CHAPTER

10

HALOALKANES AND HALOARENES

Formation of Haloalkanes and Haloarenes

Replacement Reaction

Haloalkanes: Formed by replacing a hydrogen atom in an alkane with a halogen atom (F, Cl, Br, or I).

Haloarenes: Formed by replacing a hydrogen atom in an arene with a halogen atom.

Alkane Transformation

- Alkanes serve as starting points for haloalkane formation.
- A hydrogen atom in an alkane is substituted with a halogen atom to create a haloalkane.

Arene Transformation

- Arene compounds are the basis for haloarene formation.
- A hydrogen atom in an arene is substituted with a halogen atom to produce a haloarene.

Halogen Selection

- Choice of halogen depends on desired properties and reactivity.
- Fluorine (F) is highly reactive, chlorine (Cl) and bromine (Br) are commonly used, iodine (I) is less reactive.

Mechanisms of Formation

Alkane Halogenation Mechanism

- Typically follows a free radical mechanism.
- Involves initiation, propagation, chain reaction, and termination steps.

Arene Halogenation Mechanism

- Occurs through electrophilic aromatic substitution reactions.
- An electrophile generated from a halogenating agent attacks the aromatic ring, replacing a hydrogen atom with a halogen atom.

Applications

- Used in industries as solvents, organic synthesis intermediates, refrigerants, propellants.
- Also in pharmaceuticals, pesticides, and plastics production.

Methods of Preparing Haloalkanes

From Alcohols

1. **Reagents:** Treat alcohols with HX and anhydrous zinc chloride (ZnCl2), PCl3, PCl5, or SOCl2.
    a. Example: Ethanol (CH3CH2OH) to ethyl chloride (CH3CH2Cl):
    b. CH3CH2OH + HCl → CH3CH2Cl + H2O.
2. **Nucleophilic Substitution:** Hydroxyl group (-OH) replaced by halogen (X).
3. **Catalyst:** ZnCl2 or phosphorus-based reagents.
4. **Thionyl Chloride**: Preferred for impurity removal (SO2 and HCl by-products).
5. POCl3, PBr3: Alternative reagents for alcohol conversion.

Halogenation of Alkenes

Process: Alkene halogenation.

Example: Propene (CH3CH=CH2) to 2-chloropropane (CH3CHClCH3):

CH3CH=CH2 + HCl → CH3CHClCH3.

Addition Reaction: Halogen (HCl, HBr, HI) adds across alkene double bond, forms haloalkane.

Markovnikov's Rule: Halogen adds to less hydrogenated carbon. Haloalkanes are also prepared by the action of halogen acid (HX) on alkene. The reaction follows Markownik off's rule, which states that the negative part of the reagent goes to the carbon bearing a smaller number of hydrogen atoms.

Acidic or Radical Conditions: Choice of halogen and conditions.

Swarts Reaction

Fluoroalkanes: Prepared from alkyl chlorides/bromides and metallic fluorides (AgF, HgF2, CoF2, SbF3). Reaction: R-X + AgF → R-F + AgX.

Example: Methyl chloride (CH3Cl) to methyl fluoride (CH3F) using AgF:

CH3Cl + AgF → CH3F + AgCl.

Substitution: Chlorine/bromine replaced by fluorine.

Metallic Fluorides: Act as fluorine source.

Selective Fluorination: Silver fluoride (AgF) commonly used.

Sandmeyer's Reaction

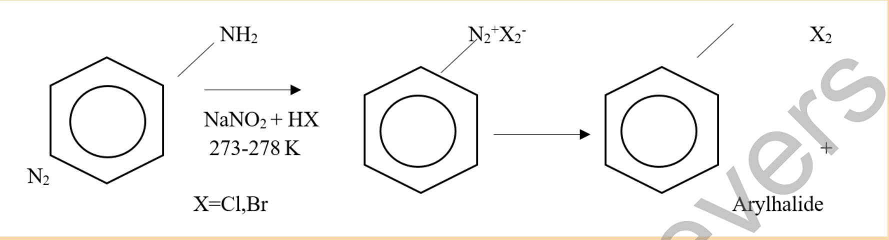
Aryl Halide Synthesis using Diazonium Salts

Aryl Diazonium Salt Formation: Aryl diazonium salts created by aromatic primary amine (aryl amine) reaction with nitrous acid (HNO2).

Example: Aniline (C6H5NH2) reacts with nitrous acid to yield benzenediazonium cation (C6H5N2+).

Role of Halide Source

- **Halide Source:** Required to replace diazonium group with halogen atom.
- **Common Sources:** Copper halides (CuX), cuprous cyanide (CuCN), alkali metal halides (MX).



Sandmeyer's Reaction Applications

- Versatility: Applicable to various aryl diazonium salts, yielding different aryl halides.
- Halide Source Influence: Type of halogen introduced determined by choice of halide source.

Finkelstein Reaction: Preparation of Alkyl Iodides

Chemical Equation: R-X + NaI → R-I + NaX

The Finkelstein reaction involves the preparation of alkyl iodides through a nucleophilic substitution process. This set of notes explores the key aspects of the Finkelstein reaction, including the chemical equation, reaction mechanism, reagents, and its significance in organic synthesis.

The Finkelstein reaction involves the substitution of an alkyl halide (R-X) with sodium iodide (NaI), leading to the formation of the corresponding alkyl iodide (R-I) and sodium halide (NaX) as a byproduct.

Example : CH3CH2Br + NaI → CH3CH2I + NaBr

(Ethyl bromide + Sodium iodide → Ethyl iodide + Sodium bromide)

Starting Materials:

- Ethyl bromide (CH_3CH_2Br): An alkyl halide serving as the initial compound for the Finkelstein reaction. It contains an ethyl group attached to a bromine atom.
- Sodium iodide (NaI): A nucleophile providing the iodine atom required for the substitution process.
- Acetone (CH_3COCH_3): Used as a solvent to facilitate the reaction.

Reaction Mechanism:

1. Sodium iodide donates an iodine ion (I^-) as a nucleophile.

2. The nucleophile attacks the electrophilic carbon atom in ethyl bromide.

3. A new covalent bond forms between the iodine atom and the carbon atom.

4. The bromine atom is displaced, creating ethyl iodide, the desired product.

5. Sodium bromide is formed as a byproduct.

Factors Influencing Reaction:

- Solubility difference: Sodium iodide's higher solubility in acetone compared to sodium bromide drives the reaction toward alkyl iodide formation.
- Heating (Δ): Applying heat accelerates the reaction by increasing molecular kinetic energy.

Significance: Alkyl iodides obtained from the Finkelstein reaction are valuable intermediates in organic synthesis, serving as building blocks for various organic compounds.

Physical Properties of Organic Compounds

1. Boiling Point:

- Halogen Atom Size: Boiling points of alkyl halides follow the sequence R-I > R-Br > R-Cl > R-F as halogen size increases.
- Larger halogens have more electrons, leading to stronger van der Waals' forces and higher boiling points.
- Smaller halogens have weaker forces and lower boiling points.
- Alkyl Group Size: For isomers with the same carbon atoms, branching reduces surface area, weakening intermolecular forces.
- More branching results in lower boiling points due to decreased van der Waals' forces.

2. **Density:**

- Fluoro and chloroalkanes have lower densities than water, making them lighter.
- Bromo, iodo, and polychloro derivatives have higher densities, making them heavier.
- Density determines whether alkyl halides float or sink in water.
- Lighter ones float, while heavier ones sink, based on atomic masses and arrangements.
- Density Variation
    a. Order: $CH3Cl > CH3F > CH3Br > CH3I$.
    b. Reason: Differences in atomic masses and arrangements

3. Alkyl halides are slightly soluble in water, because they do not form H-bonds with water.
4. Due to better symmetry of para isomers as comparedto ortho and meta isomers, para isomers have high melting points as compared to their ortho and meta isomers.

Chemical Properties of Alkyl Halides

Influence of Halogen Size on Carbon-Halogen Bond Length:

- Halogen atom size affects carbon-halogen bond length in alkyl halides.
- Larger halogens, like iodine (I), result in longer carbon-halogen bonds due to their larger atomic radius.

Reactivity Increase with Larger Halogen Atoms:

- Larger halogen atoms enhance alkyl halide reactivity.
- Weaker carbon-halogen bonds are more susceptible to nucleophilic attack or substitution reactions.

Most Reactive Alkyl Halide: R-I:

- Alkyl halides containing iodine (I) are typically most reactive.
- Longer and weaker carbon-iodine bond increases susceptibility to nucleophilic substitution reactions.

Nucleophilic Substitution Reactions: S N1 and S N2:

- Alkyl halides undergo nucleophilic substitution, where nucleophiles replace halogen atoms.
- S N1 reactions involve a two-step mechanism with carbocation intermediate formation.
- S N2 reactions occur through a single-step concerted mechanism.

Role of Carbon-Halogen Bond Length in Reactivity: Longer, weaker carbon-halogen bonds increase reactivity, enabling better nucleophile access.

Enhanced Reactivity of R-I in S N1 Reactions:

- Weaker, longer carbon-iodine bond favors carbocation intermediate formation in S N1 reactions.
- Enhances R-I reactivity compared to smaller halogen atoms.

Enhanced Reactivity of R-I in S N2 Reactions:

- Longer, weaker carbon-iodine bond facilitates nucleophile access in S N2 reactions.
- Increases reaction rate and reactivity compared to smaller halogen atoms.

Reactivity and Mechanism in Nucleophilic Substitution (S N1) Reactions

Carbocation Formation and Reactivity:

1. **Carbocation Formation as Intermediate:**

- In S N1 reactions, alkyl halides undergo heterolysis, breaking the carbon-halogen bond to generate a carbocation intermediate and a halide ion.
- The rate-determining step is the creation of the carbocation intermediate.

2. **Reactivity Based on Carbocation Stability**:

- Alkyl halide reactivity in S N1 reactions relies on the stability of the formed carbocation intermediate.
- Stability is influenced by alkyl groups that donate electron density through inductive or hyperconjugation effects, stabilizing the carbocation's positive charge.
- Alkyl halides yielding more stable carbocations exhibit higher reactivity.

3. **Order of Reactivity: 3° > 2° > 1°:**

- Reactivity order in S N1 reactions: tertiary (3°) > secondary (2°) > primary (1°).
- Tertiary alkyl halides have greater electron density due to surrounding alkyl groups, resulting in carbocation stability.
- Secondary alkyl halides are less reactive, and primary ones are least reactive due to limited electron-donating groups.

4. **Rearrangement Possibilities:**

- Carbocation intermediates in S N1 reactions allow rearrangements like hydride shifts or alkyl shifts.
- Such rearrangements lead to more stable carbocations and altered products.

5. **Racemization Product Formation:**

- Nucleophilic attack on the carbocation intermediate in S N1 reactions occurs from both sides, forming a racemic mixture.
- The product consists of equal amounts of retention and inversion configurations at the stereo enter.

6. **Solvent Effects:**

- Solvent choice influences S N1 reaction rate and outcome.
- Polar protic solvents (e.g., water, alcohols) stabilize carbocation intermediates and facilitate reactions.
- Solvent affect's reaction selectivity and nucleophile nature.

7. **Reaction Rate:**

- Rate of S N1 reactions depends solely on alkyl halide concentration; nucleophile is not involved in the rate-determining step.
- Reaction rate is unimolecular, giving the reaction its name, S N1 (Substitution Nucleophilic Unimolecular).

Reactivity and Mechanism in Nucleophilic Substitution (S N2) Reactions

1. Transition State Formation:

- In S N2 reactions, nucleophile approaches carbon while leaving group is bonded to carbon.
- Transition state represents high-energy state where nucleophile partially bonds to carbon and bond with leaving group begins breaking.
- Transition state is short-lived and leads to product formation.

2. Reactivity Based on Steric Hindrance:

- Alkyl halide reactivity in S N2 reactions hinges on steric hindrance around carbon.
- Primary alkyl halides, with fewer substituents, show less steric hindrance and are more reactive.
- Secondary alkyl halides display intermediate reactivity, while tertiary alkyl halides, with more substituents, are least reactive.

3. Inversion of Configuration:

- In S N2 reactions, nucleophile attacks carbon from opposite side of leaving group.
- Inversion of configuration at stereo enter occurs, yielding a product with opposite configuration compared to starting material.
- Inversion results from nucleophile's backside attack, switching original substituents' positions.

4. Order of Reactivity: 1° > 2° > 3°:

- Reactivity order in S N2 reactions is reverse of S N1 reactions.
- Primary alkyl halides, with less steric hindrance, are most reactive in S N2.
- Secondary alkyl halides possess slightly higher hindrance, making them less reactive; tertiary alkyl halides, with significant hindrance, are least reactive.

5. Reaction with KCN:

- In presence of polar solvent (e.g., water), KCN ionizes to provide CN− ions as nucleophiles.

  - R-Br +CN- → R-CN + Br-
- Due to C-C bond stability compared to C-N bond, cyanide (CN−) predominantly acts as nucleophile in S N2 with alkyl halides.
- Nucleophile attacks electrophilic carbon, displacing leaving group and forming new C-C bond.

6. Reaction with AgCN:

- Unlike KCN, AgCN doesn't readily ionize to form CN− ions.
- R-Br +AgCN → RNC + AgBr
- AgCN acts as nucleophile by attacking alkyl halide via nitrogen atom, yielding an isocyanide product.

Stereochemical Principles and Notation

1. Chirality Defined:

- Chirality denotes non-superimposability of an object or molecule on its mirror image.
- Chiral molecules possess unique properties due to their asymmetry.

2. Chiral Carbon:

- Chiral carbon has four different substituents.
- Molecule often becomes chiral due to presence of chiral carbon.

3. Optical Activity:

- Optically active compounds rotate plane of polarized light.
- Rotation specific to molecule's enantiomer, measured using polarimeter.

4. Racemic Mixture:

- Racemic mixture contains equal amounts of two enantiomers.

- d and l enantiomers present equally, leading to optical inactivity.

- Represented as dl or ± forms.

5. dl or ± Forms:

- dl or ± notation denotes racemic mixture.
- "d" and "
- l" represent enantiomer configuration, where "d" is dextrorotatory (right) and "l" is levorotatory (left).
- In racemic mixture, rotations cancel, causing optical inactivity.

6. Racemization:

- Racemization converts optically active compound into racemic mixture.
- Enantiomers interconvert through reaction or changing conditions.
- Results in optical inactivity and equal d and l enantiomers.

7. Resolution of Enantiomers:

- Resolution separates enantiomers into components.
- Used to isolate and purify specific enantiomers.
- Achieved via methods like crystallization, chromatography, or enzymatic reactions.

8. **Crucial Role in Biological Systems:**

- Chirality holds vital importance in biological systems.
- Biomolecules like amino acids, sugars, and nucleic acids exhibit chirality.

9. **Significance in Pharmaceuticals:**

- Chirality is profoundly significant in the pharmaceutical industry.
- Enantiomers of drugs can display distinct pharmacological activities and effects.
- Correct enantiomer selection during drug development is critical for ensuring efficacy while minimizing side effects.

10. Defining Chirality with Symmetry:

- Chiral molecules lack symmetry elements like planes of symmetry, canters of inversion, or improper rotation axes.
- Absence of these symmetry elements is a defining feature of chirality.

Characteristics of Grignard Reagents:

- Grignard reagents are potent organometallic compounds comprising an alkyl or aryl group bonded to a magnesium atom (R-X-MgX).
- General formula: RMgX, with R representing alkyl or aryl and X representing a halogen.
- Reactivity with Water: RMgX + H2O → RH + Mg(OH)X
- Reaction with Aldehydes/Ketones: Grignard + Aldehyde/Ketone → Alcohol (Grignard Reaction)
- Reaction with Esters: Grignard + Ester → Tertiary Alcohol
- Reaction with Epoxides: Grignard + Epoxide → Alcohol
- Reaction with Carboxylic Acids: Grignard + Carboxylic Acid → Tertiary Alcohol
- Halogen-Metal Exchange: Grignard + Halogen → Different Halogen or Metal
- Reactivity and Electron Density: More Substituents → More Reactivity
- Reaction with Water: Hydrocarbons + Mg(OH)X
- Sensitivity to Moisture: Handle Under Dry Conditions
- Utilized in Synthetic Organic Chemistry: Carbon-Carbon Bond Formation
- Solvent Choice: Ether Solvents (Stabilize Reagent, Prevent Air/Moisture Reaction)
- Reaction Mechanism: Organomagnesium Intermediate Formation
- Preparation: Alkyl/Aryl Halide + Mg Metal
- Synthetic Versatility: Alcohols, Carboxylic Acids, Aldehydes, Ketones
- Role in Complex Molecule Synthesis

Electrophilic Substitution:

- Electrophilic substitution swaps a hydrogen on benzene with an electrophilic species.
- Benzene (C6H6) is a common substrate for these aromatic substitution reactions.
- Electron-Rich Benzene: Susceptible to Electrophile Attack
- Mechanism: Formation of Sigma Complex Intermediate
- Electrophiles: Cl2, Br2, NO2+, Acyl Chlorides (RCOCl)
- Formation of Halobenzenes, Nitrobenzene, Aryl Ketones
- Substituent Effects: Electron-Donating ↑ Reactivity, Ortho/Para Directing
- Substituent Effects: Electron-Withdrawing ↓ Reactivity, Meta Directing
- Reaction Conditions and Regioselectivity
- Influence of Existing Substituents
- Reaction Rate and Electron Density
- Aromaticity Preservation
- Multi-Substitution and Polynuclear Compounds
- Role in Synthesis: Pharmaceuticals, Dyes, Materials

Nucleophilic Replacement of Halogen:

- Nucleophilic substitution replaces halogen in haloarenes with a nucleophile.
- Haloarenes: Aromatic Compounds with Halogen (Cl, Br, I) on Benzene Ring
- -Reaction: Ar-X + Nu → Ar-Nu + X
- Slower Reactivity Due to Electron-Withdrawing Nature
- Reactivity Order: Iodobenzene > Bromobenzene > Chlorobenzene
- Mechanism: S1 or S2
- S1 for Tertiary Haloarenes, S2 for Primary
- Regioselectivity and Electron-Withdrawing Groups
- Nucleophiles: Amines, Alkoxides, Thiolates, Organometallics
- Reaction Conditions Influence Regioselectivity and Stereochemistry
- Role in Synthesis: Pharmaceuticals, Organics

Wurtz Reaction: Alkane Synthesis from Halides:

Wurtz Reaction for Alkanes: Wurtz reaction synthesizes alkanes from alkyl halides.

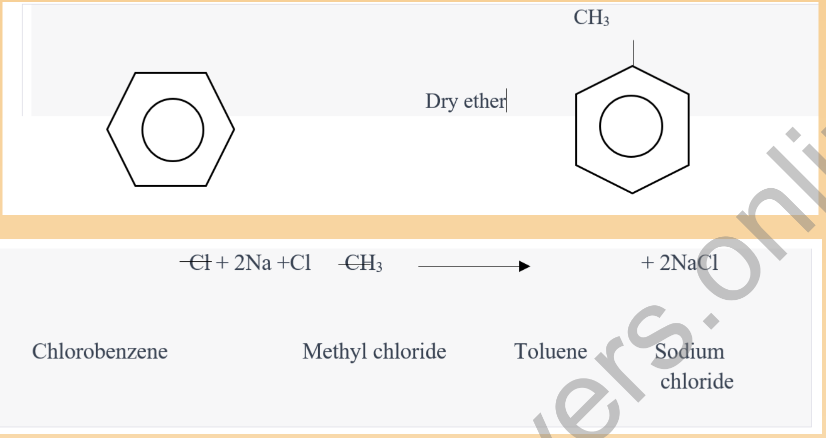
RX + 2 Na → R-R + 2 NaX (R = Alkyl, X = Halogen)

- Carbon-Carbon Bond Formation via Free Radical Mechanism
- Sodium Reducing Agent, Ether Solvent
- Symmetrical Alkanes Formation
- Dry Conditions to Avoid Unwanted Reactions
- Stoichiometry Control for Reaction
- Limited to Primary and Secondary Alkyl Halides

Wurtz-Fittig Reaction: Aryl-Alkyl Coupling:

Wurtz-Fittig Reaction for Alkylarenes: Wurtz-Fittings reaction couples aryl and alkyl halides.

Ar-X + R-X + 2 Na → Ar-R + 2 NaX (Ar = Aryl, R = Alkyl, X = Halogen)



- Carbon-Carbon Bond Formation, Radical Coupling
- Reducing Agent Sodium, Dry Ether Solvent

- Alkylarene Formation
- Regioselectivity and Stoichiometry Control
- Wide Range of Aryl and Alkyl Halides
- Applicable to Primary and Secondary Alkyl Halides
- Synthesis of Diverse Alkylarenes

Fitting Reaction

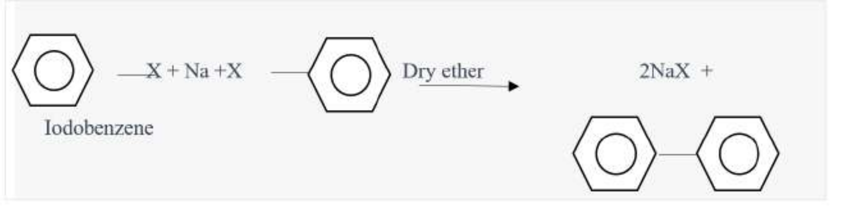
Coupling reaction involving a haloarene and sodium metal in dry ether which results in aryl group combination, forming biphenyl compound.

2 Ar-X + 2 Na → Ar-Ar + 2 NaX

Ar: aryl group, X: halogen atom (Cl, Br, I).

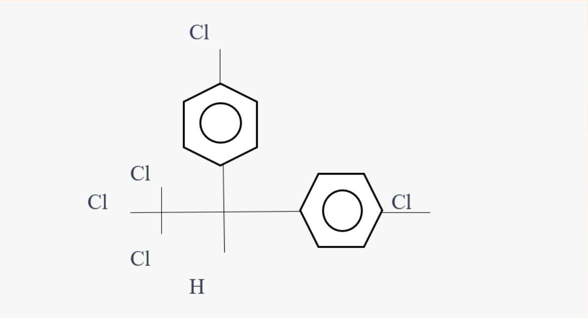
Reaction Conditions:

- Carried out in dry ether (e.g., diethyl ether) as solvent.
- Dry conditions essential to prevent side reactions with moisture.
- Sodium metal (Na) acts as reducing agent, donates electrons.
- Promotes aryl radical formation in haloarene.
- Aryl radicals undergo radical coupling, creating biphenyl.

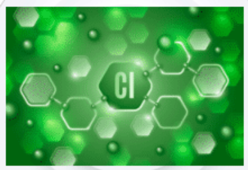


Polyhalogeno Compounds

- Polyhalogeno compounds: Carbon compounds with multiple halogen atoms.
- Examples: CHCl3 (chloroform), CHCl2F (freon), CHI3 (iodoform), CCl4 (carbon tetrachloride), DDT (p, p'-dichlorodiphenyltrichloroethane).
- Usage: Wide industrial applications due to unique properties and stability.
- Chloroform (CHCl3): Oxidizes in sunlight to form toxic COCl2 (carbonyl chloride).
- Storage: Dark bottles, full to brim, to prevent carbonyl chloride release.
- Freons: Chlorofluorocarbons from methane/ethane; used as refrigerants, propellants.
- Impact: Stratospheric reactions cause ozone layer depletion.
- Regulation: Ozone layer depletion led to bans; alternatives developed.
- DDT: Effective insecticide, toxic, stable, causing bioaccumulation.
- Use: Mosquito control, agriculture; restricted/banned due to environmental impact.
- Synthesis: Halogenation reactions add halogens to organic molecules.
- Effects: Multiple halogens impact properties like boiling point, reactivity.
- Applications: Industry uses as solvents, flame retardants, pesticides, intermediates.
- Stability: Non-reactivity beneficial for specific applications.
- Concerns: Persistence, bioaccumulation affecting ecosystems, health.
- Regulations: Countries control production, use, disposal for minimal impact.
- Research: Focus on alternatives, impact assessment, sustainable practices.
- Understanding: Crucial for environment assessment and sustainable practices.
- Governance: International agreements (Stockholm Convention) guide management.
- Studies: Monitor compound persistence, fate, transport in various environments.
- Analysis: Techniques like gas chromatography-mass spectrometry for detection.
- Consideration: Weighing risks and benefits, adopting responsible practices.
- Advancements: Research aims for sustainable alternatives, adverse effects mitigation.



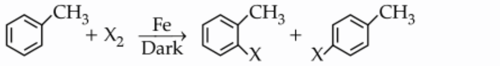
Haloalkanes and Haloarenes



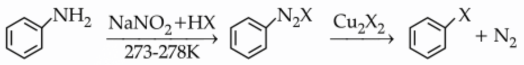
Haloalkanes

=>Preparation

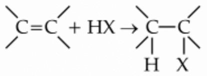
- From alcohol :
  - $R–OH + HCl \xrightarrow{ZnCl_2} R–Cl + H_2O$
  - $3R–OH + PX_3 \longrightarrow 3R–X + H_3PO_3$
  - $ROH + PCl_5 \longrightarrow R–Cl + POCl_3 + HCl$
- From hydrocarbons :
  - (a) By free radical halogenation
    $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
  - (b) By electrophilic substitution



  - (c) Sandmeyer's reaction



  - (d) From alkenes

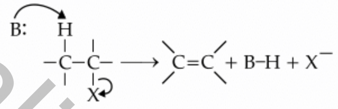


$H_2C=CH_2+Br_2 \xrightarrow{CCl_4} BrCH_2–CH_2Br$

- Halogen exchange :
  $R–X + NaI \rightarrow R – I + NaX$

=>Properties

- Physical : Colourless, volatile, sweet smell.
  Lower members are gases at room temperature while higher are solids.
  B.P : RI > RBr > RCl > RF.
  M.P : Para isomers have high m.p. than ortho and meta – isomers.
  Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.
  Solubility : Very slightly soluble in water.
- Chemical :
  - (a) Nucleophilic substitution
    $\bar{Nu} + \overset{\delta+}{C}–\overset{\delta-}{X} \longrightarrow C – Nu + X^-$
    For S_N2 reaction
    Tertiary, Secondary, Primary
    For S_N1 reaction
  - (b) Elimination reaction



    B = Base; X = Leaving group
  - (c) Reaction with metals
    $CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$
    Wurtz reaction :
    $2RX + 2Na \xrightarrow{Dry\ ether} RR + 2NaX$

Racemisation S_N1

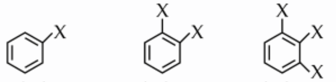
- Chiral : Objects which are non-superimposable.
- Achiral : Objects which are superimposable.

Classification

- No. of halogen atoms

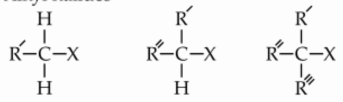
C_2H_5X Monohaloalkane

$CH_2X–CH_2X$ Dihaloalkane



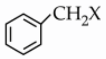
Monohaloarene Dihaloarene Trihaloarene

- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides

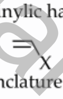


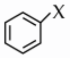
  - (b) Allylic halides

  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides
  - (b) Aryl halides

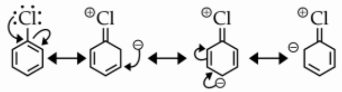




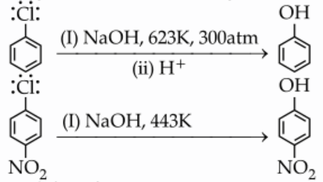
- Nomenclature
  Common name : Alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.
  IUPAC name : Numerals are used.
- Nature of C –X bond
  : Carbon –halogen bond is polarised.
  $\overset{\delta+}{C}–\overset{\delta-}{X}$

Haloarenes

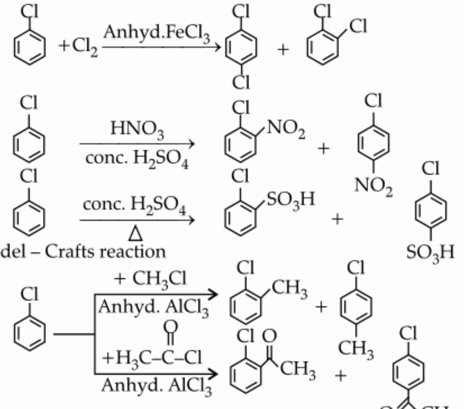
- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect



    - (ii) Hybridisation of C in C-X bond :
      Haloalkane –sp^3; Haloarene –sp^2
    - (iii) Phenyl cation unstabilised by resonance

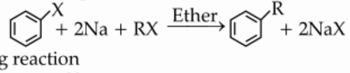


  - (b) Electrophilic substitution

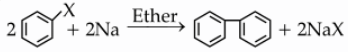


Friedel – Crafts reaction

  - (c) Reaction with metals
    Wurtz – Fitting reaction



    Fittig reaction



Polyhalogen compounds

Chloroform
- Solvent for fats, alkaloids, I etc.
- Production of freon.

Iodoform
Antiseptic

Carbon tetrachloride
- Manufacture of refrigerants and propellants.
- Cleaning fluid.

Freons
For aerosol propellants, refrigeration and air conditioning purposes.

DDT
As insecticide

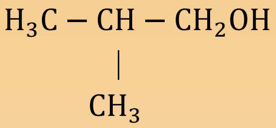
Dichloromethane
- Paint remover.
- Propellant in aerosols.
- Metal cleaning and finishing solvent.

S_N2 Stereochemical inversion

(a) Dextro (+/d)
(b) Laevo (–/l)

Trace the Mind Map
First Level Second Level Third Level

PRACTICE QUESTIONS

1. Among the following the one that gives positive iodoform test upon reaction with I_2 and Na
   a) $CH_3CH_2CH(OH)CH_2CH_3$
   b) $C_6H_5\ CH_2\ CH_2OH$
   c) 
   $\underset{\displaystyle CH_3}{H_3C - \overset{}{CH}} - CH_2OH$
   d) $PhCHOHCH_3$

2. Vicinal and geminal dihalides can be distinguished by:
   a) $KOH(aq.)$ b) KOH(alc.) c) Zn dust d) None of t

3. An alkyl halide may be converted into an alcohol by:
   a) Addition b) Substitution c) Dehydrohalogenation d) Eliminati

4. Dehydrohalogenation in haloalkanes produces:
   a) A single bond b) A double bond c) A triple bond d) Fragment

5. Chlorination of CS_2 gives:
   a) CCl_4 b) CS_2Cl_2 c) CH_4 d) $CHCl_3$

6. Methylene chloride on hydrolysis yields:
   a) HCHO b) CH_3CHO c) $CHCl_3$ d) CH_3COCl

7. The greater the ionic character of the carbon metal bond:
   a) The more reactive is the organometallic compound
   b) The less reactive is the organometallic compound
   c) Both are correct
   d) None of the above is correct

8. For the reaction,
   $C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$, the order of reactivity is:
   a) $HI > HCl > HBr$ b) $HI > HBr > HCl$ c) $HCl > HBr > HI$ d) $HBr > HI$

9. The order of reactivities of methyl halides in the formation of Grignard reagent is
   a) $CH_3I > CH_3Br > CH_3Cl$ b) $CH_3Cl > CH_3Br > CH_3I$
   c) $CH_3Br > CH_3Cl > CH_3I$ d) $CH_3Br > CH_3I > CH_3Cl$

10. The antiseptic character of iodoform is due to:
a) Its poisonous nature
b) Unpleasant smell
c) Liberation of free iodine
d) None of the above

11. On treating a mixture of two alkyl halides with sodium metal in dry ether, 2-methyl propane
The alkyl halides are
a) 2-chloropropane and chloromethane
b) 2-chloropropane and chloroethane
c) Chloromethane and chloroethane
d) Chloromethane and 1-chloropropane

12. The IUPAC name of the compound, $(CH_3)_2CHCH_2CH_2Br$ is:
a) 2-methyl-3-bromopropane
b) 1-bromopentane
c) 2-methyl-4-bromobutane
d) 1-bromo-3-methylbutane

13. The given reaction is an example of,
$C_2H_5Br + KCN(aq.) \longrightarrow C_2H_5CN + KBr$:
a) Elimination
b) Nucleophilic substitution
c) Electrophilic substitution
d) Redox change

14. Which one of the following compounds reacts with chlorobenzene to produce DDT?
a) Acetaldehyde
b) Nitrobenzene
c) m-chloroacetaldehyde
d) Trichloroacetaldehyde

15. Preparation of alkyl halides in laboratory is least preferred by:
a) Halide exchange
b) Direct halogenation of alkanes
c) Treatment of alcohols
d) Addition of hydrogen halides to alkenes

16. Which one of the following pairs is the strongest pesticide?
a) Chloroform and benzene hexachloride
b) DDT and 666
c) 666 and ether
d) isocyanides and alcohol

17. Iodoform gives a precipitate with $AgNO_3$ on heating but chloroform does not because:
   a) Iodoform is ionic
   b) Chloroform is covalent
   c) C—I bond in iodoform is weak and C—Cl bond in chloroform is strong
   d) None of the above

18. Which reagent is useful in increasing the carbon chain of an alkyl halide?
   a) HCN   b) KCN   c) NH_4CN d) AgCN

19. Chloroform on reaction with conc. HNO_3 gives an insecticide and war gas known as:
   a) Chloropicrin   b) Nitromethane   c) Picric acid   d) Acetylene

20. Aryl halides are less reactive towards electrophiles than alkyl halides due to:
   a) Resonance
   b) Stability of carbonium ions
   c) High boiling point
   d) None of the above

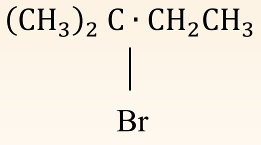
21. Carbon tetrachloride reacts with steam at 500°C to give:
   a) $COCl_2$ b) $CHCl_3$ c) Both (a) and (b)   d) None of these

22. Which of the following is a Grignard reagent?
   a) Ammoniacal solution of $AgNO_3$
   b) Ethereal solution of C_2H_5MgCl
   c) Alcoholic solution of KOH
   d) Aqueous solution of caustic soda

23. The product formed on reaction of ethyl alcohol with bleaching powder is
   a) $CHCl_3$ b) CCl_3CHO c) CH_3COCH_3 d) CH_3CHO

24. Chloral is:
   a) CCl_3CHO b) $CCl_3 \cdot CO \cdot CH_3$ c) $CCl_3 \cdot CO \cdot CCl_3$ d) $CCl_3 \cdot CH$

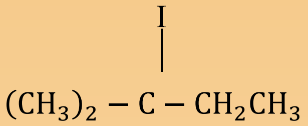
25. Which of the following compounds undergo E_2 reactions more easily?
   a)



$$\underset{\displaystyle Br}{(CH_3)_2\,\overset{}{C}} \cdot CH_2CH_3$$

   b) $CH_3(CH_2)_2CH_2Cl$

c) $CH_3(CH_2)_2CH_2I$

d)

$(CH_3)_2-\underset{}{\overset{I}{\overset{|}{C}}}-CH_2CH_3$

26. Decomposition of benzene diazonium chloride by using Cu_2Cl_2/HCl to form chlorobenzene is

a) Raschig's reaction
b) Sandmeyer's reaction
c) Kolbe's reaction
d) Cannizaro's reaction

27. Isobutyl chloride and butyl chloride are:

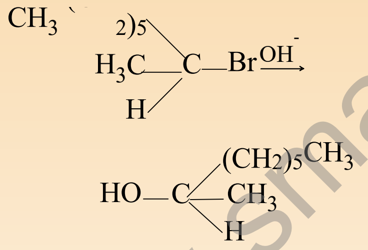
a) Position isomers
b) Chain isomers
c) Functional isomers
d) Metamers

28. $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is $[Nu^- = (A)PhO^-, (B)AcO^-, (C)HO^-, (D)CH_3O^-]$

a) $D > C > A < B$
b) $D > C > B > A$
c) $A > B > C > D$
d) $B > D > C > A$

29. The reaction described below is:

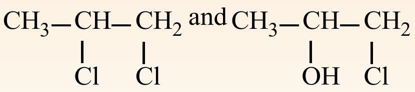


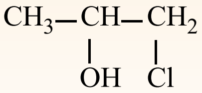
a) S_E1
b) S_N2
c) S_N1
d) S_E2

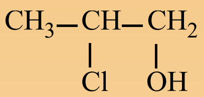
30. Identify 'Z' in the following reaction series,

$CH_3.CH_2CH_3Br \xrightarrow{aq.NaOH} (X) \xrightarrow[Heat]{Al_2O_3} (Y) \xrightarrow{HOCl} (Z)$:

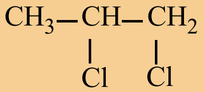
Mixture of

a)

$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$ and $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

b)

$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

c) 

$CH_3-CH(Cl)-CH_2OH$

d) 

$CH_3-CH(Cl)-CH_2Cl$

31. Which of the following when heated with KOH and primary amine gives carbylamine test
a) $CHCl_3$ b) CH_2Cl_2 c) CH_3OH d) CCl_4

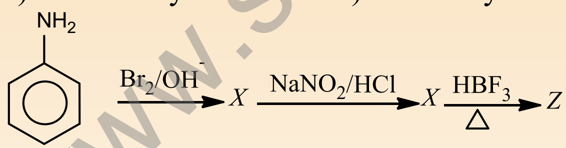
32. The reagent used for dehalogenation of 1,2-dichloropropane is:
a) Zn dust b) Zn—Hg c) Na d) Zn—Cu c

33. CH_3NH_2 reacts with CH_3MgX to give:
a) Acetone b) Alcohol c) Methane d) Ethane

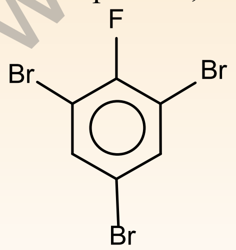
34. Which of the following haloalkanes is most reactive?
a) 1-chloropropane b) 1-bromopropane c) 2-chloropropane d) 2-bromopr

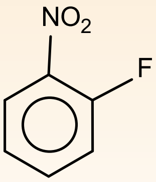
35. Iodoform is formed when ethanol is heated with:
a) Potassium iodide and sodium hydroxide
b) Iodine and aqueous potassium hydroxide
c) Chloroform and iodine
d) Iodine and potassium iodide

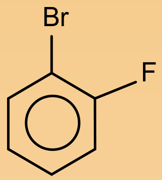
36. Tertiary alkyl halides are practically inert to S_N2 mechanism because of:
a) Insolubility b) Instability c) Inductive effect d) Steric hin

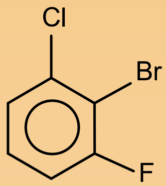
37. 

The final product, is

a) 

b) 

c) 

d) 

38. Carbon tetrachloride on treatment with Fe/H_2O gives:
    a) Chloromethane b) Methane c) Chloroform d) Methylen

39. Which group is displaced by a halogen group?
    a) Hydroxyl (OH) group
    b) Aldehyde (—CHO) group
    c) Nitro (—NO_2) group
    d) Keto (C=O) group

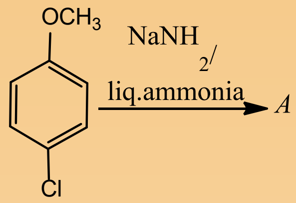
40. Which of the following statements regarding the S_N1 reaction shown by alkyl halide is not
    a) The added nucleophile plays no kinetic role in S_N1 reaction.
    b) The S_N1 reaction involves the inversion of configuration of the optically active substrate
    c) The S_N1 reaction on the chiral starting material ends up with racemization of the produc
    d) The more stable the carbocation intermediate the faster the S_N1 reaction.

41. Pick up the correct statement about alkyl halides:
    a) They show H-bonding.
    b) They are soluble in water.
    c) They are soluble in organic solvents.
    d) They do not contain any polar bond.

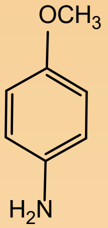
42. The product of reaction between alcoholic silver nitrite with ethyl bromide is
    a) Ethene b) Ethane c) Ethyl nitrile d) Nitro etha

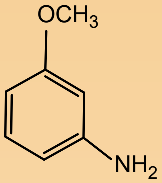
43. 1-phenyl, 2-chloropropane on treating with alc. KOH gives mainly:
    a) 1-phenylpropene
    b) 2-phenylpropene
    c) 1-phenylpropan-2-ol
    d) 1-phenylpropan-1-ol

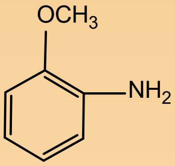
44. In the reaction,

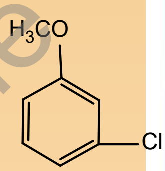


The major product *A* is

a) 

b) 

c) 

d) 

45. $(CH_3)_3CMgCl$ on reaction with D_2O gives:

a) $(CH_3)_3CD$ b) $(CH_3)_3OD$

c) $(CD_3)_3CD$ d) $(CD_3)_3OD$

46. Grignard reagent shows addition on:

a) $>C=O$ b) $-C\equiv N$

c) $>C=S$ d) All of these

47. When tetrahydrofuran is treated with excess HI, the product formed is

a) 1, 4-diiodobutane b) 1, 4-butanediol

c) 2-iodotetrahydrofuran d) 4-iodo-1-butanol

48. Iodoform can be used in medicine as:

a) Anesthetic b) Antiseptic

c) Analgesic d) Antifebrin

49. A mixture of two organic compounds was treated with sodium metal in ether solution. Is obtained as a product. The two chlorine compounds are:

a) Methyl chloride and propyl chloride

b) Methyl chloride and ethyl chloride

c) Isopropyl chloride and methyl chloride

d) Isopropyl chloride and ethyl chloride

50. Wurtz's reaction involves the reduction of alkyl halide with

a) Zn/HCl b) HI

c) Zn/Cu couple d) Na in ether

51. In the following sequences of reactions;

$$CH_3CH_2CH_2Br \xrightarrow{KOH(alc.)} (A) \xrightarrow{HBr} (B) \xrightarrow{KOH(aq.)} (C)$$

the end product (C) is :

a) Propene

b) Propyne

c) Propane-l-o l

d) Propan-2-ol

52. When $CHCl_3$ is boiled with NaOH, it gives

a) Formic acid

b) Trihydroxy methane

c) Acetylene

d) Sodium format

53. Which of the following compounds has the highest boiling point?

a) $CH_3\ CH_2CH_2Cl$

b) $CH_3CH_2CH_2CH_2Cl$

c) $CH_3CH(CH_3)CH_2Cl$

d) $(CH_3)_3\ CCl$

54. Which one is liquid at room temperature?

a) CH_3Cl

b) C_2H_5Cl

c) CH_3Br

d) C_2H_5Br

55. The organic chloro compound, which shows complete stereochemical inversion during an S_N2 reaction is

a) $(C_2H_5)_2\ CHCl$

b) $(CH_3)_3CCl$

c) $(CH_3)_2\ CHCl$

d) CH_3Cl

56. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with

a) PCl_3

b) PCl_5

c) $SOCl_2$ in presence of pyridine

d) dry HCl in the presence of anhydrous $ZnCl_2$

57. Which compound is used in cooling?

a) $CHCl_3$

b) CCl_4

c) CF_4

d) CCl_2F_2

58. Which is finally produced when acetylene reacts with HCl?

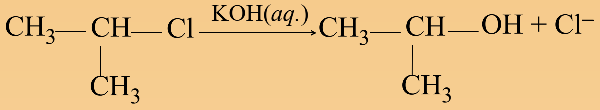
a) $CH_2{=}CHCl$

b) CH_3CHCl_2

c) $ClCH{=}CHCl$

d) None of these

59. The reaction,



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Cl \xrightarrow{KOH(aq.)} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + Cl^-$$

shows:

a) Reduction

b) Oxidation

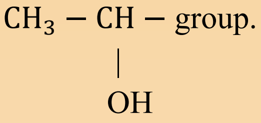
c) Neutralisation

d) Nucleophilic substitution

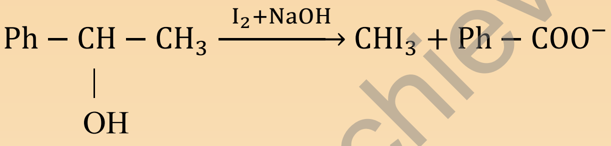
HINTS ANS SOLUTIONS

1 **(d)**

For positive iodoform test, alcohol molecule must have



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-$ group.



$$Ph-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{I_2+NaOH} CHI_3+Ph-COO^-$$

2 **(a)**

$$CH_2ClCH_2Cl \xrightarrow{KOH(aq.)} \underset{\text{Ethane}-1,2-\text{diol}}{CH_2OHCH_2OH}$$

$$CH_3CHCl_2 \xrightarrow{KOH(aq.)} \underset{\text{Ethanal}}{CH_3CHO}$$

3 **(b)**

$$R-X \xrightarrow{KOH(aq.)} R-OH$$

4 **(b)**

$$CH_3CH_2Cl \xrightarrow{KOH(alc.)} CH_2=CH_2+HCl$$

5 **(a)**

$$CS_2+2Cl_2 \longrightarrow CCl_4+2S$$

6 **(a)**

$$CH_2Cl_2 \xrightarrow{HOH} CH_2(OH)_2 \xrightarrow[-H_2O]{} HCHO$$

7 b) The less reactive is the organometallic compound

8 **(b)**

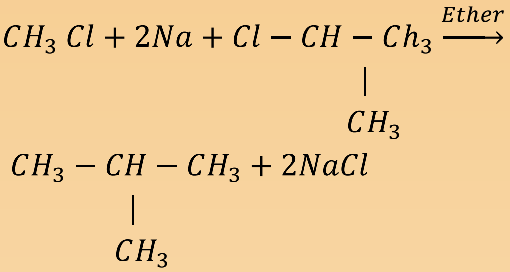
HI reacts with C_2H_5OH even in absence of ZnX_2. Larger is bond length, more is reactivity.

9 **(a)**Among alkyl halides, iodides are least stable, hence these form Grignard reagents easily. Hence, the correct order of reactivity in formation of Grignard reagent is

$CH_3I > CH_3Br > CH_3Cl$

10 **(c)**The I_2 has antiseptic nature.

11 **(a)**This is Wurtz reaction. 2-chloropropane and chloromethane reacts in presence of dry ether t form 2-methyl propane.



$$CH_3\,Cl + 2Na + Cl - \underset{\displaystyle CH_3}{\underset{|}{CH}} - Ch_3 \xrightarrow{Ether}$$

$$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3 + 2NaCl$$

12 **d) 1-bromo-3-methylbutane**

The IUPAC name "1-bromo-3-methylbutane" indicates that there is a bromine atom (bromo) attached to the first carbon in a chain of four carbons (butane), and there is a methyl group (methyl) attached to the third carbon.

13 **(b)**Br is replaced by a nucleophile CN^-.

14 c) m-chloroacetaldehyde

m-chloroacetaldehyde is the compound that reacts with chlorobenzene to produce DDT.

15 **(b)**A mixture of halides is formed.

16 **(b)**DDT and 666 ($C_6H_6Cl_6$ or benzene hexachloride) is the pair of strongest pesticides.

17 **c)** C—I bond in iodoform is weak and C—Cl bond in chloroform is strong

This is because the carbon-iodine (C—I) bond in iodoform is weaker compared to the carbon-chlorine (C—Cl) bond in chloroform. As a result, iodoform reacts with silver nitrate (AgNO3) to form a precipitate of silver iodide (AgI) upon heating, while chloroform does not undergo this reaction.

18. a) HCN: Hydrogen Cyanide (HCN) is a reagent that can be used to increase the carbon chain of an alkyl halide through a nucleophilic addition reaction.

19. a) Chloropicrin: When chloroform reacts with concentrated nitric acid (HNO3), it forms chloropicrin, which is both an insecticide and a chemical warfare agent.

20. a) Resonance: Aryl halides are less reactive towards electrophiles compared to alkyl halides because the benzene ring in aryl halides stabilizes positive charge through resonance, making it harder for electrophiles to attack. This reduces the reactivity of aryl halides in electrophilic aromatic substitution reactions.

21 **(a)**

$CCl_4 + H_2O(v) \longrightarrow COCl_2 + 2HCl$

22 **(b)**

R —MgX are obtained as ethereal solution.

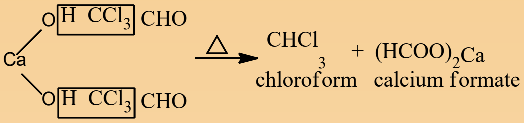
(ii) $CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + 2HCl$

oxidation step

(iii) $CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$

chloral

chlorination step

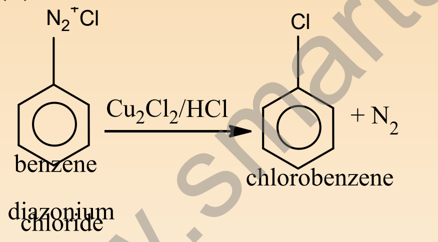
(iv) 

23 **b)** CCl3CHO (Trichloroacetaldehyde)
Ethyl alcohol reacts with bleaching powder (CaOCl2) to form trichloroacetaldehyde, which has the chemical formula CCl3CHO.

24 **(a)**
Chloral is commercial name of CCl_3CHO.

25 **(d)**
C—I bond is broken easily as well as ease of reaction is *t*-alkyl halide > *s*-alkyl halide >
p-alkyl halide.

26 **(b)**

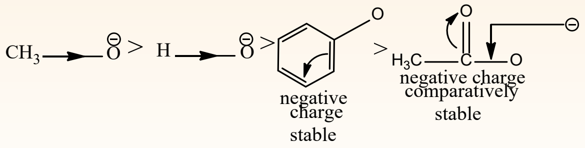


This reaction is known as Sandmeyer's reaction.

27 **(b) Chain Isomers**
$(CH_3)_2CHCH_2Cl$ and $CH_3CH_2CH_2CH_2Cl$; only chain is different.

28 **(a)**

Nucleophilicity order is ;



$D > C > A < B$

29 **(a)**

$$CHCl_3 + RNH_2 + 3KOH \longrightarrow \underset{\text{Foul smell}}{RNC} + 3KCl + 3H_2O$$

31 c) CH3OH (Methanol).

When methanol is heated with KOH and a primary amine, it undergoes a reaction that produces a foul-smelling isocyanide compound, giving a positive carbylamine test. This reaction is characteristic of compounds containing a -NH2 group, which is found in primary amines.

32 **(a)**Zn dust removes X_2 from molecule.

33 a) Acetone. CH3NH2 reacts with CH3MgX (a Grignard reagent) to give acetone through nucleophilic addition followed by dehydration.

34 b) 1-bromopropane. Among the given options, 1-bromopropane is the most reactive haloalkane due to the lower bond dissociation energy of C-Br bond compared to C-Cl or C-F bonds.

35 b) Iodine and aqueous potassium hydroxide. Iodoform is formed when ethanol is heated with iodine and aqueous potassium hydroxide. This is known as the iodoform test.

36 **(b)**$R - X \xrightarrow{\text{KOH(aq.)}} R - OH$

37 **(d)** Reactivity of t-alkyl halides to show S_N2 mechanism is least due to steric hinderance.

38 **(c)** $CCl_4 + [H] \xrightarrow{Fe/H_2O(v)} CHCl_3$

39 **(a)** $R - OH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$

40 **(b)** Statement (b) is not correct regarding the S_N1 reaction for alkyl halide because in S_N1 reaction no inversion takes place. The removal of X and the attachment of OH^- will take place from the same side.

$$R - X \xrightarrow{Slow} R^+ + X^-$$

$$R^+ + OH^- \xrightarrow{Fast} ROH$$

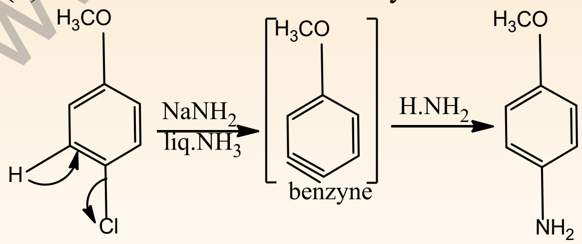
41 **(c)**Alkyl halides are soluble in organic solvents.

42 **(d)** $C_2H_5Br + AgNO_2(alc.) \rightarrow C_2H_5NO_2 + AgBr$

nitro ethane

43 **c) 1-phenylpropan-2-ol**

44 **(a)** This reaction follows benzyne mechanism.

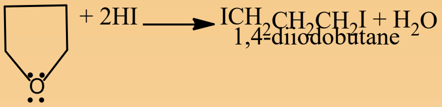


45 **b) $((CH_3)_3OD)$**

46 **(d)** Grignard reagent give nucleophilic addition (of R^-) at +ve centre.

47 **(a)**

Tetrahydrofuran when treated with excess HI, give 1, 4-diiodobutane.



48 **(b)**

I_2 possesses antiseptic nature.

49 **d)** Isopropyl chloride and ethyl chloride.

When a mixture of isopropyl chloride and ethyl chloride is treated with sodium metal in ether solution, isobutane is obtained as a product through the Wurtz reaction.

50 **(d)**

Wurtz's reaction involves the reduction of alkyl halide with Na in ether.

51 **(d)**

$$\underset{(aq)}{CHCl_3 + 4NaOH} \rightarrow \underset{\text{sodium formate}}{HCOONa} + 3NaCl + 2H_2O$$

52 **b)** Trihydroxy methane: Boiling CHCl3 with NaOH leads to the formation of trihydroxy methane, commonly known as glycerol or glycerin.

53 **(b)**

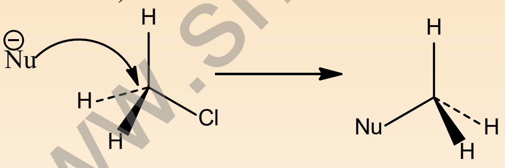
Straight chain alkyl halides have greater boiling point than their isomers. Therefore, $CH_3CH_2CH_2CH_2Cl$ has highest boiling point.

54 **(d)**

CH_3Cl, C_2H_5Cl and CH_3Br are gases at room temperature.

55 **(d)**

Nucleophilic substitution bimolecular (S_N2) prefers less sterically hindered site to attack. Lesser the steric hindrance better the S_N2 reaction. So, ease of reaction is $1^\circ > 2^\circ > 3^\circ$. S_N2 involves inversion of configuration stereochemically (Walden inversion)



56 **(c)**

The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with $SOCl_2$ in the presence of pyridine.

$$ROH + SOCl_2 \rightarrow RCl + HCl + SO_2$$

The other products being gases escape leaving behind pure alkyl halide.

57 **(d)**

Freon, CCl_2F_2 is used in cooling.

58 **(b)**

$CH\equiv CH + 2HCl \longrightarrow CH_3CHCl_2$

59 **(d)**

Cl^- is replaced by OH^- , *i.e.*, nucleophilic substitution.