3 ⟶ CH2=C(CH3)2 + H⁺

Key Points:

- Two steps ⟶ carbocation intermediate.
- Molecularity = 1 (unimolecular).
- Leads to more substituted, stable alkenes (Saytzeff's rule).

Future	**E2 (Bimolecular)**	**E1 (Unimolecular)**
Steps	1 (concerted)	2 (via carbocation)

Molecularity	2	1
Kinetics	Second-order	First-order
Favored Substrate	Primary alkyl halide	Tertiary alkyl halide
Base Strength	Strong	Weak
Stereochemistry	Anti-periplanar required	Not specific

✦ **Summary:**

- **β-Elimination:** removal of leaving group and β-hydrogen → formation of alkene.
- **E2 mechanism:** one step, strong base, primary halides, second-order.
- **E1 mechanism:** two steps, carbocation intermediate, tertiary halides, first-order.

🌟 **Q.11. What products are formed when the following compounds are treated with ethyl magnesium bromide (C_2H_5MgBr), followed by hydrolysis in the presence of an acid?**

❖ **Answer:**

Grignard reagents are highly nucleophilic and react with electrophilic carbon atoms in compounds such as aldehydes, ketones, carbon dioxide, and cyanides. After reaction with

Grignard reagent, hydrolysis with an acid gives alcohols, carboxylic acids, or ketones depending on the starting material.

i) Reaction with HCHO (formaldehyde):

- Ethyl magnesium bromide attacks the carbonyl carbon of formaldehyde. After hydrolysis with an acid, primary alcohol is formed.

Reaction:

$$HCHO + C_2H_5MgBr \longrightarrow [H^+] \longrightarrow CH_3CH_2OH$$

Product: Ethyl alcohol (Primary alcohol)

ii) Reaction with CH_3CHO (acetaldehyde):

- Grignard reagent attacks the carbonyl carbon of acetaldehyde. Hydrolysis gives a secondary alcohol.

Reaction:

$$CH_3CHO + C_2H_5MgBr \longrightarrow [H^+] \longrightarrow CH_3CH(OH)CH_2CH_3$$

Product: 2-Butanol (Secondary alcohol)

iii) Reaction with CO_2 (carbon dioxide):

- The Grignard reagent reacts with CO_2 to form a carboxylic acid after hydrolysis.

Reaction:

$$CO_2 + C_2H_5MgBr \longrightarrow [H^+] \longrightarrow CH_3CH_2COOH$$

Product: Propanoic acid

iv) Reaction with $(CH_3)_2CO$ (acetone):

- Grignard reagent attacks the carbonyl carbon of the ketone. After hydrolysis, a tertiary alcohol is produced.

Reaction:

$$(CH_3)_2CO + C_2H_5MgBr \longrightarrow [H^+] \longrightarrow (CH_3)_2C(OH)CH_2CH_3$$

Product: 2-Methyl-2-butanol (Tertiary alcohol)

v) Reaction with CH_3CH_2CHO (propionaldehyde):

- Grignard reagent reacts with the aldehyde. Hydrolysis gives a secondary alcohol.

Reaction:

$$CH_3CH_2CHO + C_2H_5MgBr \longrightarrow [H^+] \longrightarrow CH_3CH_2CH(OH)CH_2CH_3$$

Product: 2-Pentanol (Secondary alcohol)

vi) Reaction with ClCN (cyanogen chloride):

- Grignard reagent attacks the carbon of the cyanide group. Hydrolysis converts it into a ketone.

Reaction:

$$ClCN + C_2H_5MgBr \longrightarrow [H^+] \longrightarrow CH_3CH_2C(=O)Cl$$

Product: Propanoyl chloride (Ketone)

✦ **Summary:**

Grignard reagents attack electrophilic carbon atoms.

- **Formaldehyde** ⟶ Primary alcohol
- **Aldehydes** ⟶ Secondary alcohols
- **Ketones** ⟶ Tertiary alcohols
- **CO_2** ⟶ Carboxylic acids
- **Cyanides** ⟶ Ketones

🌟 Q.12. How will you carry out the following conversions?

i) $CH_4 \longrightarrow CH_3CH_2COOH$

Stepwise conversion:

1. Chlorination of methane:

$CH_4 + Cl_2 \longrightarrow CH_3Cl$ (in presence of UV light)

2. Formation of ethyl cyanide via nucleophilic substitution:

$CH_3Cl + NaCN \longrightarrow CH_3CN$

3. Hydrolysis of nitrile to carboxylic acid:

$CH_3CN + 2[H_2O] \longrightarrow CH_3CH_2COOH$ (acidic medium)

Product: Propanoic acid

ii) $CH_3\text{-}CH_3 \longrightarrow (CH_3\text{-}CH_2)_4N^+Br^-$

Stepwise conversion:

1. Bromination of ethane:

$CH_3\text{-}CH_3 + Br_2 \longrightarrow CH_3CH_2Br$ (UV light)

2. Reaction with excess ammonia:

$CH_3CH_2Br + 4\ NH_3 \longrightarrow (CH_3CH_2)_4N^+Br^-$

Product: Tetraethylammonium bromide

iii) $CH_2{=}CH_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$

Stepwise conversion:

1. Addition of HBr to ethene:

$CH_2=CH_2 + HBr \longrightarrow CH_3CH_2Br$

2. Reaction with NaOH (aq) or KOH (aq):

$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH$

3. Chain elongation via Grignard reagent with formaldehyde:

$CH_3CH_2MgBr + HCHO \longrightarrow CH_3CH_2CH_2OH$ (after hydrolysis)

Product: Butanol

iv) $CH_3CH_2CH_2Cl \longrightarrow CH_3\text{-}CH=CH_2$

Stepwise conversion (β-elimination):

1. Treatment with alcoholic KOH:

$CH_3CH_2CH_2Cl + KOH(alc) \longrightarrow CH_3\text{-}CH=CH_2 + HCl$

Product: Propene

v) $CH_3COOH \longrightarrow CH_3CH_2COOH$

Stepwise conversion:

1. Reduction of acetic acid to ethanol:

$$CH_3COOH + LiAlH_4 \longrightarrow CH_3CH_2OH$$

2. Halogenation to form ethyl halide:

$$CH_3CH_2OH + PBr_3 \longrightarrow CH_3CH_2Br$$

3. Reaction with NaCN to form ethyl cyanide:

$$CH_3CH_2Br + NaCN \longrightarrow CH_3CH_2CN$$

4. Hydrolysis of nitrile to carboxylic acid:

$$CH_3CH_2CN + 2[H_2O] \longrightarrow CH_3CH_2COOH$$

Product: Propanoic acid

Summary of Methods Used:

- **Halogenation** + Nucleophilic substitution ⟶ Cyanides ⟶ Carboxylic acids
- **Alcohol formation** + Halogenation ⟶ Carbon chain elongation
- **β-Elimination** ⟶ Formation of alkenes
- **Grignard** reagent with formaldehyde ⟶ Chain extension

Note:

This chapter is designed to provide a solid foundation of knowledge, with the goal of deepening understanding and encouraging further exploration of the subject. The content has been carefully selected to support effective learning and inspire students to engage with the topic more deeply.

Author: Muhammad Asghar

Purpose: To contribute to education by offering insightful, valuable content that enhances learning and understanding.