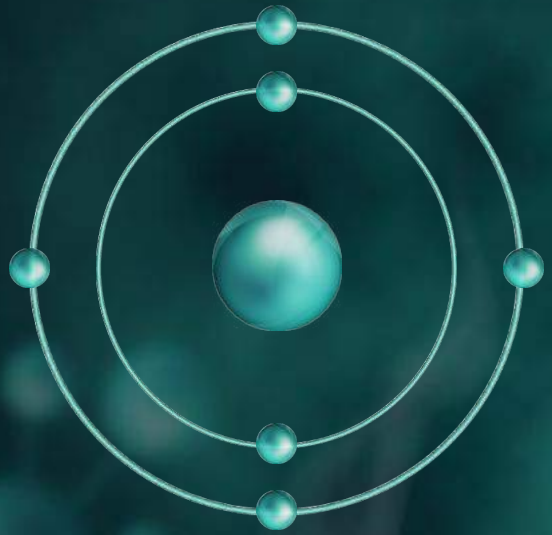
BYJU'S Classes

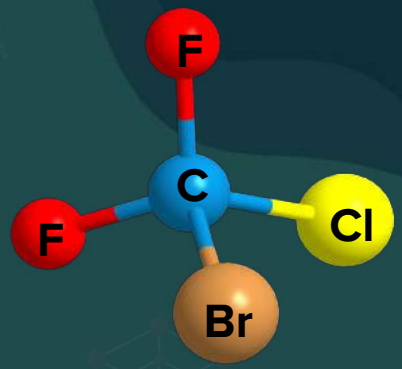
Haloalkanes & Haloarenes



Haloalkanes & Haloarenes

Haloalkanes and haloarenes are the hydrocarbons in which one or more hydrogen atoms have been replaced with halogen atoms. The primary difference between haloalkanes and haloarenes is that haloalkanes are derived from open-chain hydrocarbons (alkanes) whereas haloarenes are derived from aromatic hydrocarbons.

Example



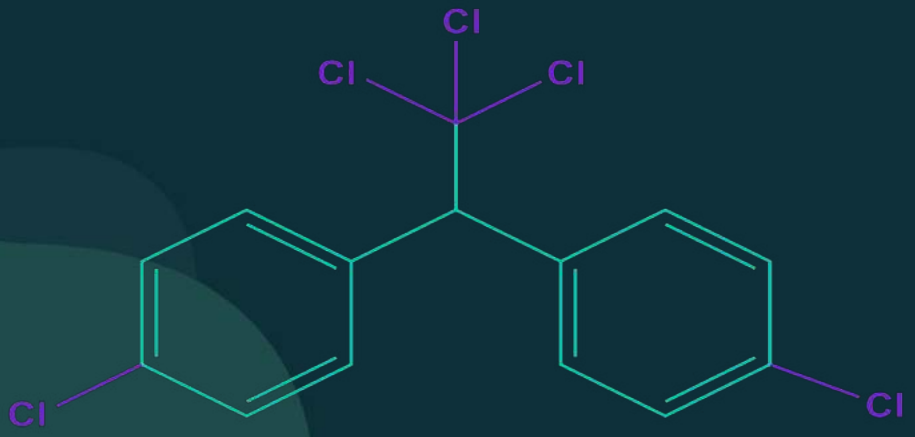
Bromochlorodifluoromethane

Halon: Halon, a chemical compound formerly used in firefighting. A halon may be group of organohalogen compounds containing bromine and fluorine and one or two carbons.

The effectiveness of halons in extinguishing fires arises from their action in interrupting chain reactions that propagate the combustion process.

Haloalkanes & Haloarenes

- **DDT (Dichloro-Diphenyl Trichloroethane):** DDT, a synthetic insecticide belonging to the family of organic halogen compounds, highly toxic toward a wide variety of insects as a contact poison.



Biological Importance of Haloalkanes & Haloarenes

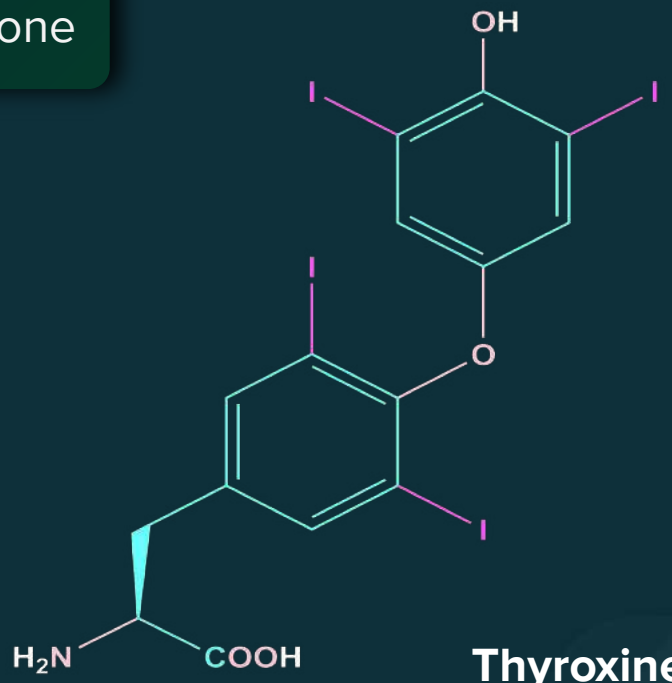
Goiter is caused due to the deficiency of hormone

↓

Thyroxine

↓

contains **iodine**

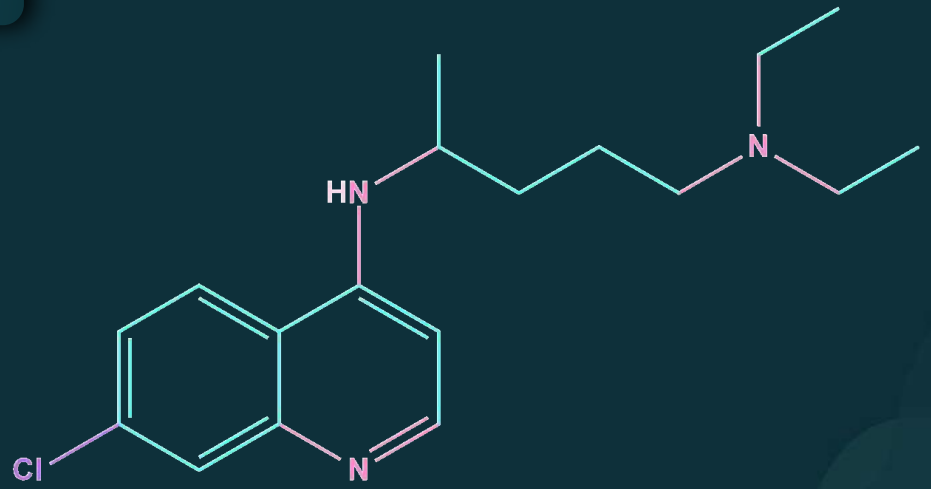


Thyroxine

Biological Importance of Haloalkanes & Haloarenes

Malaria is treated using Chloroquine

which contains chlorine

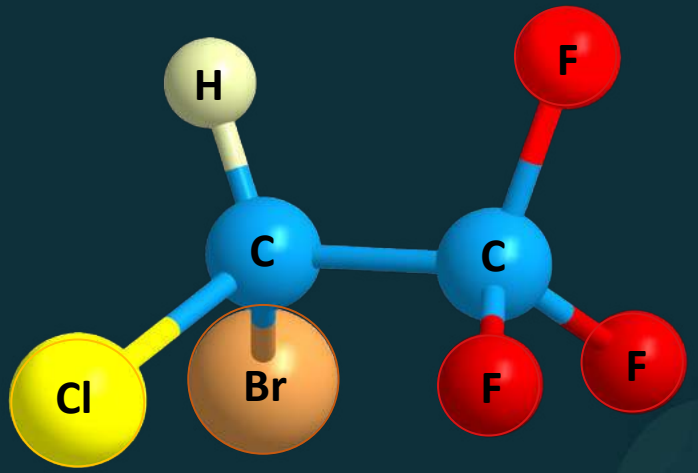


Chloroquine

Biological Importance of Haloalkanes & Haloarenes

Halothane is used as an **anaesthetic** during surgery.

It contains **fluorine, chlorine, and bromine.**

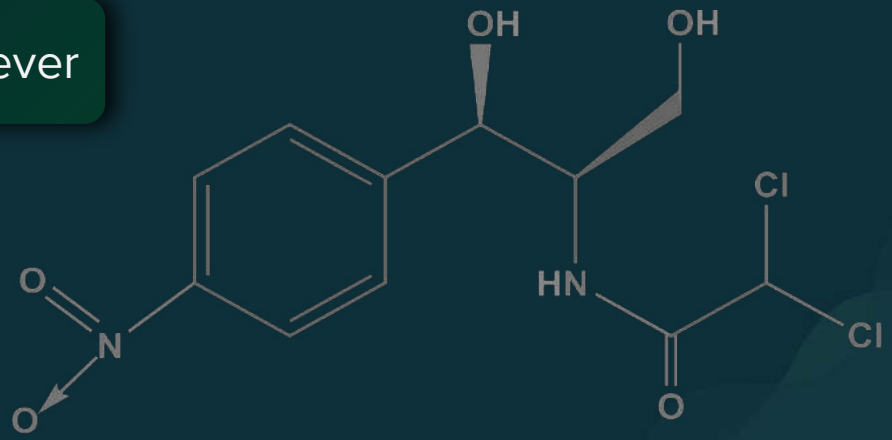


Halothane

Biological Importance of Haloalkanes & Haloarenes

Chloramphenicol – Chlorine containing antibiotic

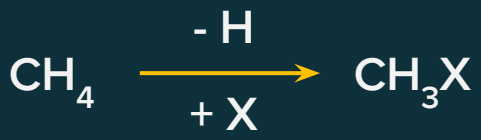
Used for the treatment of **typhoid** fever



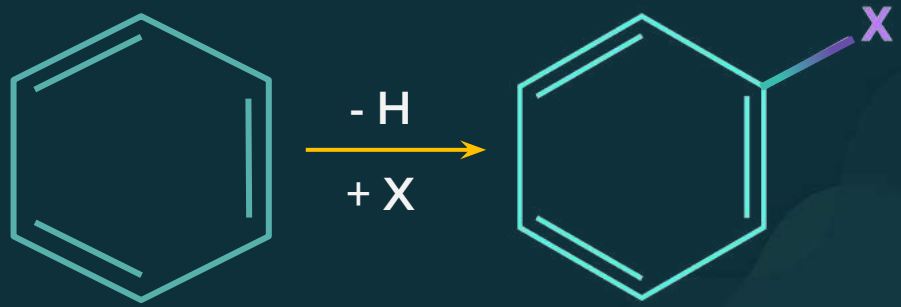
Chloramphenicol

Haloalkanes and Haloarenes

Haloalkanes/haloarenes are compounds in which **at least one halogen atom replaces hydrogen atom** of an alkane/aromatic compound.



Haloalkanes



Haloarenes

Haloalkanes and Haloarenes

Classification

- Number of halogens present
- Hybridisation of 'C' in C—X bond

1. Depending on the number of halogens present

- Monohaloalkane/ monohaloarene
- Dihaloalkane/ dihaloarene
- Polyhaloalkane/ polyhaloarene

Classification of Haloalkanes and Haloarenes

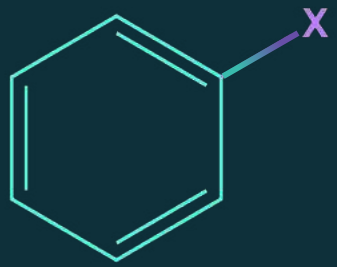
Monohaloalkane

Example

Number of halogens (X) = 1

Monohaloarene

Example

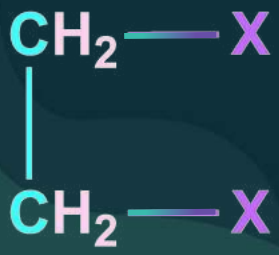


Number of halogens (X) = 1

Classification of Haloalkanes and Haloarenes

Dihaloalkane

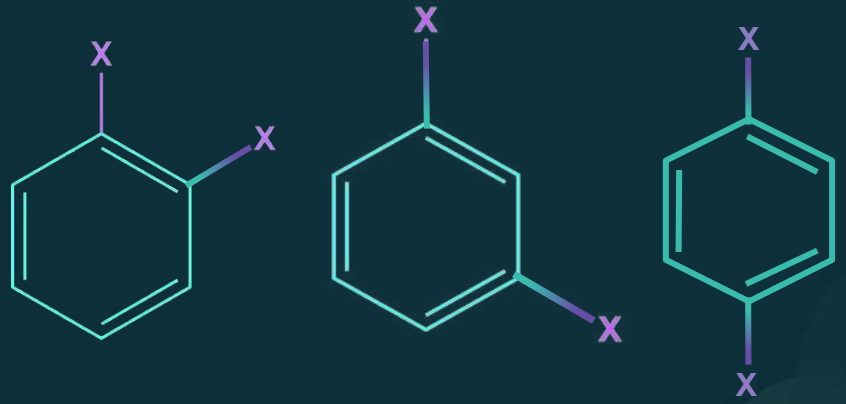
Example



Number of halogens (X) = 2

Dihaloarene

Example

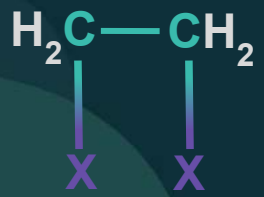


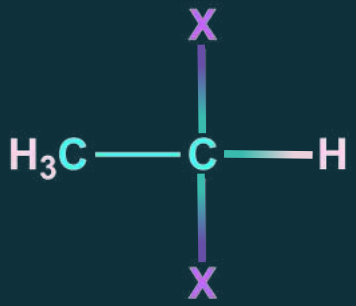
Number of halogens (X) = 2

Classification of Haloalkanes and Haloarenes

Dihaloalkane

- Vicinal dihalide
- Geminal dihalide





Classification of Haloalkanes and Haloarenes

Polyhaloalkane/Polyhaloarene

Number of halogens (X) present in the compound **>** 2

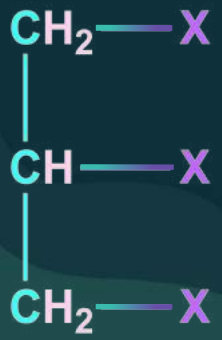
Polyhalogen compounds can be named as **tri, tetra**, etc.

Trihaloarene

Classification of Haloalkanes and Haloarenes

Polyhaloalkane

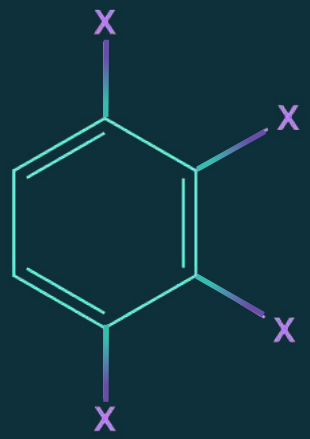
Example



Number of halogens (X) = 3

Polyhaloarene

Example



Number of halogens (X) = 4

Classification of Haloalkanes and Haloarenes

2. Hybridisation of 'C' in C—X bond

A. **Compound containing sp^3 C-X bond**

- Alkyl halides
- Allylic halides
- Benzylic halides

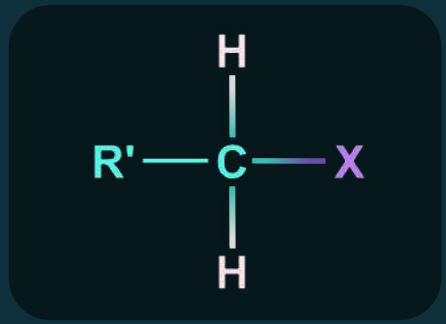
Classification of Haloalkanes and Haloarenes

Alkyl halides

- Primary (1°)
- Secondary (2°)
- Tertiary (3°)

Primary Alkyl halides

Number of carbons attached to the C-atom of sp^3 C-X bond = **1**

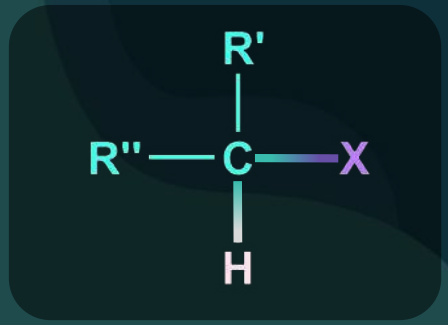


Primary (1°)

Classification of Haloalkanes and Haloarenes

Secondary Alkyl halides

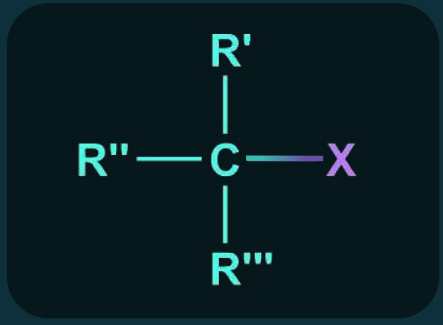
Number of carbons attached to the C-atom of sp^3 C-X bond = **2**



Secondary (2°)

Tertiary Alkyl halides

Number of carbons attached to the C-atom of sp^3 C-X bond = **3**

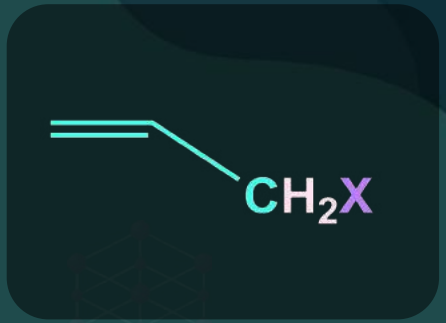


Tertiary (3°)

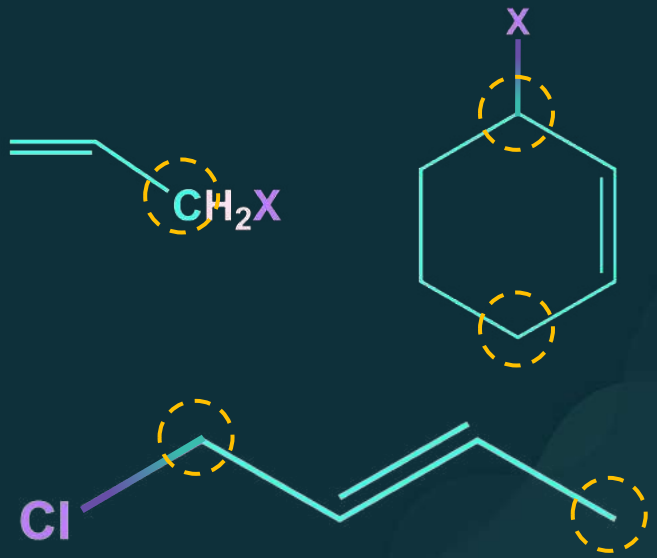
Classification of Haloalkanes and Haloarenes

Allylic halides

Halogen atom bonded to an sp^3-C atom which is directly attached to a carbon-carbon double bond **(C=C)**



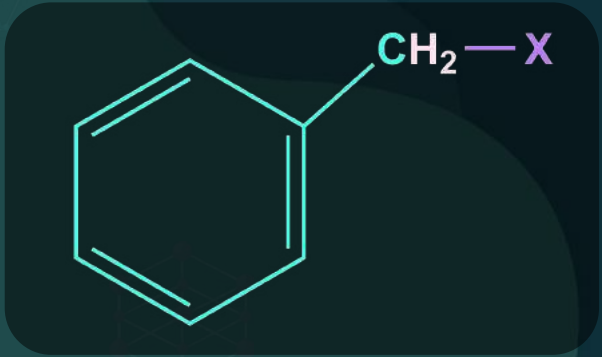
Allylic carbon



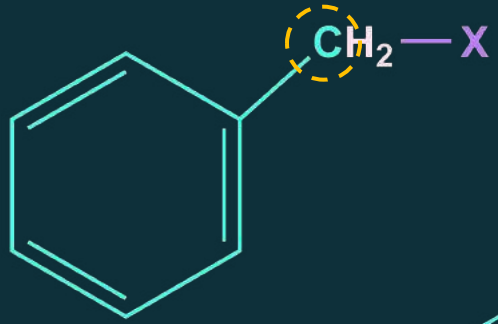
Classification of Haloalkanes and Haloarenes

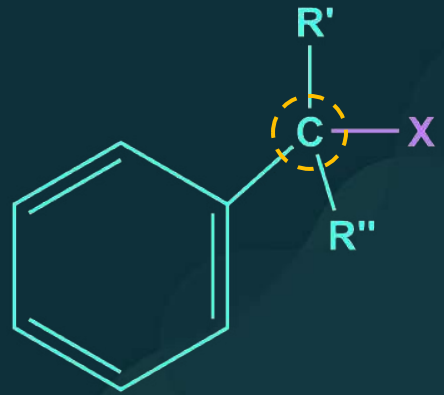
Benzylic halides

Halogen atom bonded to a sp^3-C atom which is directly attached to a **benzene ring.**



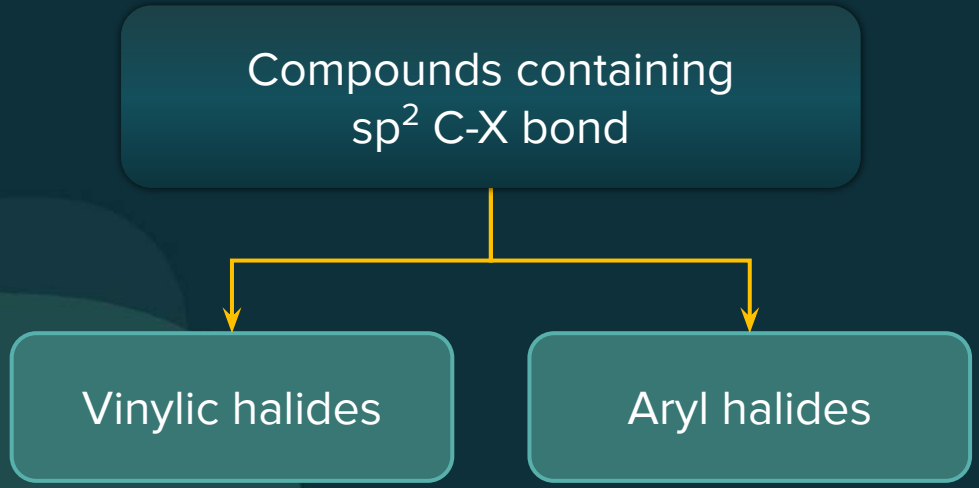
Benzylic carbon





Classification of Haloalkanes and Haloarenes

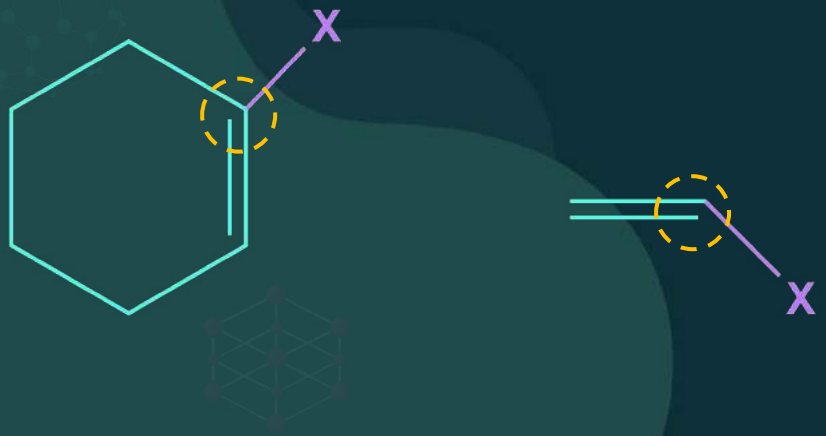
B. **Compound containing sp^2 C-X bond**



Classification of Haloalkanes and Haloarenes

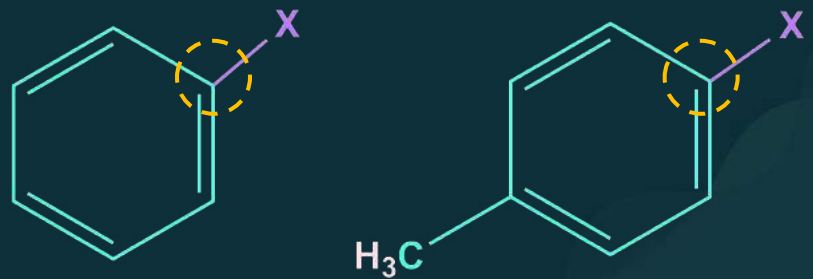
Vinylic halides

Halogen atom is attached to a sp^2-C atom of **C=C.**



Aryl halides

Halogen atom is **bonded to a sp^2-C atom** of an aromatic ring.



Which of the following is an example of aryl halide?

(a) Bromobenzene

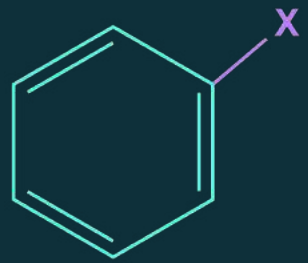
(b) Chlorobenzene

(c) Allyl chloride

(d) Both (a) and (b)

Solution

X = Cl; Allyl chloride



X = Br; Bromobenzene
X = Cl; Chlorobenzene

Bromobenzene and chlorobenzene are aryl halide as halogen atom is **bonded to a sp^2-C atom** of an aromatic ring, while allyl chloride is not.

Hence, option (d) is the correct answer.

When two halogens are attached to same carbon atom, it is known as:

(a) vic-dihalide

(b) gem-dihalide

(c) α,ω-dihalide

(d) α,β-dihalide

Solution

Vic-dihalide: In this case the two halogen atoms are on the adjacent carbons.

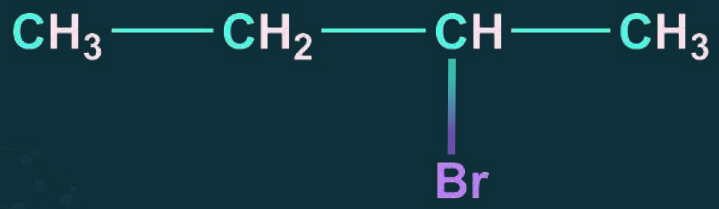
Gem-dihalide: Geminal dihalides are those dihalides in which the two halogen atoms are present on the same carbon atom.

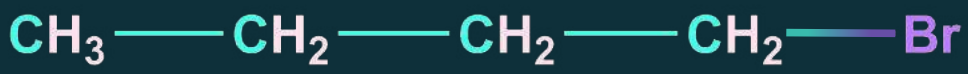
α,ω-dihalide: If halogen atom is attached to first and fifth carbon atom, such dihalide is called α,ω-dihalide.

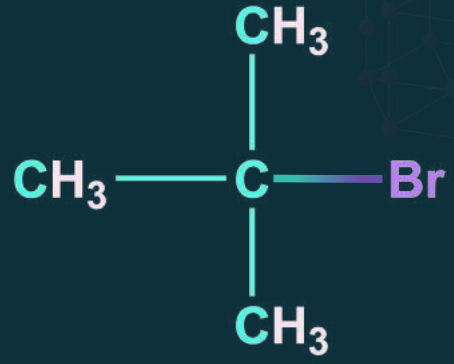
α,β-dihalide: They are the vicinal dihalide (In this case, two halogen atoms are on adjacent carbons).

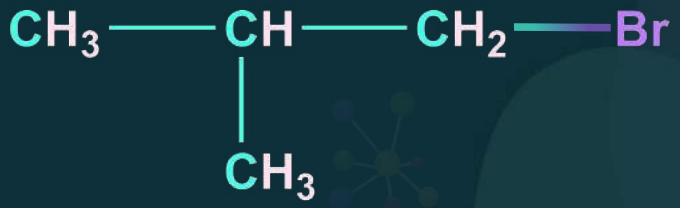
Hence, option (b) is the correct answer.

Which of the following halides is iso-butyl bromide?

(a) 

(b) 

(c) 

(d) 

Solution

Option (a) is 2-bromobutane or sec-butyl bromide. So it is incorrect.

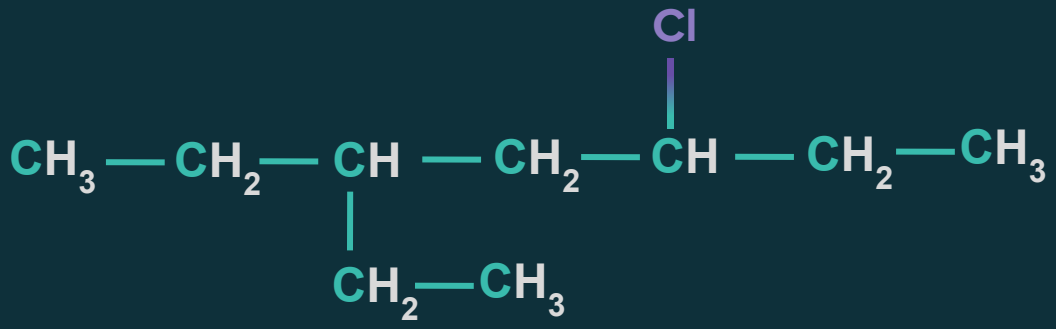
Option (b) is 1-bromobutane. So it is incorrect.

Option (c) is 2-bromo-2-methylpropane or tert-butyl bromide. So it is incorrect.

Option (d) is 1-bromo-2-methylpropane or iso-butyl bromide. So it is correct.

Hence, option (d) is the correct answer.

The IUPAC name of the compound is:



Solution

The parent chain consists of seven carbons. While numbering, chloro group will get the preference so we start numbering from the right side. Hence IUPAC nomenclature of the given compound is **3-chloro-5-ethylheptane.**

The correct structure of 4-bromo-3-methylbut-1-ene is:

(a) $Br-CH=C(CH_3)_2$

(c) $CH_2=C(CH_3)CH_2CH_2Br$

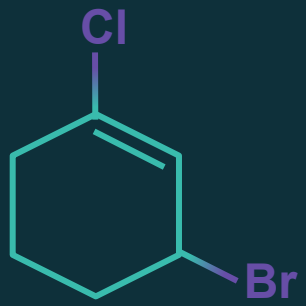
(c) $CH_2=CH-CH(CH_3)-CH_2Br$

(d) $CH_3-C(CH_3)=CHCH_2-Br$

Solution

Option (a): The IUPAC name is 1-bromo-2-methylprop-1-ene. So this is incorrect.
Option (b): The IUPAC name is 4-bromo-3-methylbut-1-ene. So this is correct.
Option (c): The IUPAC name is 4-bromo-2-methylbut-1-ene. So this is incorrect.
Option (d):The IUPAC name is 1-bromo-3-methylbut-2-ene. So this is incorrect.
Hence, option (b) is the correct answer.

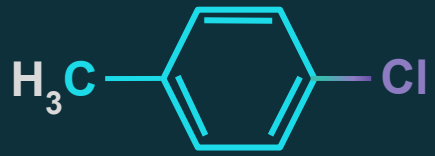
The IUPAC name of the compound is:



Solution

The parent chain is cyclohexene. Double bond is given preference over halogen atom. Hence, IUPAC nomenclature of the given compound is **3-bromo-1-chlorocyclohex-1-ene.**

The IUPAC name of the given compounds are:

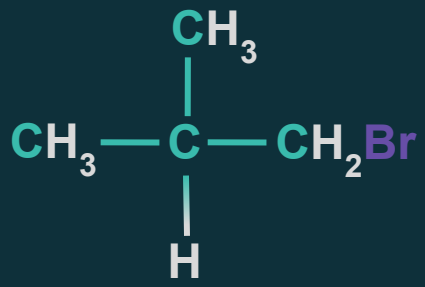


Solution

(I) Here, bromine is attached to cyclopentadiene. Double bond is given preference over halogen atom. Hence, IUPAC nomenclature of the given compound is **5-bromocyclopenta-1,3-diene.**

(II) Here, chlorine and methyl group is attached on the benzene ring. Chloro group is given preference over methyl group according to alphabetical order. Hence, IUPAC nomenclature of the given compound is **1-chloro-4-methylbenzene.**

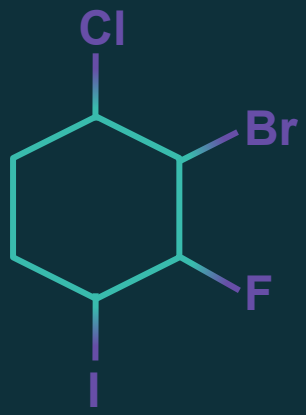
The IUPAC name of the compound is:



Solution

The parent chain is propane. Halogen atom is given preference over methyl group. Hence, IUPAC nomenclature of the given compound is **1-bromo-2-methylpropane.**

The IUPAC name of the compound is:



Solution

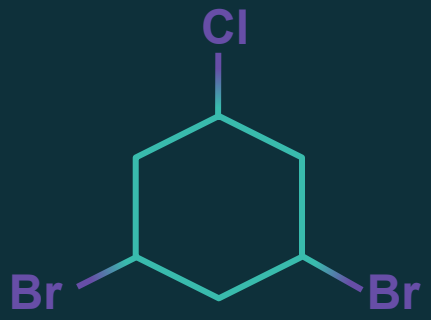
The parent chain is cyclohexane. There are 4 halogen atoms. Numbering is given according to alphabetical order. Hence, IUPAC nomenclature of the given compound is **2-bromo-1-chloro-3-fluoro-4-iodocyclohexane.**

The IUPAC name of the compound is:

Solution

Halogen atom is attached in the branched chain, so it will be the parent chain. Hence, IUPAC nomenclature of the given compound is **(3-chloropentyl)cyclopropane.**

The IUPAC name of the compound is:



Solution

The parent chain is cyclohexane. Numbering is given according to alphabetical order of halogens. Hence, IUPAC nomenclature of the given compound is **1,3-dibromo-5-chlorocyclohexane.**

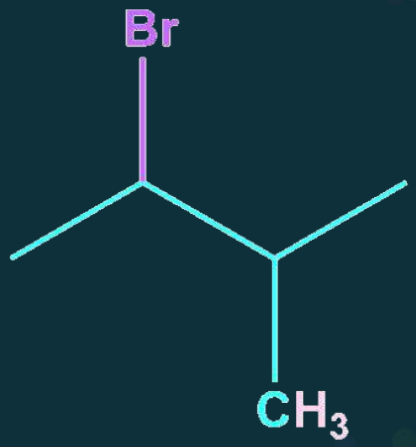
The structure for 2-bromo-3-methylbutane is:

Solution

Step 1 : Butane means the given molecule has four carbon.

Step 2 : 2-Bromo means bromine group at the second position.

Step 3 : 3-methyl means CH_3 group at third position.

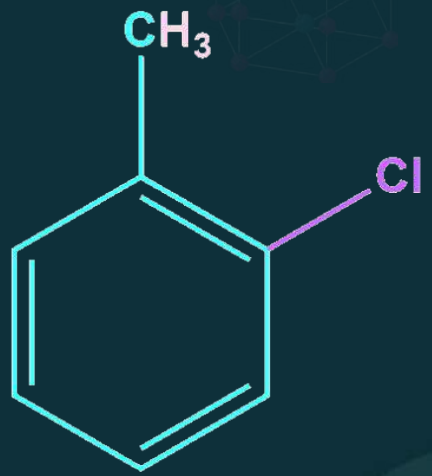


The structure for 2-chlorotoluene is:

Solution

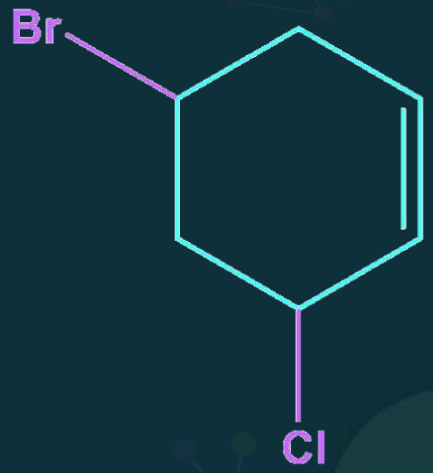
Step 1 : Toluene is the molecule when the benzene ring is attached to the methyl group.

Step 2 : At 2^{nd} position, a chlorine atom is attached to the benzene ring.



The structure for 5-Bromo-3-chlorocyclohex-1-ene is:

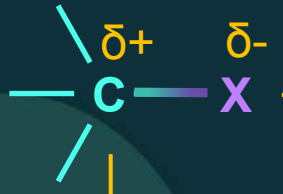
Solution



Step 1 : Cyclohex-1-ene means ring of 6 carbons with a double bond.

Step 2 : Number 1 will be given to double bond (alkene), chlorine atom is attached at 3^{rd} position and bromine is attached at 5^{th} position.

Nature of C-X Bond



More electronegative

Less electronegative

Generally,

Electronegativity difference ↑ → Polarisation of C-X bond ↑

Bond length

Down the group → C-X bond length ↑

C-F < C-Cl < C-Br < C-I

Increasing bond length

Nature of C-X Bond

Generally,

Bond length ↑ → Bond enthalpy ↓

C-F > C-Cl > C-Br > C-I

Increasing bond enthalpy

Dipole moment of a bond depends on

- |Δ E.N.|
- Bond length

CH_3 - Cl > CH_3 - F > CH_3 - Br > CH_3 - I

The correct statement is:

(a) Dipole moment only depends on difference in electronegativity between atoms.

(b) Dipole moment of C-F bond is more than that of C-Cl.

(c) Bond enthalpy of C-F bond is more than that of C-Cl bond.

(d) None of these

Solution

Option (a) is incorrect as dipole moment depends on both the electronegativity difference and bond length.

Option (b) is incorrect as dipole moment of carbon fluorine is less than that of carbon chlorine bond because of large bond length of carbon chlorine bond.

Option (c) is correct because smaller is the bond length larger will be the bond enthalpy.

Hence, option (c) is the correct answer.

The incorrect statement is:

(a) Chloramphenicol is used for the treatment of typhoid fever.

(b) Malaria is treated using chloroquine.

(c) Goiter is caused due to the deficiency of iodine containing hormone.

(d) None of these

Solution

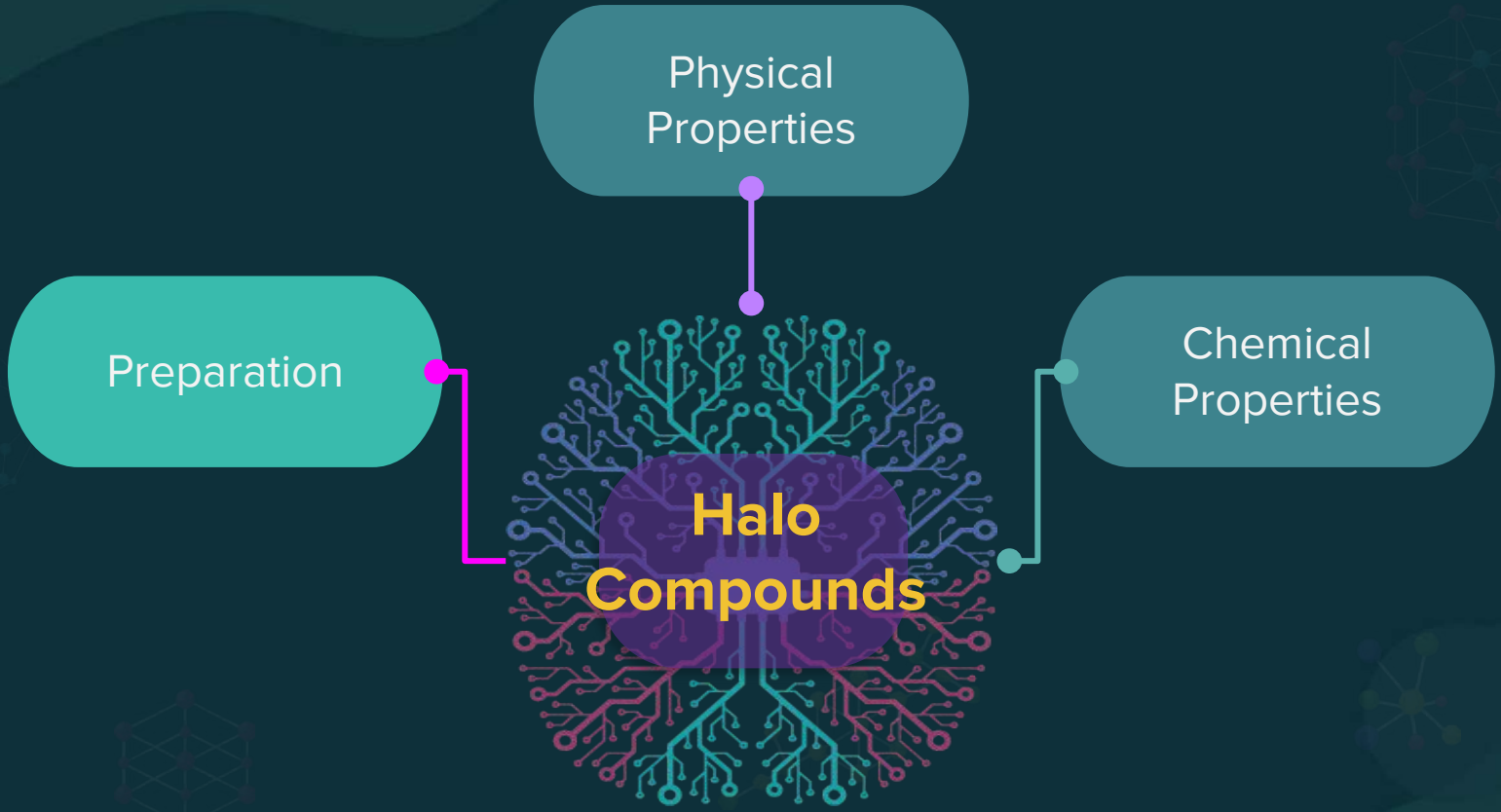
Option (a): Chloramphenicol is used for the treatment of typhoid fever. So it cannot be the correct choice.

Option (b): ‘Malaria is treated using chloroquine’ is the correct statement. So it cannot be the correct choice.

Option (c): ‘Goiter is caused due to the deficiency of iodine containing hormones’ is the correct statement. So it cannot be the correct choice.

Hence, option (d) is the correct answer.

Preparation of Halo Compounds



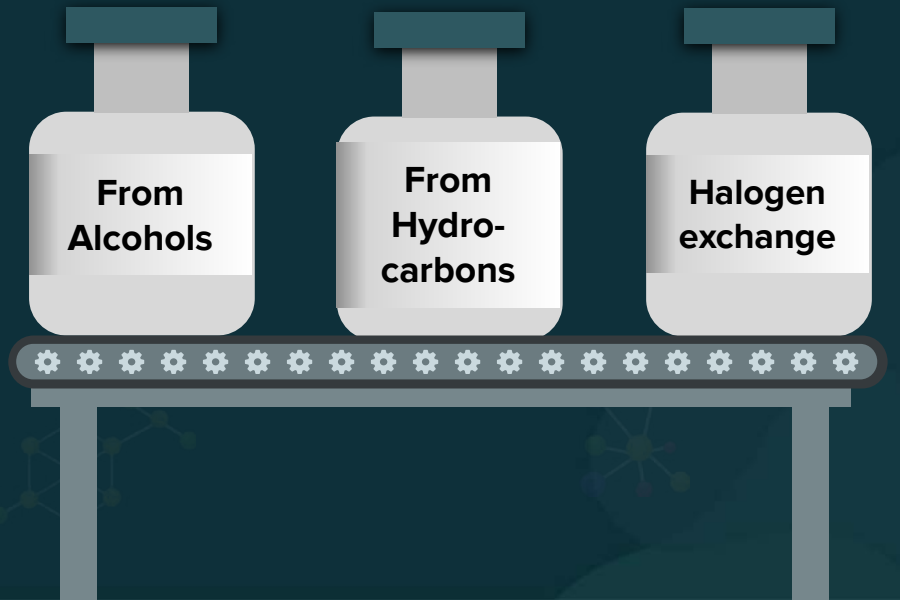
Preparation of Halo Compounds

Preparation

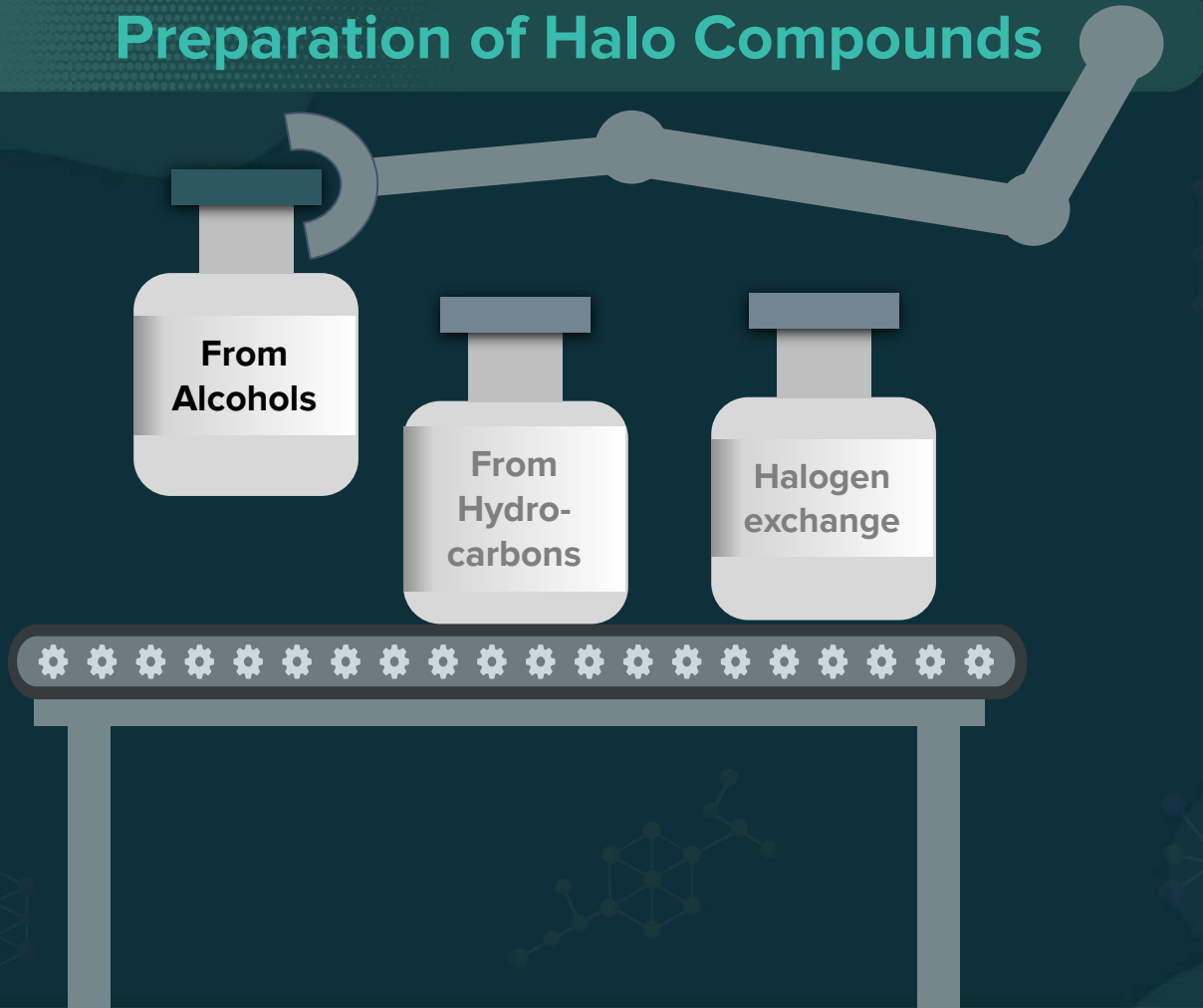
Types of Halo Compounds

- Alkyl halides
- Aryl halides

Preparation of alkyl halides



Preparation of Halo Compounds

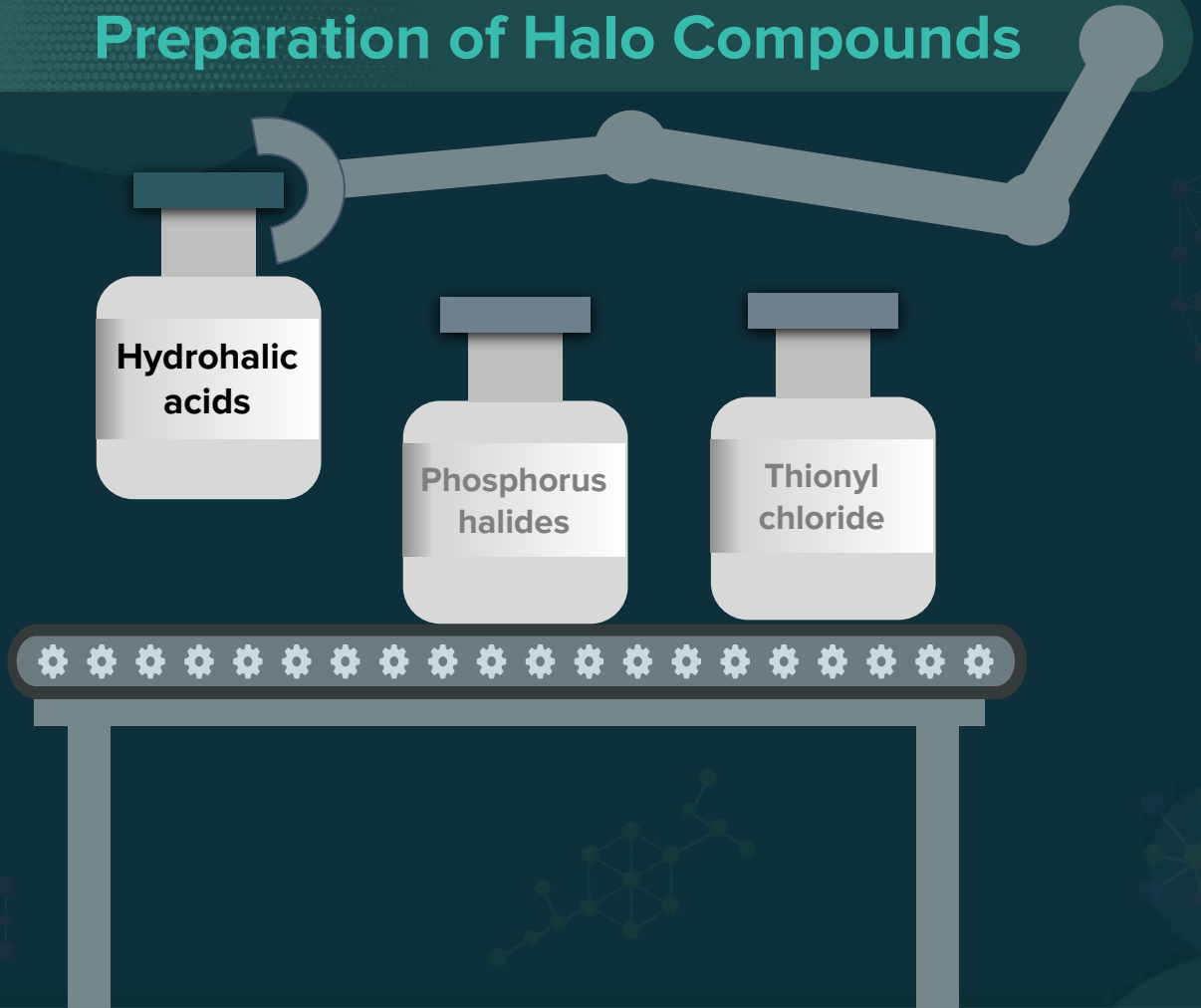


Preparation of Halo Compounds

Preparation from alcohols

Reagents used	Hydrohalic acid, Phosphorus halides and Thionyl chloride

Preparation of Halo Compounds



Preparation of Halo Compounds

Alcohols with hydrohalic acid (HCl)

General reaction

Alcohols with Hydrohalic acid (HCl)

Preparation of Halo Compounds

Reactivity of HX

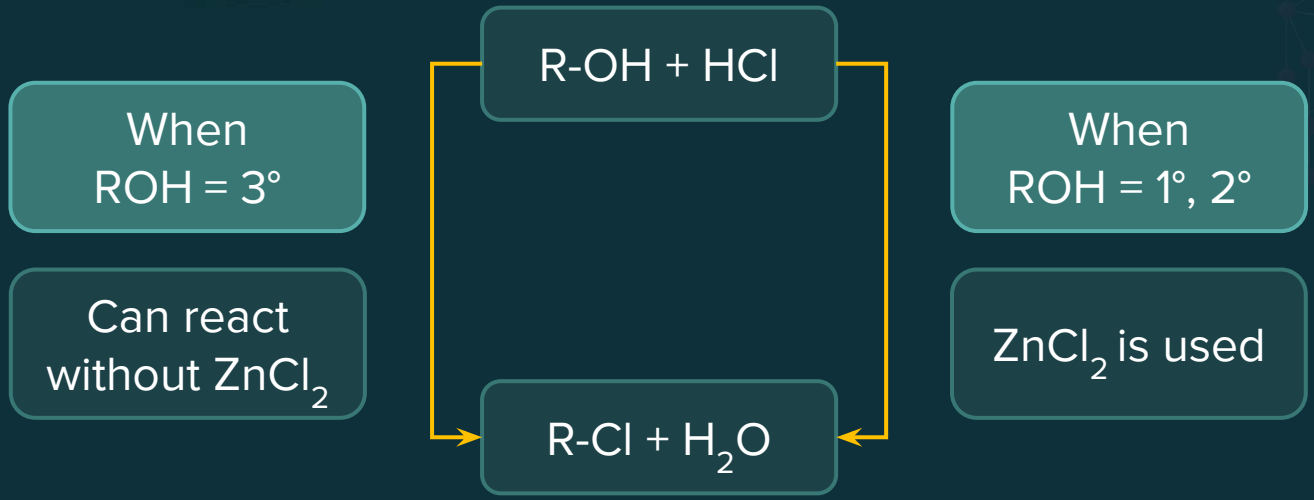
HI > HBr > HCl

Reactivity of ROH

3° > 2° > 1°

Rate of the reaction can be increased by using $ZnCl_2$ as a **catalyst.**

Preparation of Halo Compounds

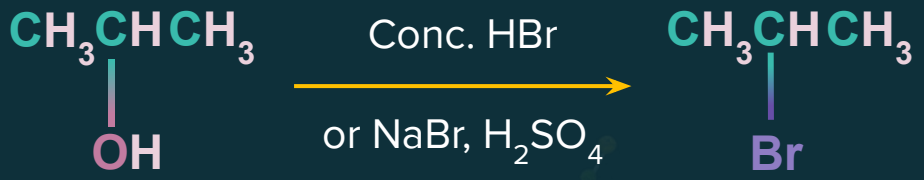


A mixture of concentrated hydrochloric acid and anhydrous zinc chloride is called the **Lucas reagent.**

Preparation of Halo Compounds

Alcohols with other hydrohalic acids

HI and HBr are often **generated in situ** from the **halide ion** and an **acid** such as phosphoric or sulfuric acid.



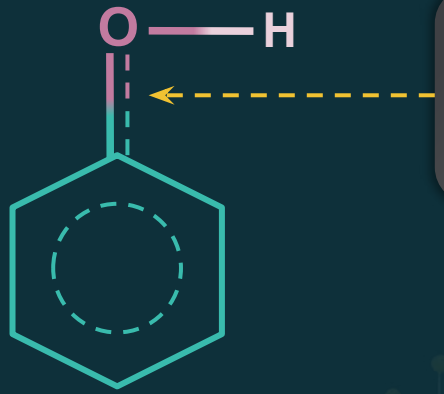
Preparation of Halo Compounds

HI is generated from **KI** and **H_3PO_4**

To prepare HI, **KI** is **not** made to react with conc. **H_2SO_4 or HNO_3** as they are **oxidising agents** and thus oxidise iodide ions to iodine (I_2).

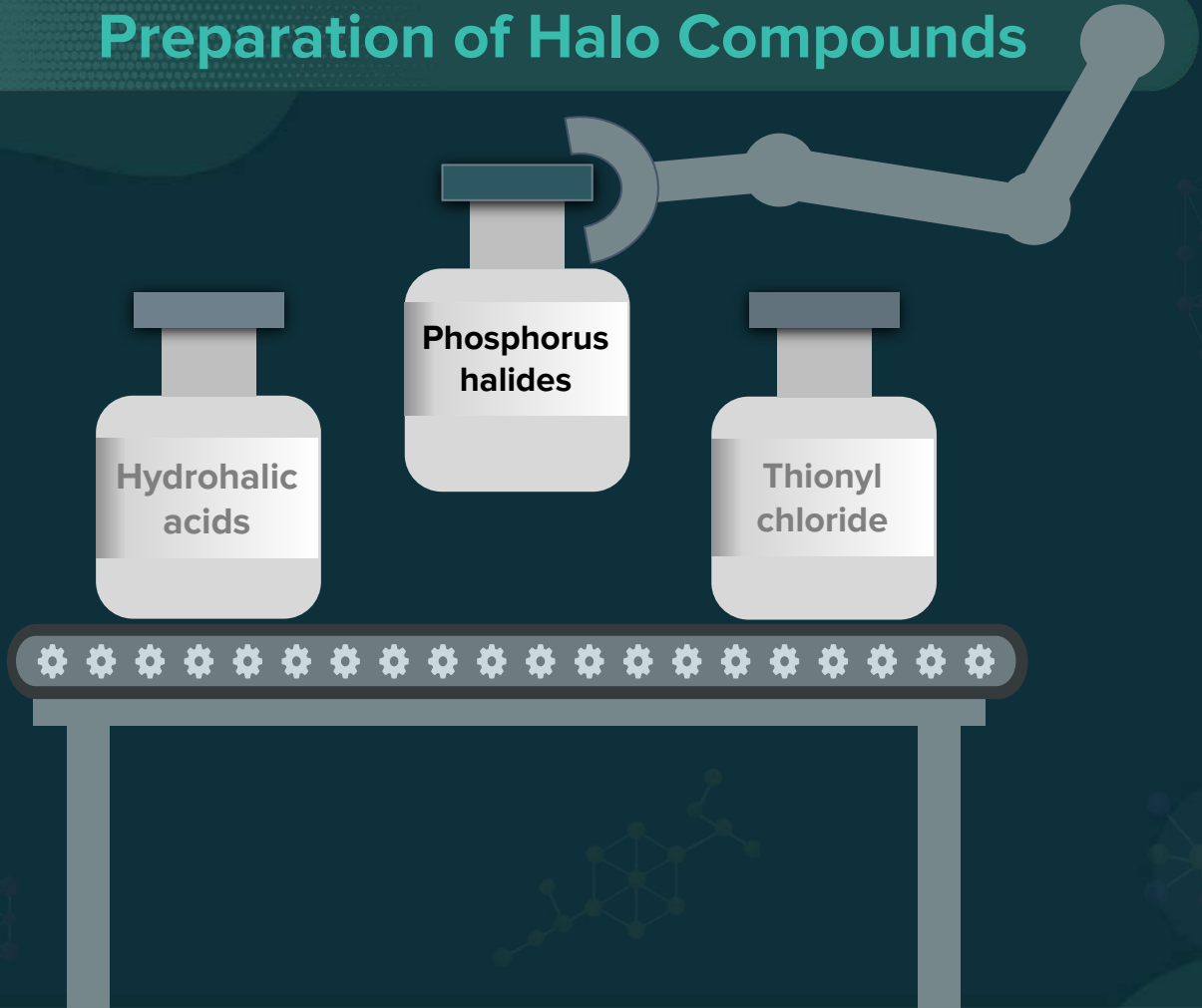
Preparation of Halo Compounds

Aryl halides **cannot be prepared** from phenol.



Partial double bond which is difficult to break

Preparation of Halo Compounds



Preparation of Halo Compounds

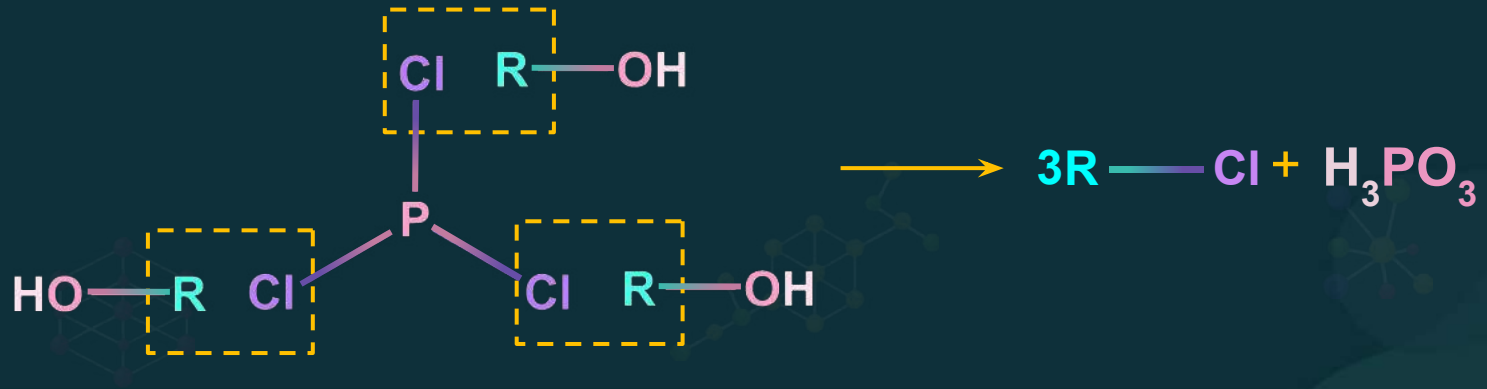
Alcohols with phosphorus halides

$$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$$

X: Cl, Br, I

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

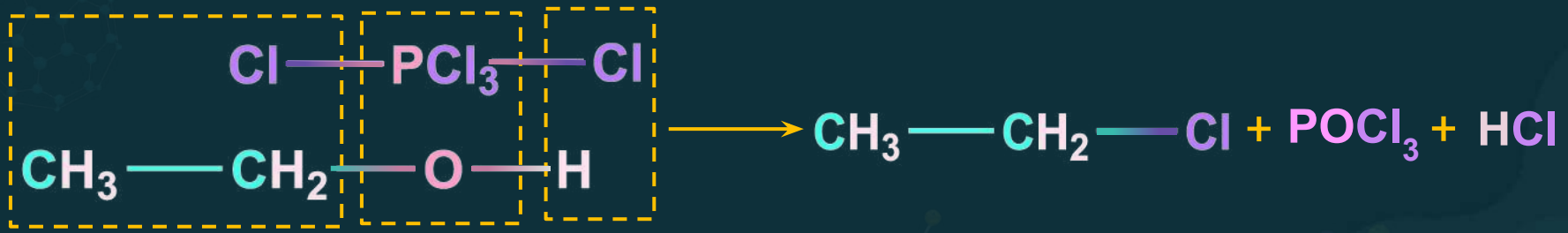
Short trick



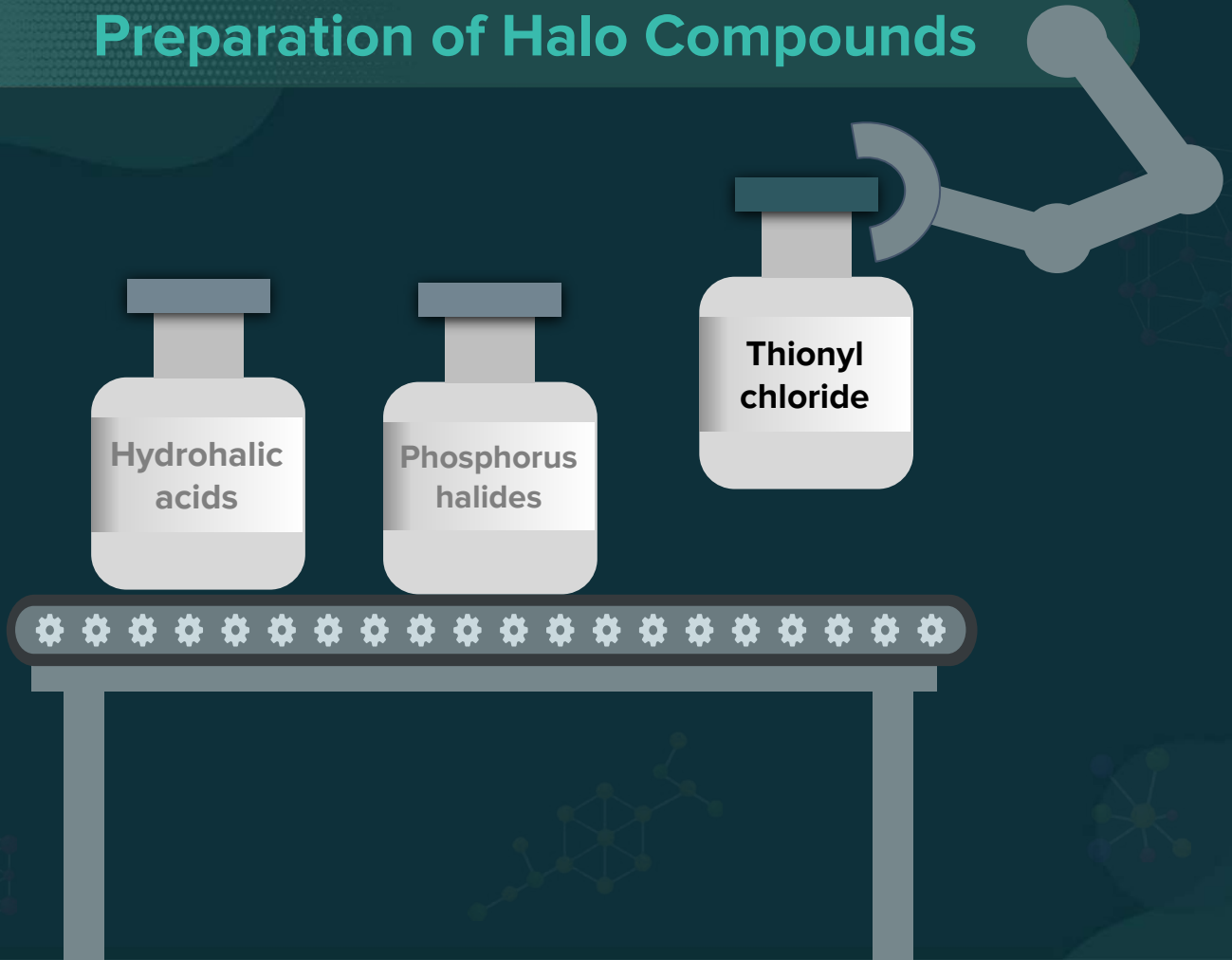
Preparation of Halo Compounds

$$ROH + PCl_5 \longrightarrow RCl + HCl + POCl_3$$

Short trick



Preparation of Halo Compounds



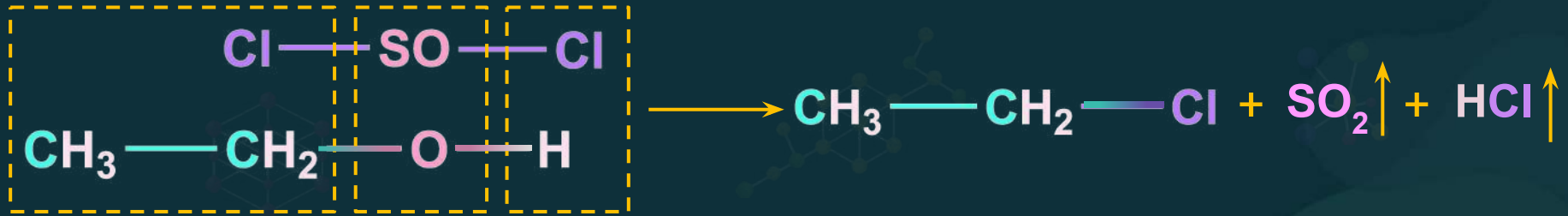
Preparation of Halo Compounds

Alcohols with thionyl chloride

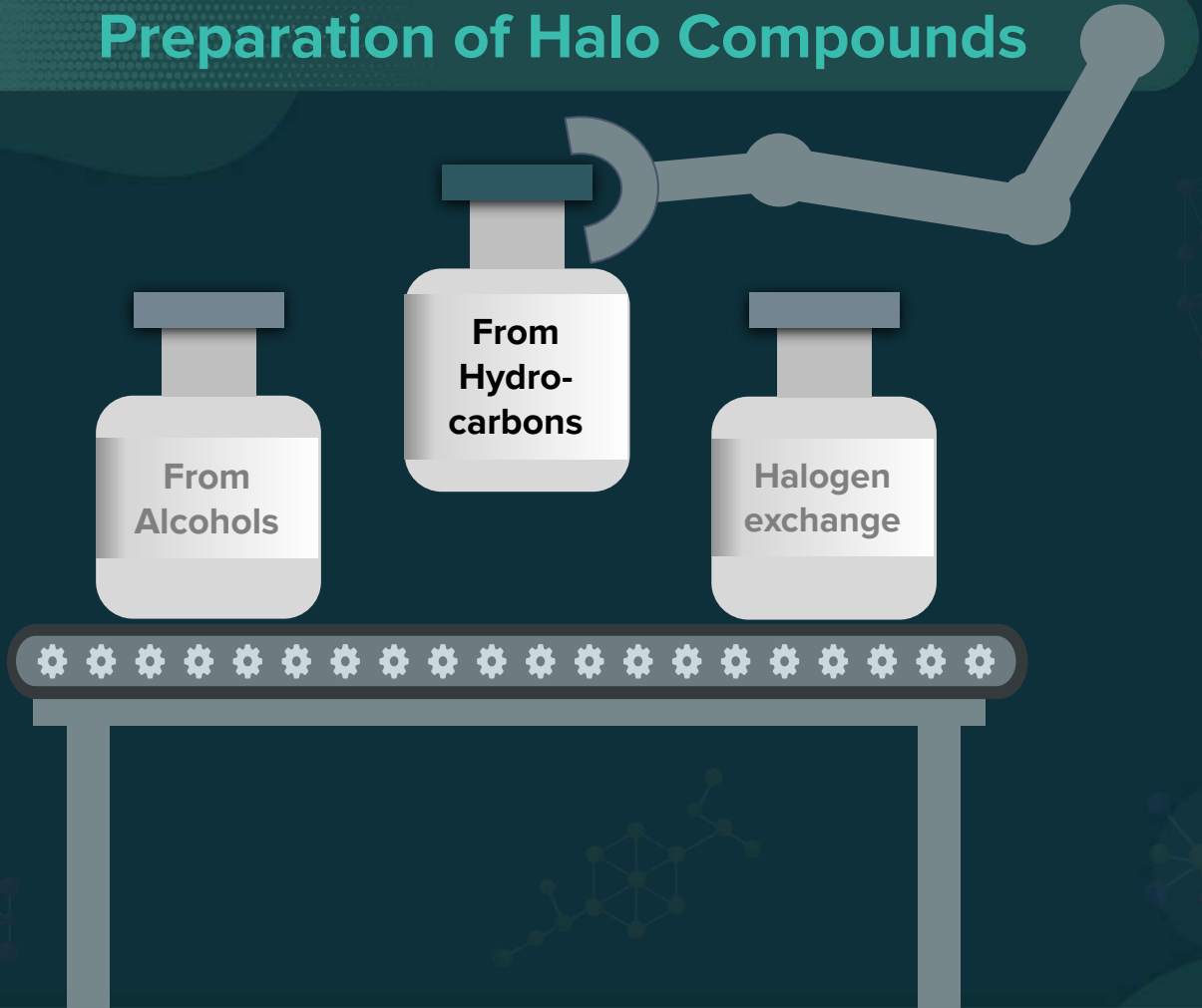
General reaction

Good method for the preparation of alkyl halide.
By-products are gaseous in nature.

Short trick



Preparation of Halo Compounds



Preparation of Halo Compounds

Preparation from hydrocarbons

From Hydrocarbons

From alkanes

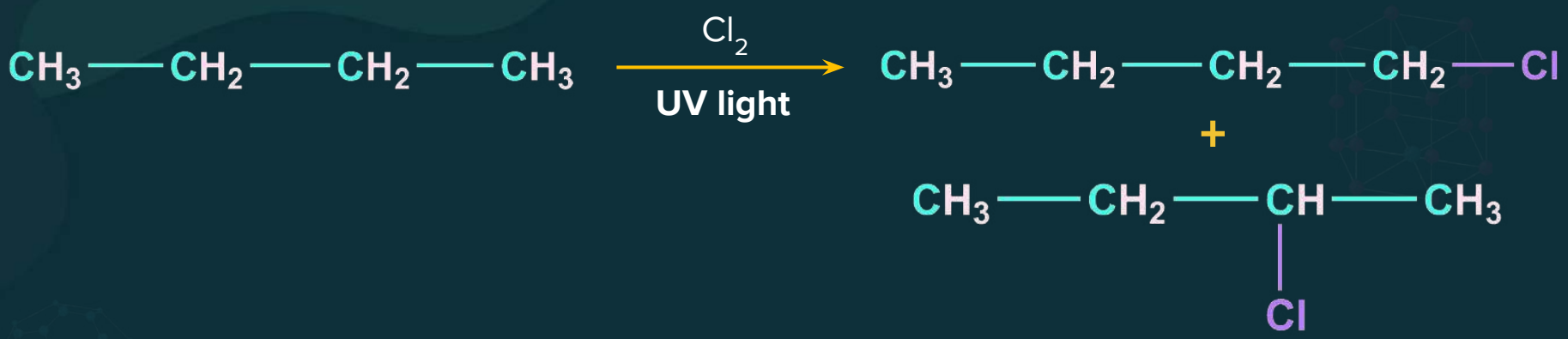
From alkenes

From alkanes

Halogenation of alkanes by **free radical** mechanism

Generates a mixture of **mono/poly** haloalkanes

Preparation of Halo Compounds



Rate of reaction of **halogens**

F_2 > Cl_2 > Br_2 > I_2

Reactivity of **H**

3° > 2° > 1°

$H_3C - CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3$, obtained by chlorination of butane will be:

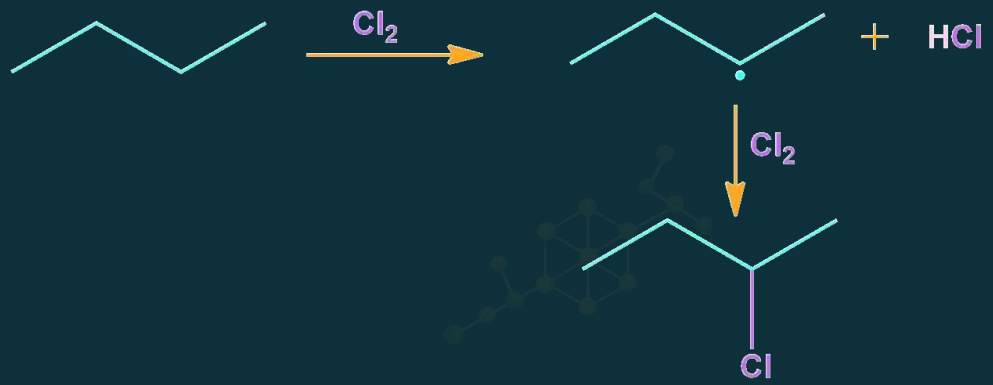
a) Meso form

b) Racemic mixture

c) d-form

d) *l*-form

Solution



- According to the mechanism free radical is formed (Sec butyl radical) in the first step.
- Carbon radical is planar in nature and because of this, the attack of Cl radical from both sides is possible (above and below).
- So we will get 50% mixture dextro and 50% laevo, so the resultant mixture will be **racemic in nature.**

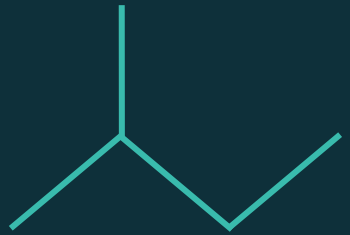
Hence, option (b) is the correct answer.

A gaseous hydrocarbon ‘X’ on reaction with bromine in light forms a mixture of two monobromo alkanes and HBr. The hydrocarbon ‘X’ is:

a) $CH_3—CH_3$

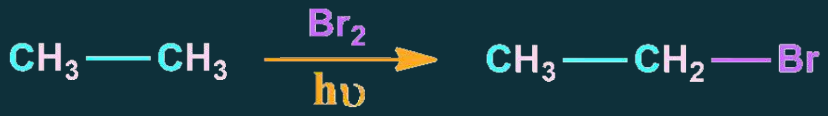
b) 

c) 

d) 

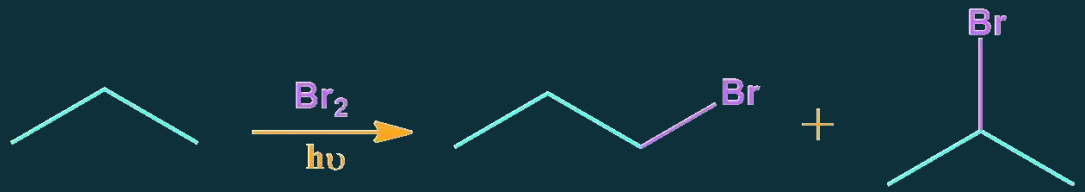
Solution

Option (a): On monohalogenation it forms only one types of product. So this is not correct choice.

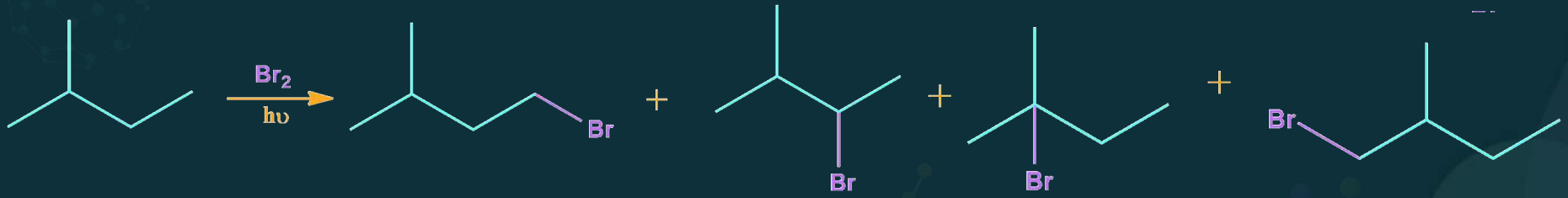


Option (b): On monohalogenation it only forms three types of product.

Option (c): On monohalogenation it only forms two types of products. So this is correct choice.



Option (d): On monohalogenation it only forms four types of product .



Hence, option (c) is the correct answer.

The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is:

a) 3

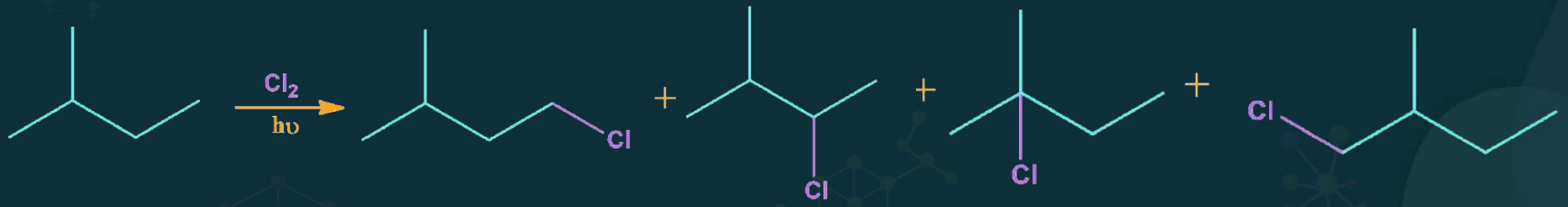
b) 4

c) 1

d) 2

Solution

It has four types of products on monochlorination.



Hence, option (b) is the correct answer.

Preparation of Halo Compounds

From Hydrocarbons

From alkanes

From alkenes

From alkanes

Alkyl halides are prepared from alkenes in two ways

Mono haloalkanes

Addition of HX

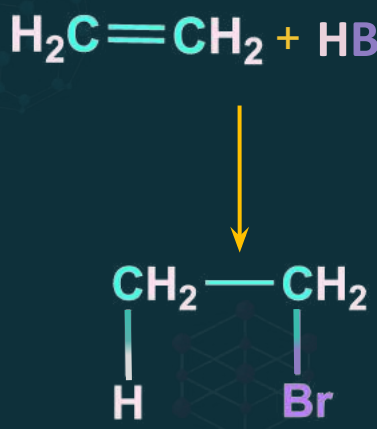
Dihaloalkanes

Addition of X_2

Preparation of Halo Compounds

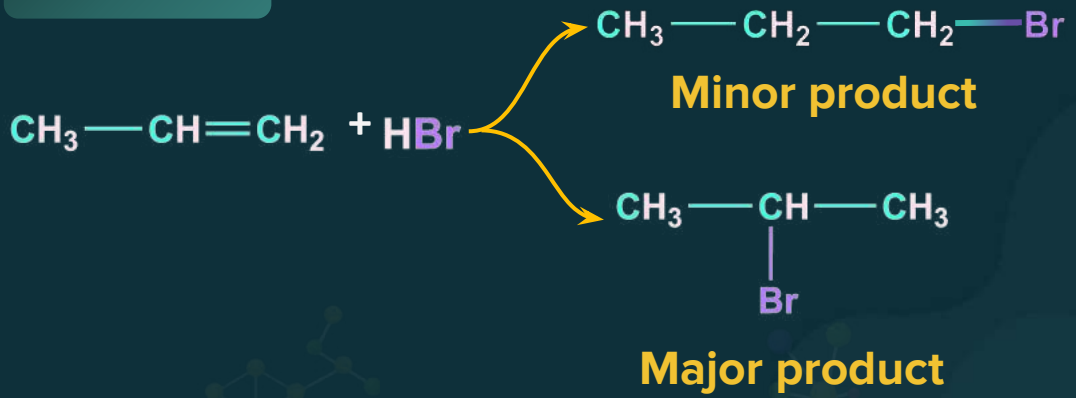
Addition of HX

Addition of HBr to a **symmetrical** alkene



Addition of HBr to **an unsymmetrical** alkene (Markovnikov's rule)

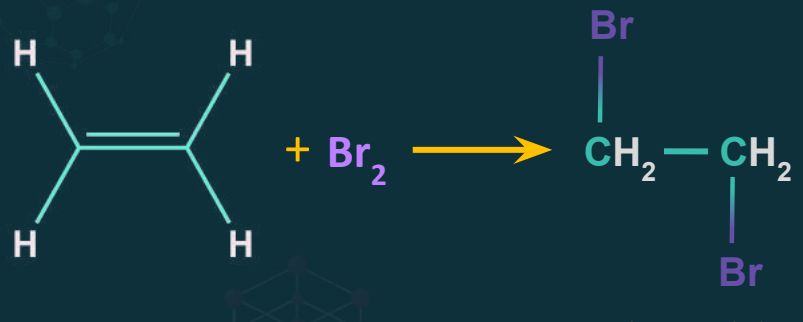
Example



Preparation of Halo Compounds

Addition of X_2

Halogens (Cl_2, Br_2) add up to alkenes to form **vicinal dihalides**.



Anti-addition

Addition of halogens to alkenes is an example of **electrophilic addition reaction.**

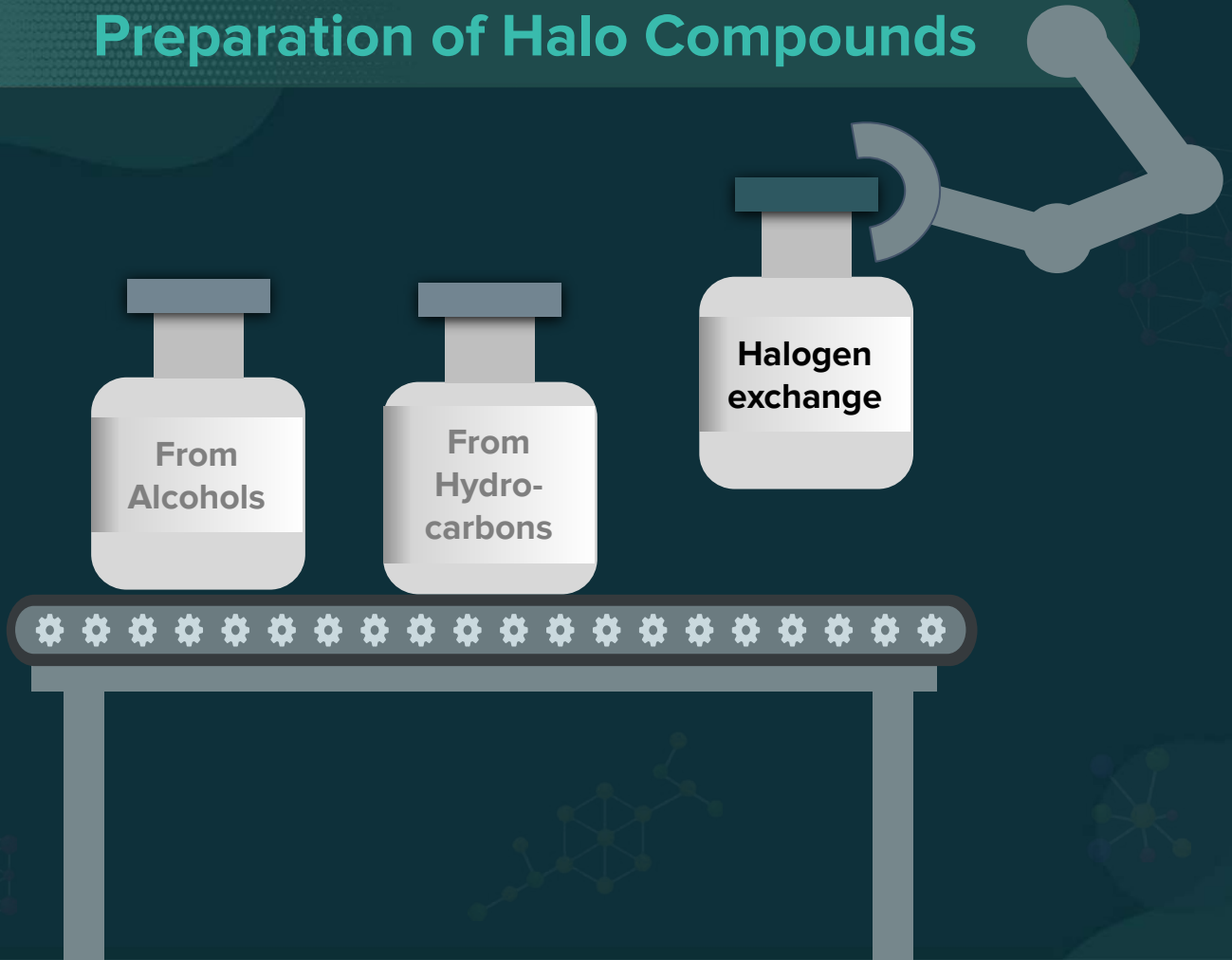
Involves **halonium ion** formation

Preparation of Halo Compounds

Addition of halogens to alkenes is an example of **electrophilic addition reaction.**

Involves **halonium ion** formation

Preparation of Halo Compounds



Preparation of Halo Compounds

Preparation by halogen exchange

Halogen exchange method is used to obtain alkyl halides by

- Finkelstein reaction
- Swarts reaction

Finkelstein reaction

$$RX + NaI \underset{}{\overset{\text{Acetone}}{\rightleftharpoons}} RI + NaX$$

X: Cl, Br

Unlike NaI, NaCl or NaBr is **not soluble** in acetone.

Preparation of Halo Compounds

When RCl or RBr is treated with a solution of **NaI** in acetone

Equilibrium is shifted by the **precipitation** of NaCl or NaBr

Swarts reaction

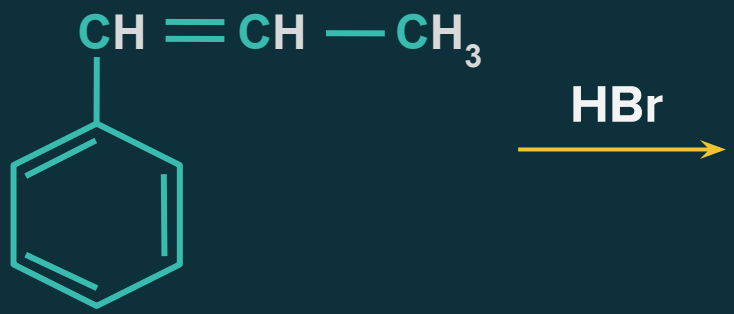
R-**Br**/R-**Cl** ⟶ R-**F**

Reagents used AgF, CoF_2, Hg_2F_2

Example

CH_3-Br + AgF ⟶ CH_3-F + AgBr↓

The major product of the following reaction is:

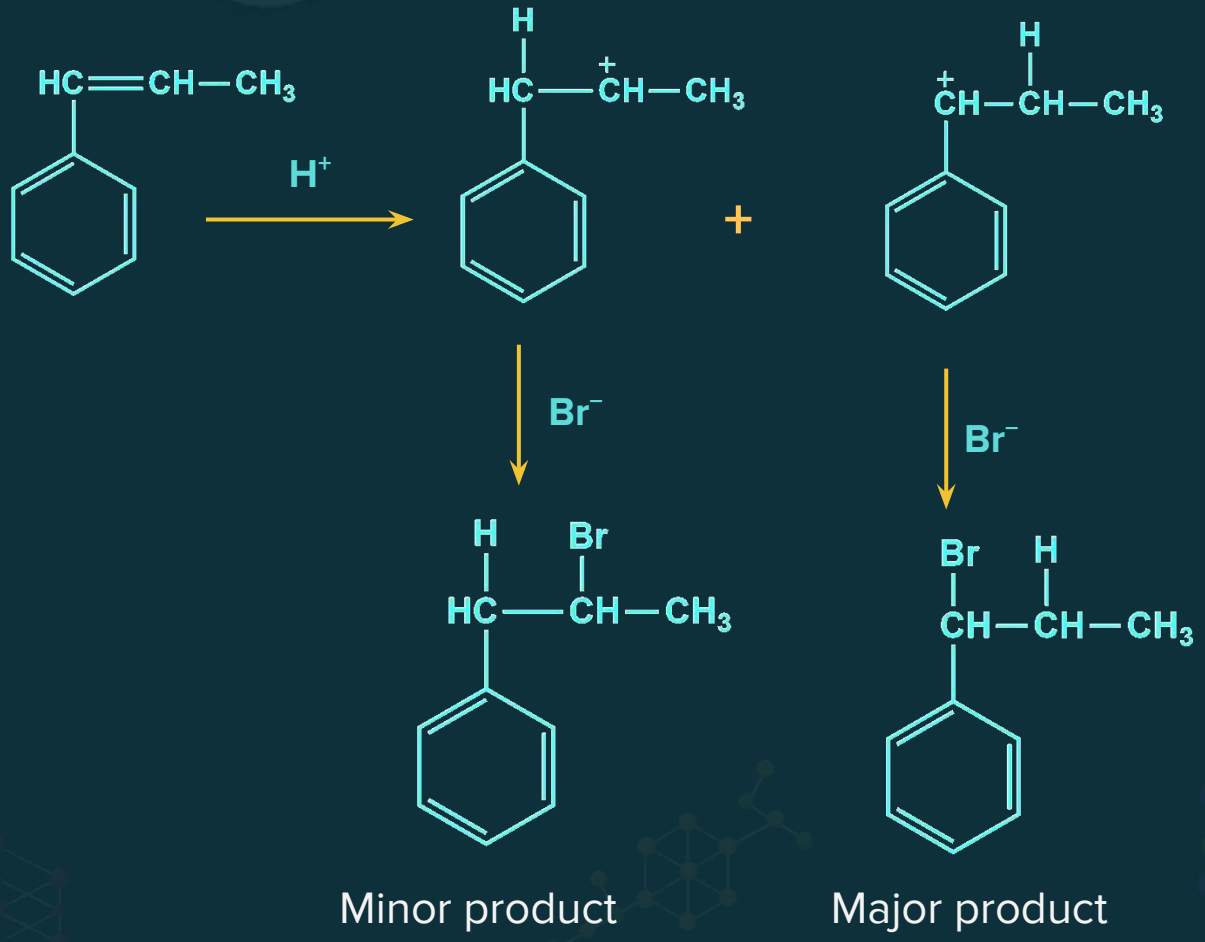


Solution

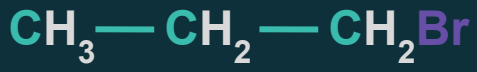
On attack of H^+, there are two possibilities of forming the carbocation.

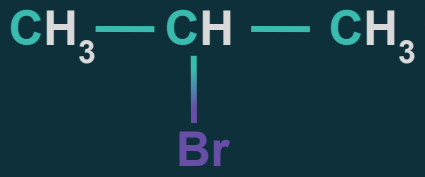
(I) Secondary carbocation

(II) Secondary carbocation and benzylic too. This forms major product as it is more stable.


HC═CH—CH3
H+
H
HC—+CH—CH3
+
H
+CH—CH—CH3
Br−
Br−
H
Br
HC—CH—CH3
Br
H
CH—CH—CH3
Minor product
Major product

The product obtained by treating:

a) 

b) 

c) 

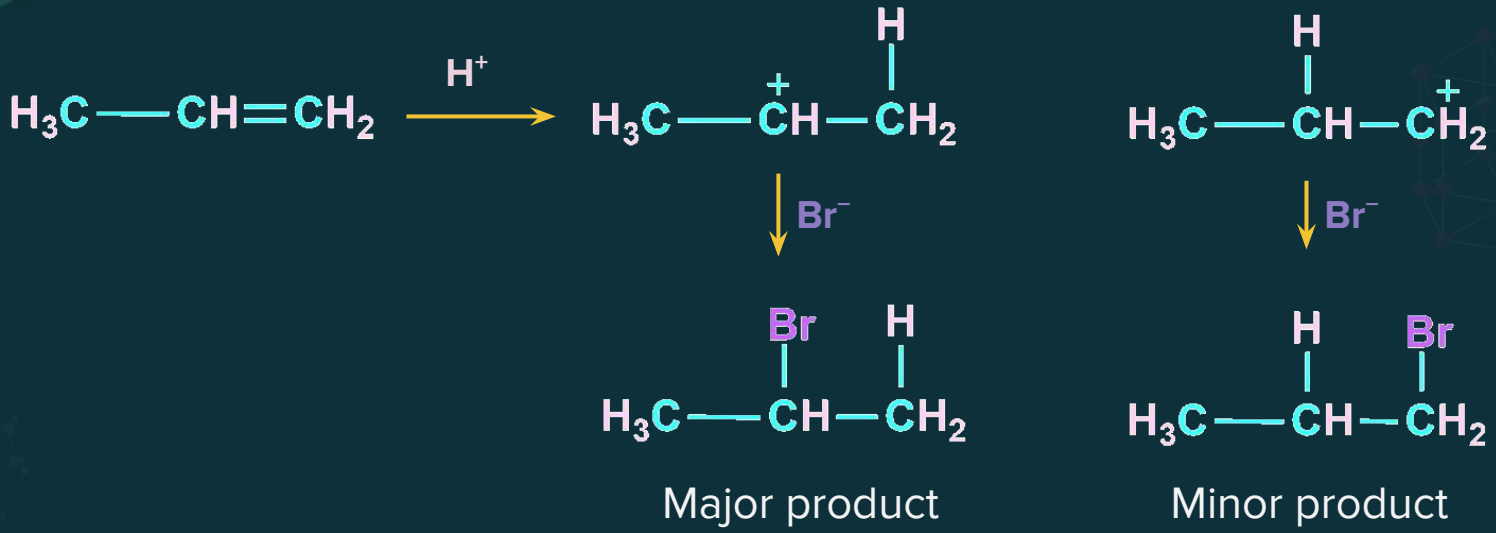
d) 

Solution

On attack of H^+, there are two possibilities of forming the carbocation.

(I) Secondary carbocation (More stable) - It forms major product.

(II) Primary carbocation (less stable) - It forms minor product.



Hence, option (b) is the correct answer.

The synthesis of alkyl fluorides is best accomplished by:

a) Finkelstein reaction

b) Swarts reaction

c) Free radical fluorination

d) All of the above

Solution

Swarts Reaction is used for the preparation of alkyl fluorides.

R-**Br**/R-**Cl** ⟶ R-**F**

Reagents used AgF, CoF_2, Hg_2F_2

Hence, option (b) is the correct answer.

Lucas reagent is:

a) Anhy. $AlCl_3$ + conc. HCl

b) Anhy. $AlCl_3$ + conc. HNO_3

c) Anhy. $ZnCl_2$

d) Anhy. $ZnCl_2$ + conc. HCl

Solution

Anhydrous $ZnCl_2$ and concentrated HCl is called as Lucas reagent.

Hence, option (d) is the correct answer.

Lucas test is used for the detection of:

a) Alcohols

b) Alkyl halides

c) Phenols

d) Aldehydes

Solution

Lucas test is used to distinguish between primary, secondary and tertiary alcohols.

Hence, option (a) is the correct answer.

Assertion: Alkyl iodide can be prepared by treating alkyl chloride/bromide with NaI in acetone.

Reason: NaCl/NaBr are soluble in acetone while NaI is not.

a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

c) If the Assertion is correct but Reason is incorrect.

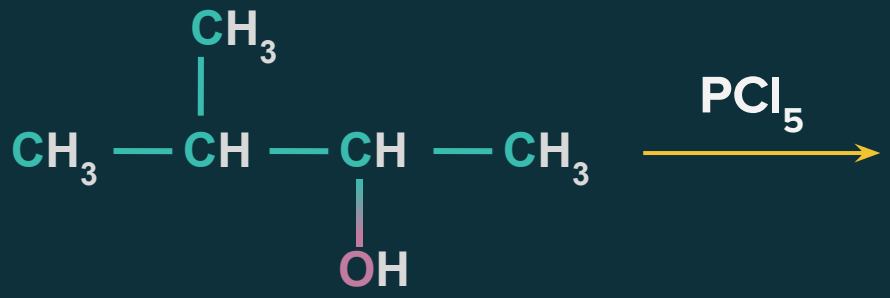
d) If both the Assertion and Reason are incorrect.

Solution

- Alkyl iodide can be prepared by treating alkyl chloride/bromide with NaI in acetone. This method is called Finkelstein Reaction. Therefore, assertion is true.
- NaI is soluble in acetone while NaCl and NaBr are not soluble in acetone. Hence the reason statement is false.
- Assertion is correct but Reason is incorrect.

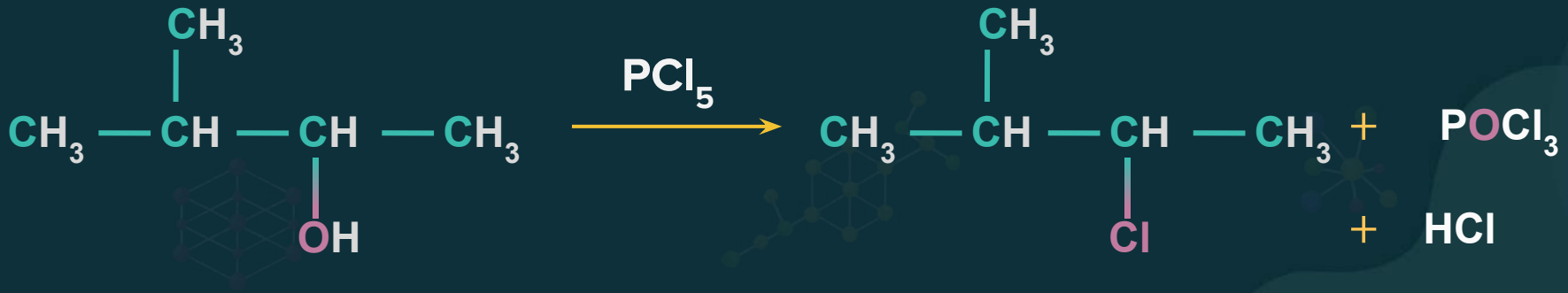
Hence, option (c) is the correct answer.

What will be the major product of the following reaction?



Solution

On reaction with PCl_5, alcohol is converted to alkyl halide, HCl and $POCl_3$.



Which of the following reaction(s) can be used for the preparation of alkyl halides?

(I) $CH_3CH_2OH + HCl \xrightarrow{\text{anhy. } ZnCl_2}$

(II) $CH_3CH_2OH + HCl \longrightarrow$

(III) $(CH_3)_3COH + HCl \longrightarrow$

(IV) $(CH_3)_2CHOH + HCl \xrightarrow{\text{anhy. } ZnCl_2}$

a) (I) and (II) only

b) (IV) only

c) (III) and (IV) only

d) (I), (III), and (IV) only

Solution

(I) The reaction (I) is Lucas test. The product obtained will be alkyl halides.
The reaction is :

$$CH_3CH_2OH + HCl + \text{Anhydrous } ZnCl_2 \rightarrow CH_3CH_2Cl + H_2O$$

(II) The primary alcohol on reaction with conc. HCl will produce alkyl halide only in the presence of Anhydrous $ZnCl_2$.
Hence The reaction (II) will not produce alkyl halide.

(III) The tertiary alcohol on reaction with conc. HCl will produce the alkyl halide even in the absence of Anhydrous $ZnCl_2$. Hence The reaction (III) will produce alkyl halide.

The reaction is :

$$(CH_3)_3COH + HCl \longrightarrow (CH_3)_3CCl + H_2O$$

(IV) The reaction (IV) is Lucas test involving secondary alcohol. The product obtained will be alkyl halides.

The reaction is :

$$(CH_3)_2CHOH + HCl + \text{Anhydrous } ZnCl_2 \longrightarrow (CH_3)_2CHCl + H_2O$$

Reactions (I), (III) and (IV) produces alkyl halides.

Hence, option (d) is the correct answer.

The compound which reacts fastest with Lucas reagent at room temperature is:

a) Butan-1-ol

b) Butan-2-ol

c) 2-Methylpropan-1-ol

d) 2-Methylpropan-2-ol

Solution

The rate of reaction of alcohol with Lucas reagent is 3^{o} alcohol > 2^{o} alcohol > 1^{o} alcohol.

- Butan-1-ol is a primary alcohol
- Butan-2-ol is a secondary alcohol
- 2-Methylpropan-1-ol is a primary alcohol
- 2-Methylpropan-2-ol is a tertiary alcohol

Tertiary alcohol reacts with Lucas reagent fastest.

Hence, option (d) is the correct answer.

HBr reacts fastest with:

a) 2-Methylpropan-1-ol

b) Methylpropan-2-ol

c) Propan-2-ol

d) Propan-1-ol

Solution

The reaction will be fastest with the alcohol that forms the stable carbocation.

- 2-Methylpropan-1-ol forms primary carbocation
- Methylpropan-2-ol forms tertiary carbocation
- Propan-2-ol forms secondary carbocation
- Propan-1-ol forms primary carbocation

Tertiary carbocation is most stable among others mentioned here.

Hence, option (b) is the correct answer.

Preparation of Halo Compounds

Preparation of Aryl Halide

- Halogenation of arenes
- Via diazonium salts

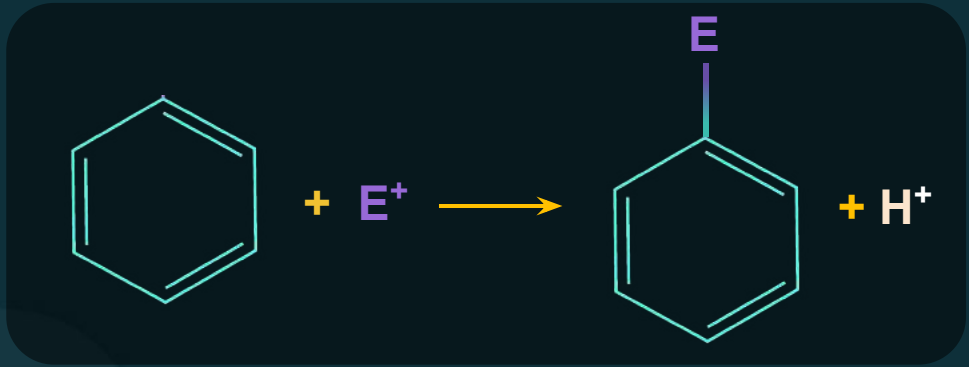
Halogenation of arenes

Chlorine and bromine in presence of Lewis acid (like $AlCl_3$, $FeCl_3$) react with benzene by **electrophilic substitution reaction.**

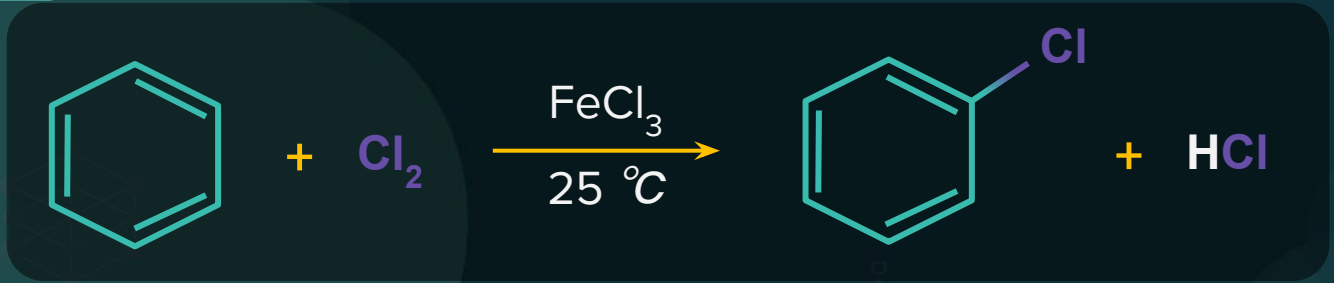
Preparation of Halo Compounds

Electrophilic substitution reaction (ESR)

General reaction



Example



Preparation of Halo Compounds

Reactivity of halogens in ESR

Electrophilicity

- F_2 → Fluorination is highly reactive
- Cl_2, Br_2
- I_2 → Iodination is very slow

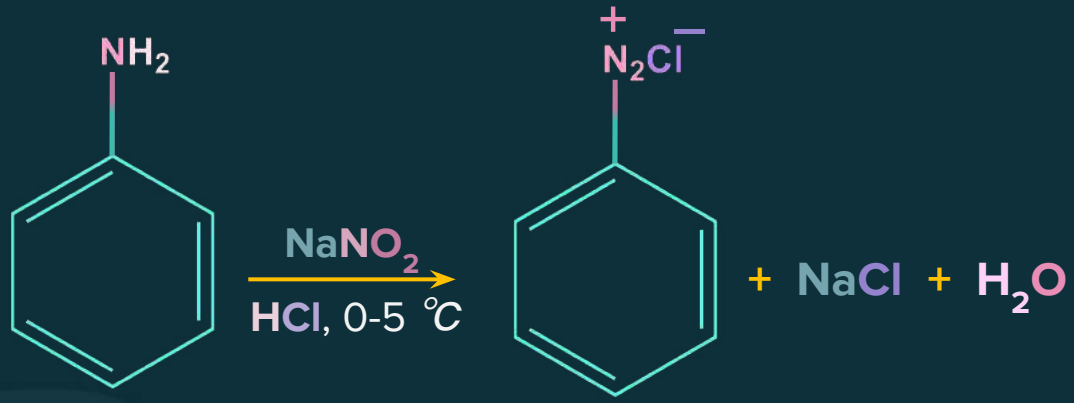
Via diazonium salts

Diazotisation reaction

Primary aromatic amines react with nitrous acid at low temperature (273-278 *K*) to give aromatic diazonium salts.

Preparation of Halo Compounds

Preparation of diazonium salt



Aniline

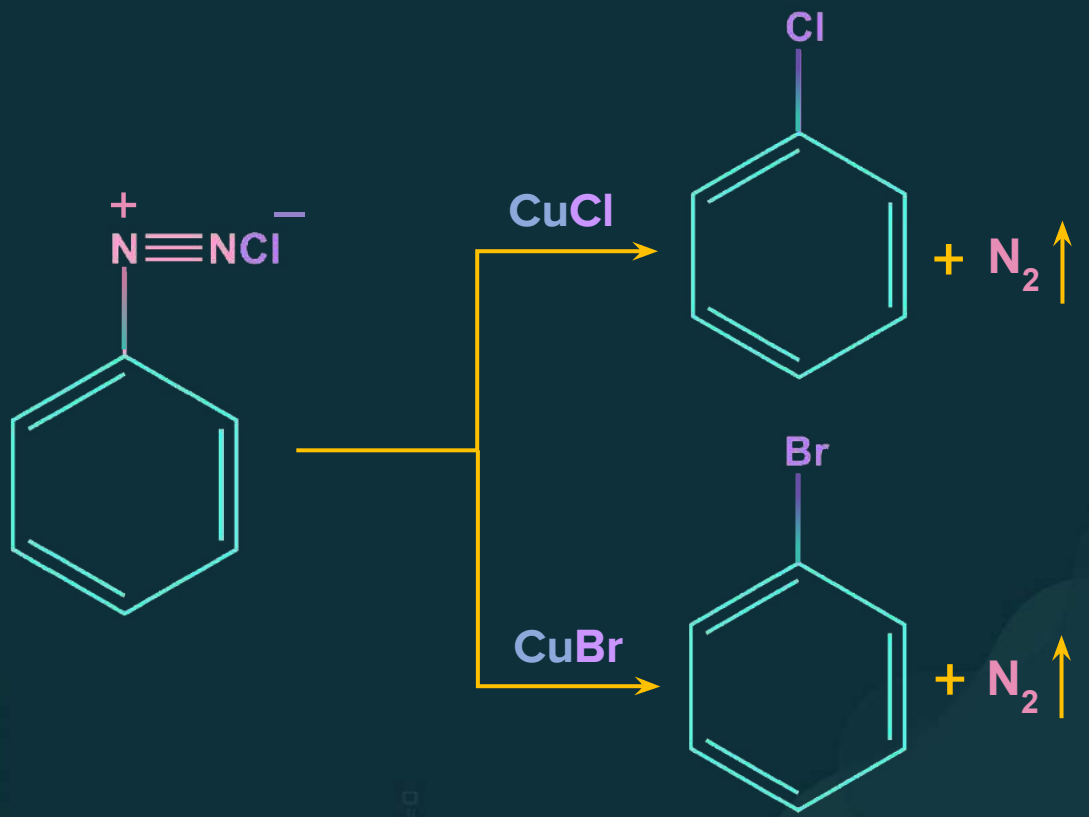
Benzene diazonium chloride

Here, primary aromatic amines react with nitrous acid at low temperature (273-278 *K*) to give aromatic diazonium salts. Treatment of diazonium salts with cuprous chloride or bromide leads to aryl chlorides or bromides, respectively.

Preparation of Halo Compounds

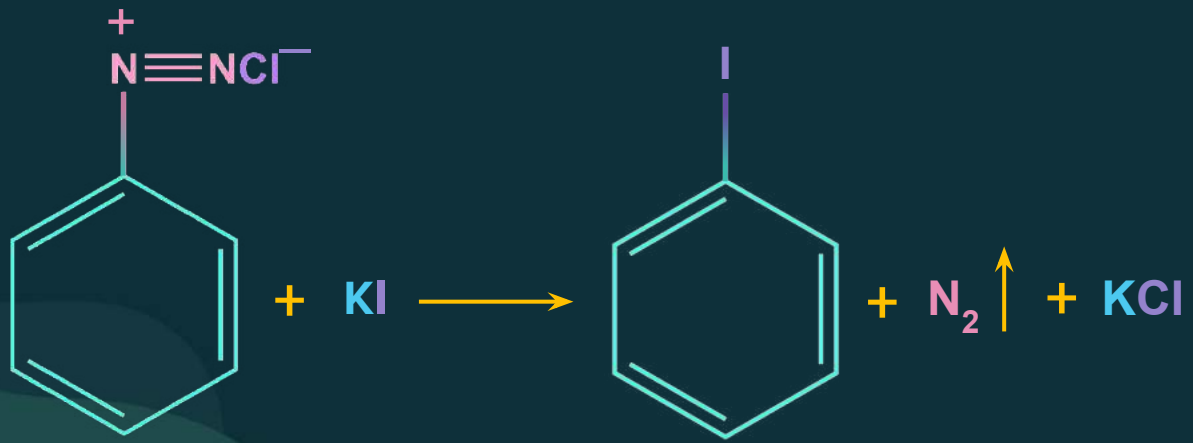
Sandmeyer Reaction

Treatment of **diazonium salts** with cuprous chloride or bromide leads to aryl chlorides or bromides, respectively.



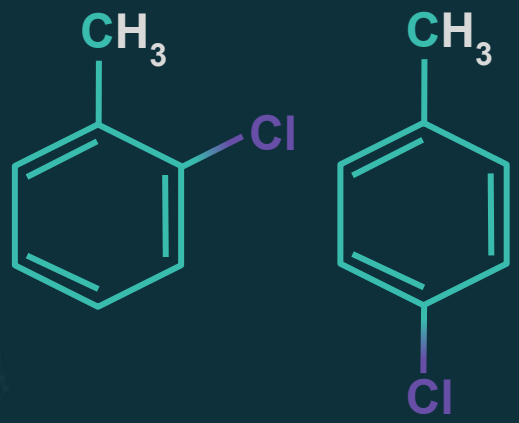
Preparation of Halo Compounds

Replacement of diazonium group with iodine does not require cuprous iodide. It **can be done with KI.**

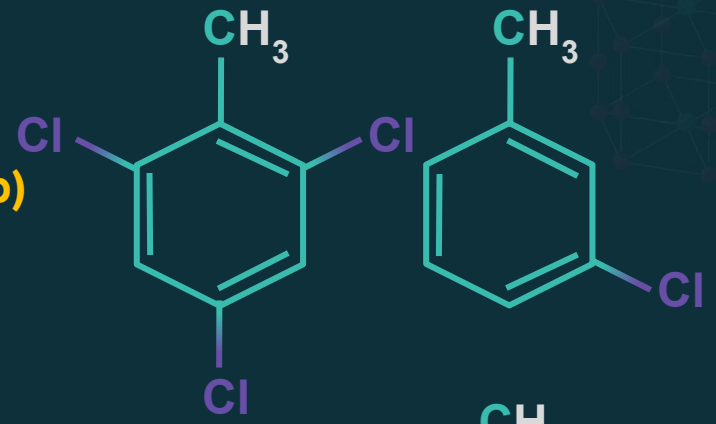


A compound ‘X’ with molecular formula C_7H_8 is treated with Cl_2 in presence of $FeCl_3$. Which of the following compounds are formed during the reaction?

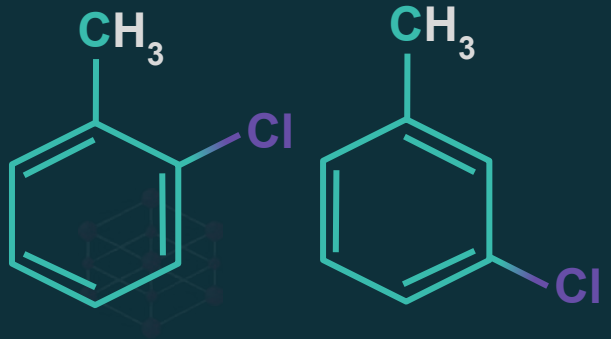
(a)



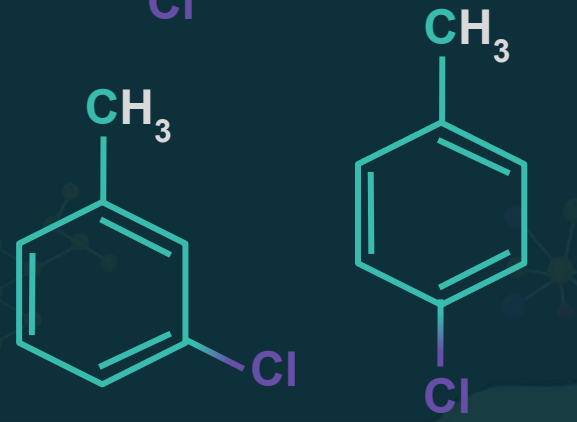
(b)



(c)



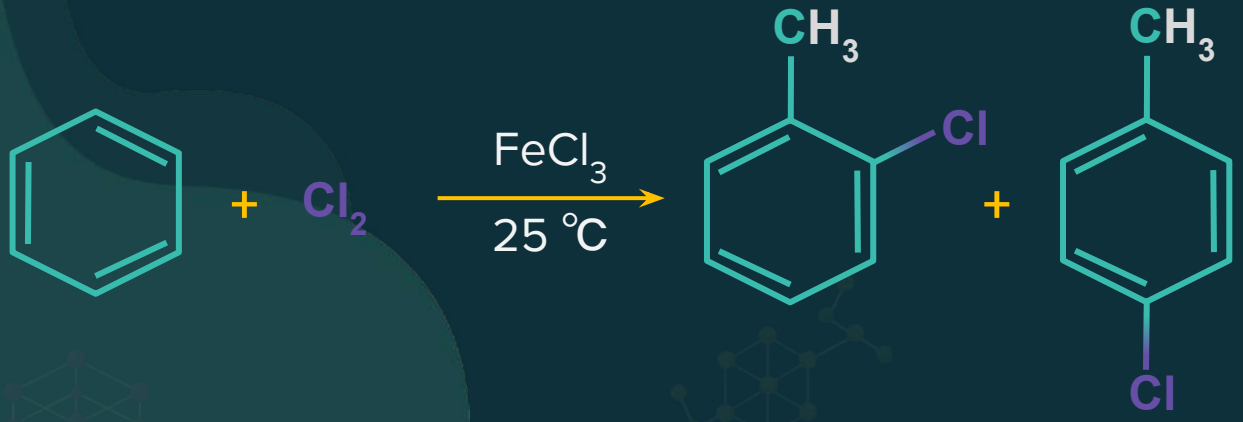
(d)



Solution

X (C_7H_8) should be toluene. In X, benzene has -CH_3 group attached to it, and CH_3 group is o,p-directing group.

Therefore, electrophilic substitution reaction will occur on ortho and para position.



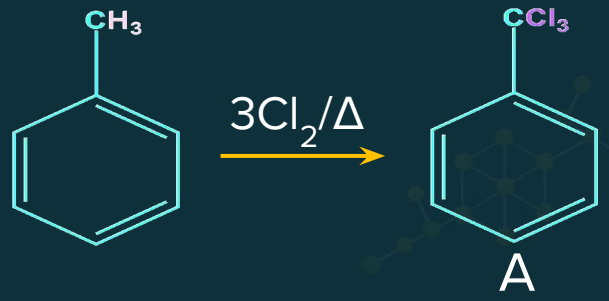
Hence, option (a) the correct answer.

A compound C_7H_8 undergoes the following reactions, the product 'A' and 'B' are:

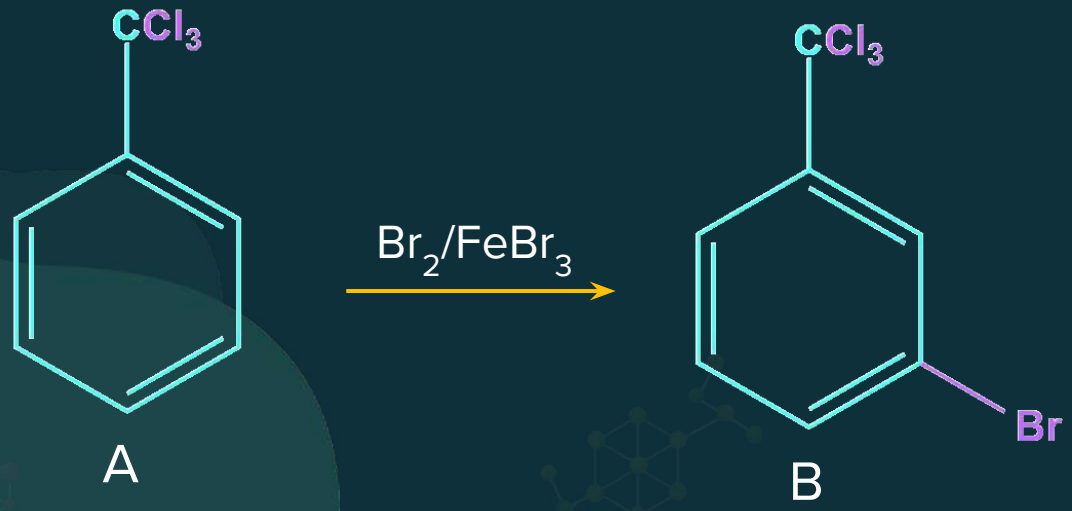
$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/FeBr_3} B$$

Solution

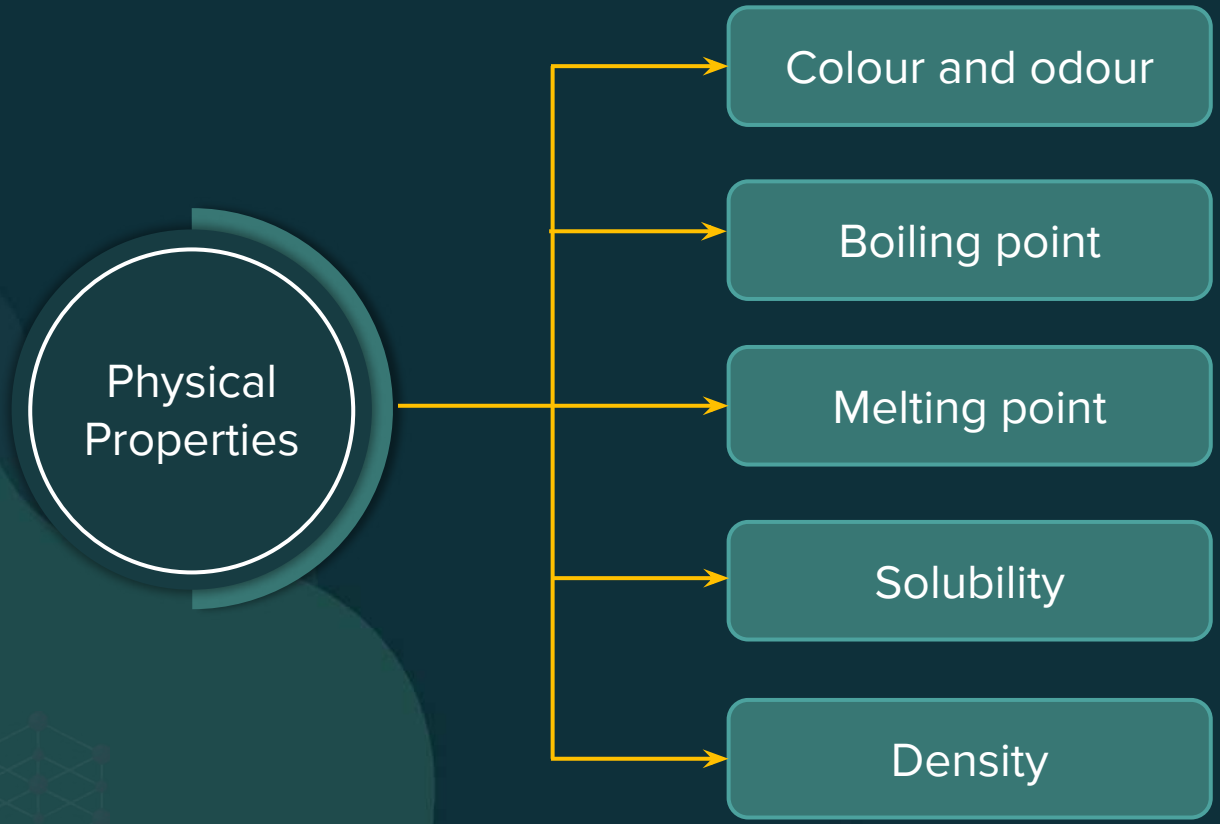
Step 1: Since the reaction is occuring in presence of heat then it must be via the free radical mechanism as the electrophilic substitution reaction does not occur in presence of heat and light. So, in presence of Cl_2, there will be a formation of **benzotrichloride (BTC)** which is the product 'A'.



Step 2: In compound A , the three Cl are showing -I effect, so this group will be meta directing in nature. Therefore, the Br atom will substitute the meta hydrogen and we get product ‘B’ which is **m-bromobenzotrichloride**.



Physical properties of Halo Compounds



Physical properties of Halo Compounds

Colour and odour

Generally, alkyl halides are **colourless** in their pure form.

But **bromides & iodides** develop colour when exposed to light.

Generally, volatile halogen compounds have a **sweet smell**.

Physical properties of Halo Compounds

Boiling point

Factors affecting Boiling Point of Haloalkanes

- Polarity and molar mass of the compound
- Branching of parent chain

Physical properties of Halo Compounds

Polarity and molar mass of the compound

Polarity of C—X bond

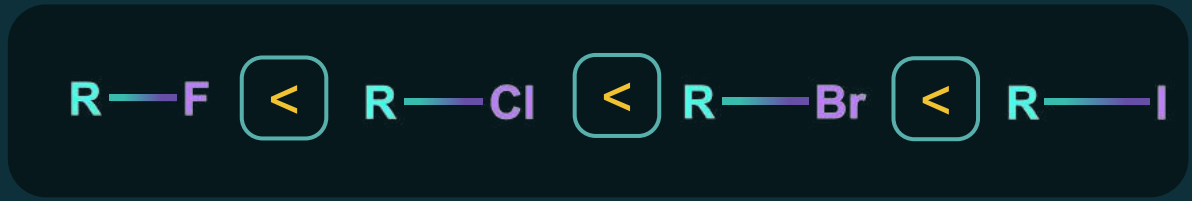
C—I < C—Br < C—F < C—Cl

Polarity depends upon both electronegativity difference and distance of bond as well. Thus experimentally:

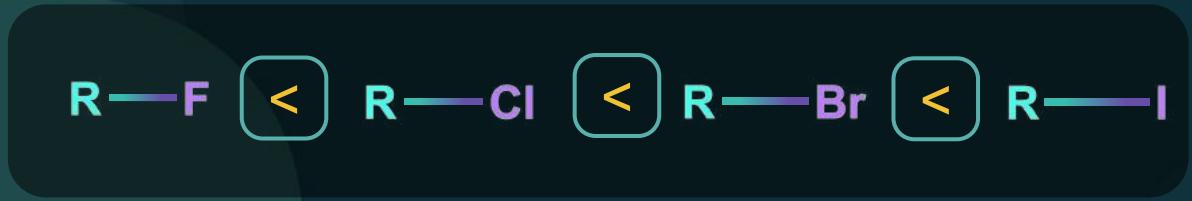
C—F < C—Cl

Physical properties of Halo Compounds

Order of **van der Waals forces**

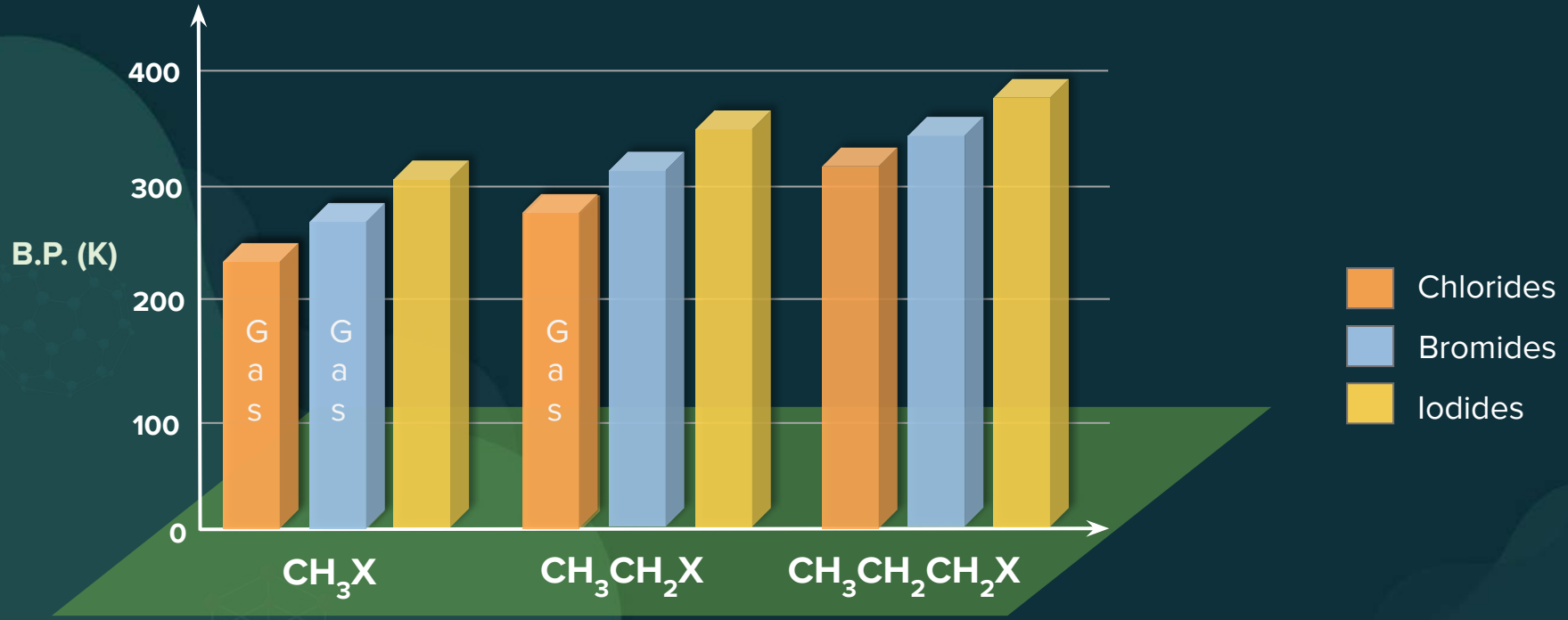


Order of **B.P.**



Physical properties of Halo Compounds

Let's understand the boiling points of alkyl halides with graphs.

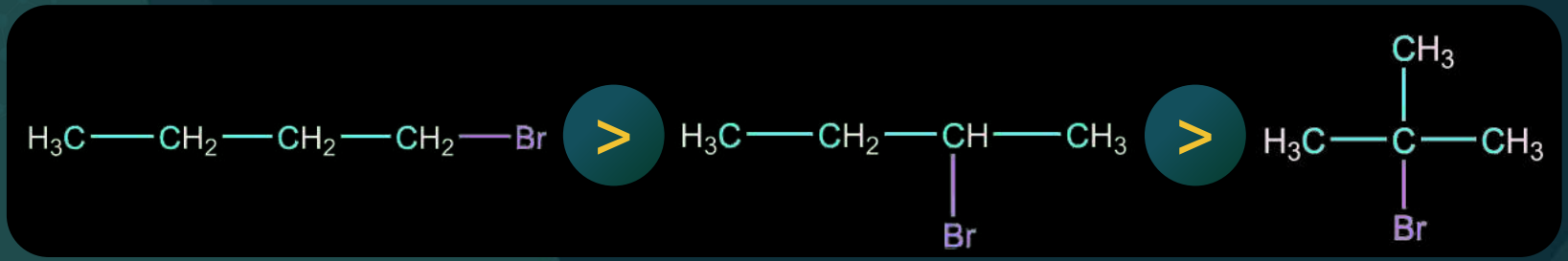


Compounds with **higher molar mass** have **higher boiling points**.

Physical properties of Halo Compounds

Branching of parent chain

$$\text{Boiling point} \propto \frac{1}{\text{Branching}}$$



B.P. (*K*):	375	364	346

Physical properties of Halo Compounds

Boiling points of haloalkanes vs hydrocarbon

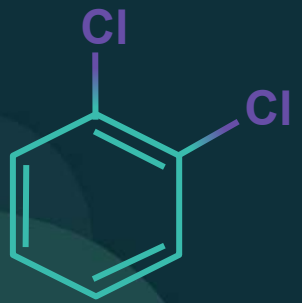
Haloalkanes have **greater polarity** and **higher molar mass** compared to parent hydrocarbon.

B.P. of haloalkanes is **greater** than their parent hydrocarbon due to

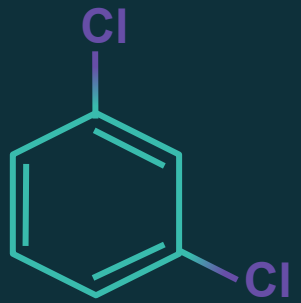
Strong intermolecular force of attraction (**Dipole–dipole** and **van der Waals** forces)

Physical properties of Halo Compounds

Boiling points of isomeric dihalobenzenes are **nearly the same.**



B.P.: 453 *K*



B.P.: 446 *K*

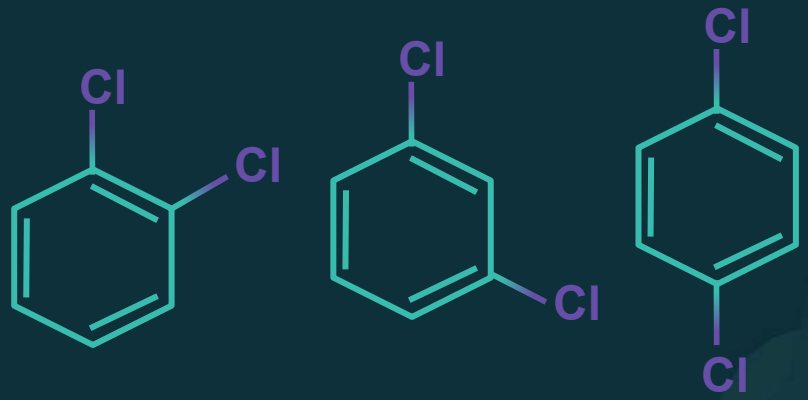
B.P.: 448 *K*

Physical properties of Halo Compounds

Melting point

Molecules with **better packing** have **higher** melting point.

Para-isomers have **high M.P.** as compared to their ortho and meta-isomers.



M.P.: 256 *K*

M.P.: 249 *K*

M.P.: 323 *K*

Physical properties of Halo Compounds

Solubility

Solubility of haloalkanes in water

Energy required to overcome **attractions between haloalkane molecules** + Energy required to **break H-bonds between H_2O** molecules
is **greater** than
Energy released when new bonds are setup **between haloalkane and H_2O** molecules

Hence, solubility of haloalkanes in water is **low.**

Physical properties of Halo Compounds

Solubility of haloalkanes in organic solvents

Energy required to overcome **attractions between haloalkane molecules** +
Energy required to overcome interactions between **organic solvent**
is **nearly same** as
Energy released when new bonds are setup **between haloalkanes & organic solvent**

Hence, haloalkanes are
soluble in organic solvents.

Physical properties of Halo Compounds

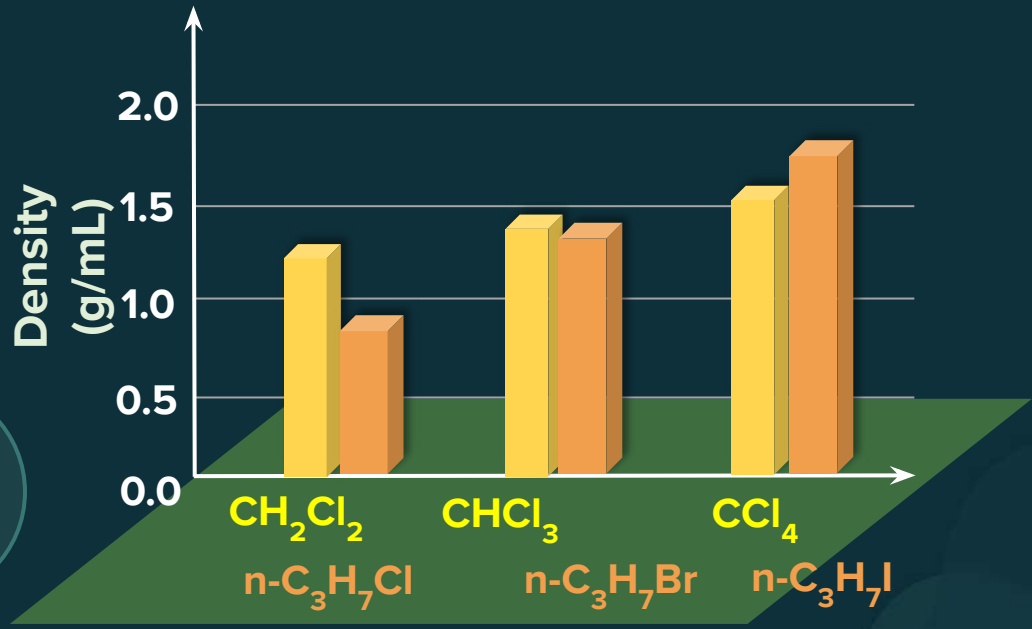
Density

Bromo, iodo, & polychloro derivatives of hydrocarbons are **heavier** than water.

Number of carbon/halogen atoms & atomic mass of the halogen atoms ↑

↓

Density ↑



The correct statement is:

(a) Molecules with better packing have lower melting point.

(b) Haloalkanes are insoluble in organic solvents.

(c) As branching of parent chain increases, boiling point decreases.

(d) All of these

Solution

- Option (a) is incorrect as better packing molecules have more melting point.
- Option (b) is incorrect as haloalkanes are soluble in organic solvents.
- Option (c) is correct as boiling point decreases as the branching of parent chain increases due to decrease in surface area.

Hence, option (c) is the correct answer.

Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reactions?

(a) Birch reduction

(b) Friedel-Crafts

(c) Sandmeyer

(d) Wurtz

Solution

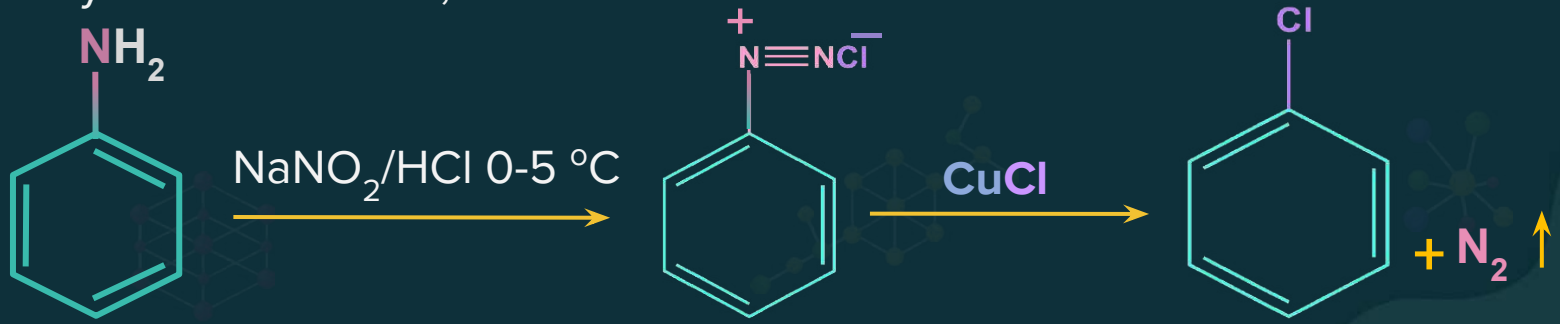
Conversion of benzene diazonium chloride to chlorobenzene is an example of Sandmeyer's reaction.

Hence, option (c) is the correct answer.

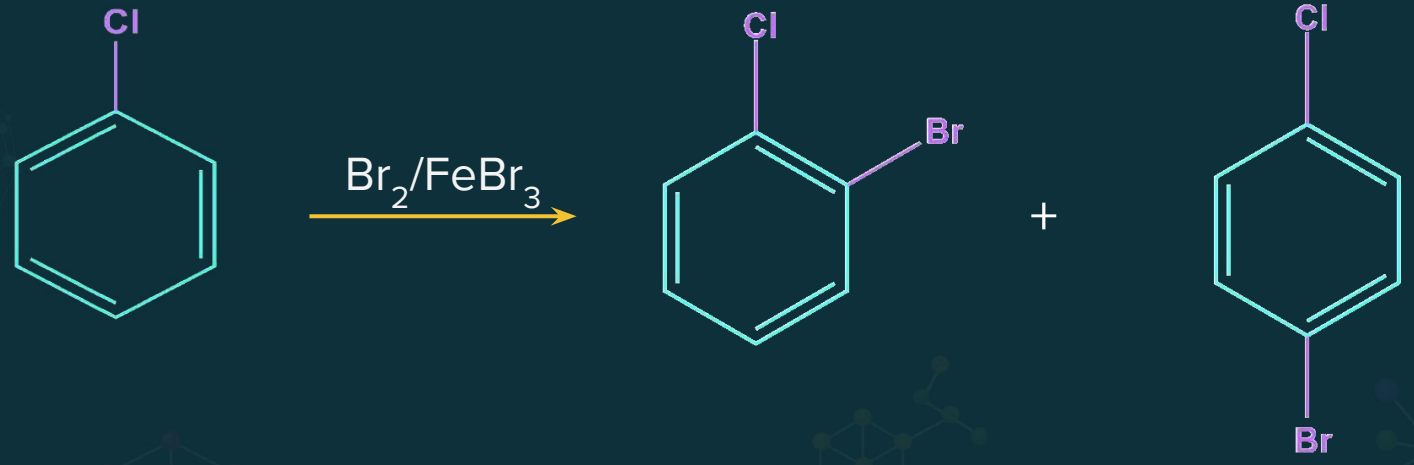
The products are:

Solution

The first step is diazotization which forms chlorobenzene. This reaction is known as Sandmeyer's reaction. So, A will be **chlorobenzene**.



The second step is bromination. As chlorine is a deactivating group, but it directs ortho and para products. Therefore, B and C are **1-bromo-2-chlorobenzene** and **1-bromo-4-chlorobenzene**.



(B) (C)

Which of the following is involved in Sandmeyer's reaction?

(a) Ferrous salt

(b) Diazonium salt

(c) Ammonium salt

(d) Cuprammonium salt

Solution

Treatment of diazonium salts with cuprous chloride or bromide leads to aryl chlorides or bromides, respectively. This reaction is known as Sandmeyer's reaction. So, diazonium salt is involved in Sandmeyer's reaction.

Hence, option (b) is the correct answer.

Which of the following compounds has the highest boiling point?

(a) $CH_3CH_2CH_2Cl$

(b) $CH_3CH_2CH_2CH_2Cl$

(c) $CH_3CH(CH_3)CH_2Cl$

(d) $(CH_3)_3CCl$

Solution

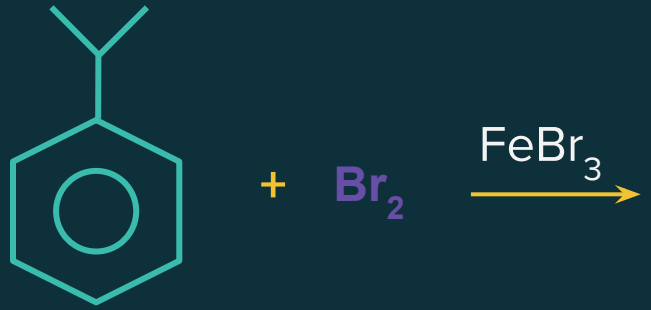
Higher the molar mass and lesser the branching, higher will be the boiling point.

Option (a) has less boiling point as it has three carbon atoms whereas others have four carbon atoms.

Option (b) has highest boiling point as it contains more number of carbon atoms and less branching when compared to others.

Hence, option (b) is the correct answer.

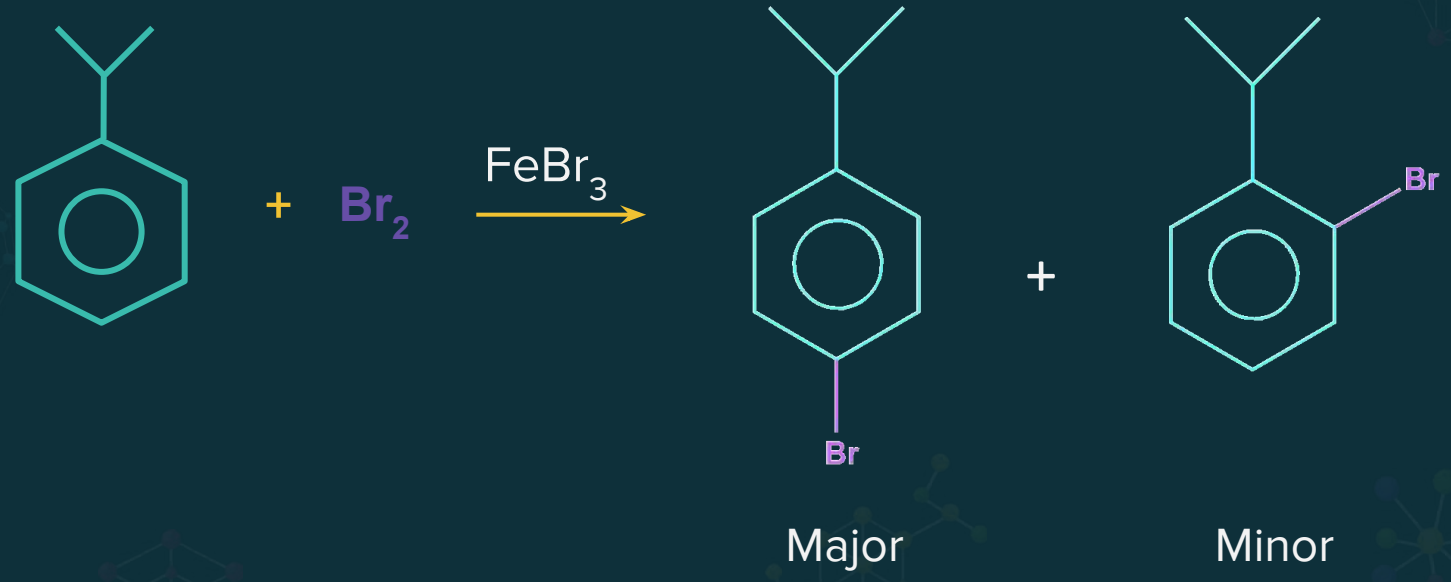
The product(s) of the following reaction is/are _____.



Solution

- This reaction is electrophilic aromatic substitution.
- Isopropyl group is ortho-para directing group, which is activating group.

- As Isopropyl group is bulky group, it will form para as major product and ortho as minor product.



Arene diazonium salt results from reaction of nitrous acid with:

(a) 1° Aliphatic amine

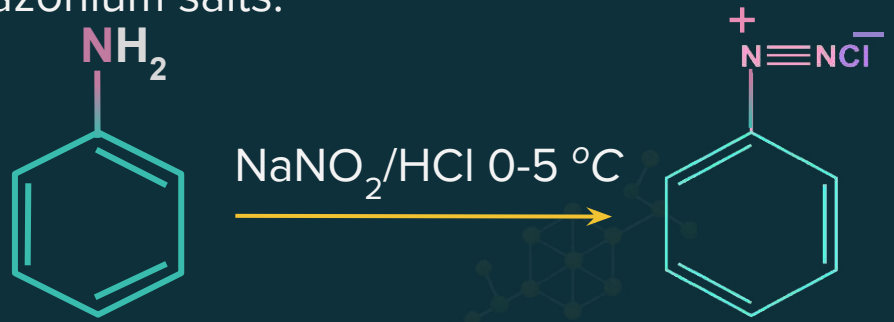
(b) 2° Aromatic amine

(c) 1° Aromatic amine

(d) 1° Aromatic amide

Solution

Primary (1°) aromatic amines react with nitrous acid at low temperature (273-278 *K*) to give aromatic diazonium salts.



Hence, option (c) is the correct answer.

Arrange each set of compounds in increasing order of their boiling points.

Chloromethane ? Bromomethane ? Dibromomethane ? Bromoform

Solution

Higher the molar mass, higher will be the boiling point.

- Since bromoform ($CHBr_3$) has 3 bromines attached to it, it's molar mass will be maximum and hence it will have maximum boiling point.
- Chloromethane has one chlorine attached to it which has less molar mass than bromine. So, it will have lowest boiling point. The order of boiling points will be:

Chloromethane < Bromomethane < Dibromomethane < Bromoform

Arrange each set of compounds in increasing order of their boiling points.

Isopropylchloride ? 1-Chloropropane ? 1-Chlorobutane

Solution

Higher the molar mass and lesser the branching, higher will be the boiling point.

Isopropyl chloride has lowest boiling point due to more branching and 1-chlorobutane has maximum boiling point due to more number of carbon atoms.

Thus, the order of B.P. will be **isopropylchloride < 1-chloropropane < 1-chlorobutane.**

Arrange each set of compounds in the order of their boiling points.

Fluoroethane ? Chloroethane ? Bromoethane ? Iodoethane

Solution

Higher the molar mass, higher will be the boiling point.

The order of molar mass of halogens is F < Cl < Br < I.

Therefore, the order of boiling point will be **fluoroethane < chloroethane < bromoethane < iodoethane**.

Which of the following statements is/are correct?

(a) Boiling points of isomeric dihalobenzenes are almost the same.

(b) Melting point of para isomer of dichlorobenzene is more than that of ortho and meta isomers.

(c) Haloalkanes are soluble in organic solvents.

(d) All of these

Solution

a) Boiling points of isomeric dihalobenzenes are almost the same. So, option (a) is correct.

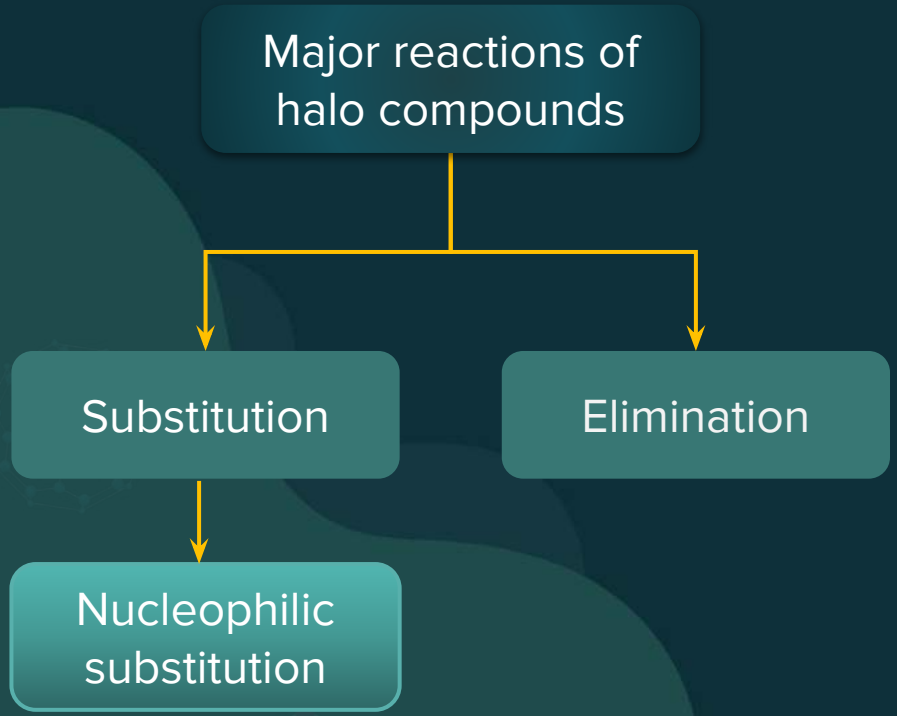
b) Melting point of para isomer of dichlorobenzene is more than that of ortho and meta isomers due to better packing. So, option (b) is correct.

c) Haloalkanes are soluble in organic solvents. So, option (c) is correct.

d) All the statements are correct.

Hence, option (d) is the correct answer.

Chemical properties of Halo Compounds



Nucleophilic substitution reaction

Replacement of an atom or group **by any other atom or group** in a molecule is known as **substitution reaction**.

If substitution reaction is brought about by a **nucleophile,** then it is known as **nucleophilic substitution reaction**.

Chemical properties of Halo Compounds

Generally, substitution takes place at **sp^3 carbon.**

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

Ig Leaving group

Nu Nucleophile

1. Nucleophile

Electron rich species having **at least one unshared** pair of electron.

- Neutral or negatively charged
- Always a lewis base

Example CN^-, OH^-, Br^-, I^-, NH_3, H_2O etc.

Chemical properties of Halo Compounds

Ambident Nucleophiles

Some nucleophiles have a pair of electrons on each of **two or more atoms**, or canonical forms can be drawn in which two or more atoms bear an unshared pair of electrons.

Nucleophiles which have **two attacking sites,** one **negatively charged** and **one neutral** site, are known as ambident nucleophiles.

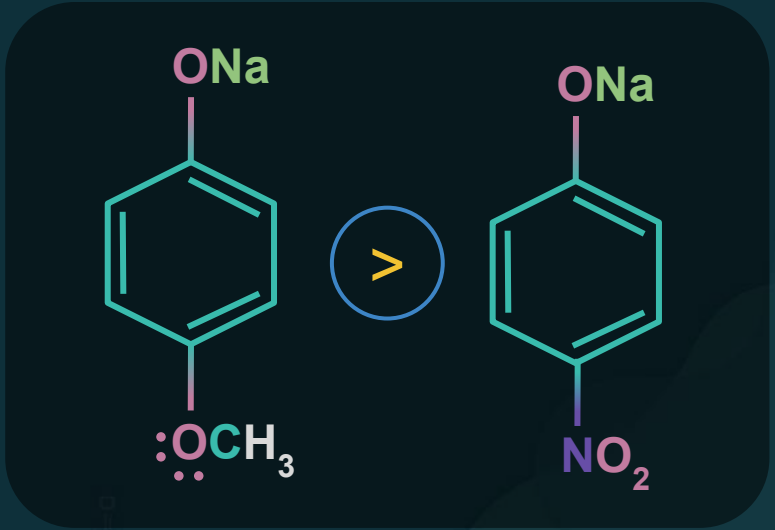
Chemical properties of Halo Compounds

Nucleophilicity

Tendency to **give electron pair** to an electron deficient atom.

Criteria for Nucleophilicity

01 Factors that **increase electron density** at donor atom, increases nucleophilicity.



Chemical properties of Halo Compounds

02 The **more polarisable** donor atom is the **better nucleophile**.

Size of donor atom ↑ → Nucleophilicity ↑

SH^- > OH^-

03 **Periodicity**

Along the period → Nucleophilicity ↓

CH_3^- > NH_2^- > OH^- > F^-

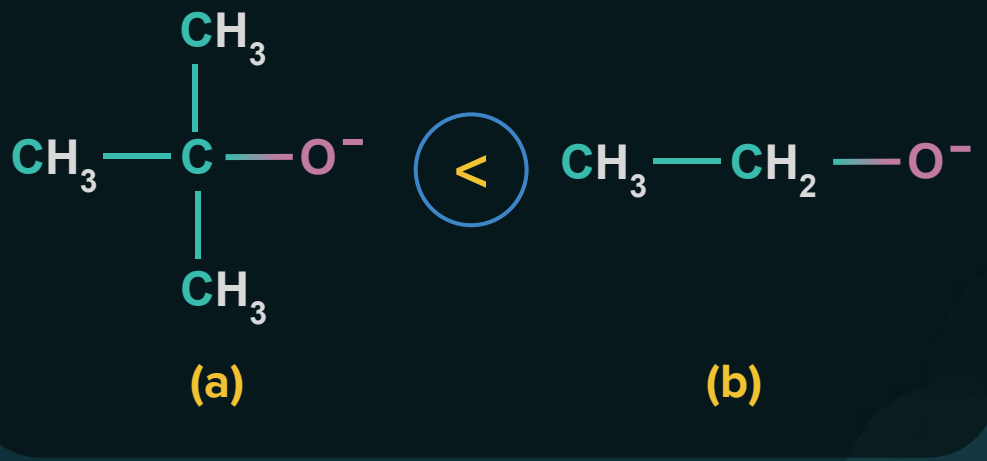
Chemical properties of Halo Compounds

04 Polar protic solvent

Down the group → Nucleophilicity ↑

$F^- < Cl^- < Br^- < I^-$

05 Steric effect on nucleophilicity



Nucleophile (a) **cannot approach electrophile easily.**

Chemical properties of Halo Compounds

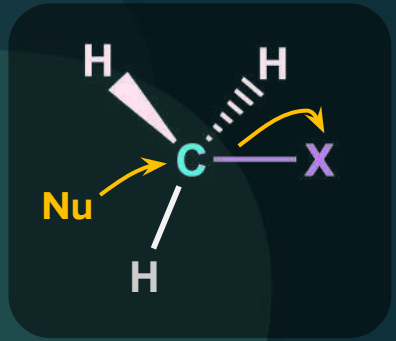
Nucleophilicity & Basicity

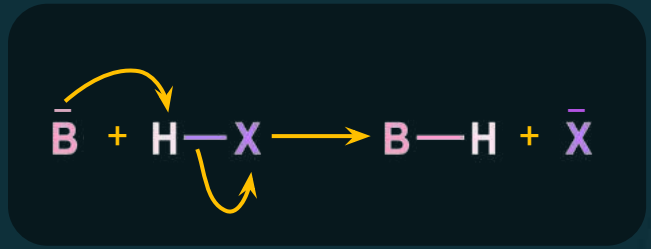
Nucleophilicity

Measure of how readily a species is able to **attack** an electron-deficient atom.

Basicity

Measure of how well a species **abstracts** a proton.





The most reactive nucleophile among the following is:

(a) CH_3O^-

(b) $C_6H_5O^-$

(c) $(CH_3)_2CHO^-$

(d) $(CH_3)_3CO^-$

Solution

- As the steric hindrance or bulkiness increases, the reactivity decreases.
- The order of nucleophilicity is : (a) > (c) > (d) > (b).

It is due to the participation of a lone pair of O atoms with benzene ring in the +M effect.

Hence, option (a) is the correct answer.

Which of the following is ambident nucleophile?

(a) NO_2^-

(b) OH^-

(c) Cl^-

(d) None of these

Solution

NO_2^- is an ambident nucleophiles as it can donate its lone pair from both nitrogen and oxygen.

Hence, option (a) is the correct answer.

Chemical properties of Halo Compounds

2. Leaving Group

In a reaction in which the substrate molecule becomes **cleaved**, smaller part of it is usually called the leaving group.

Generally, **leaving group** carries away an electron pair.

Weaker bases are good leaving groups.

Chemical properties of Halo Compounds

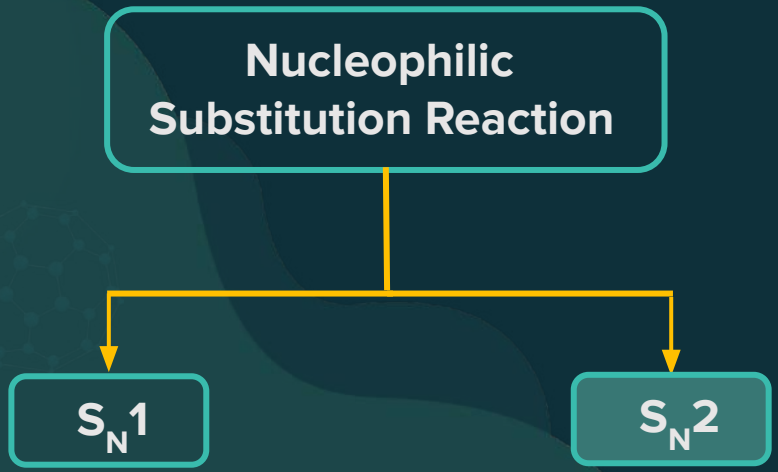
Examples

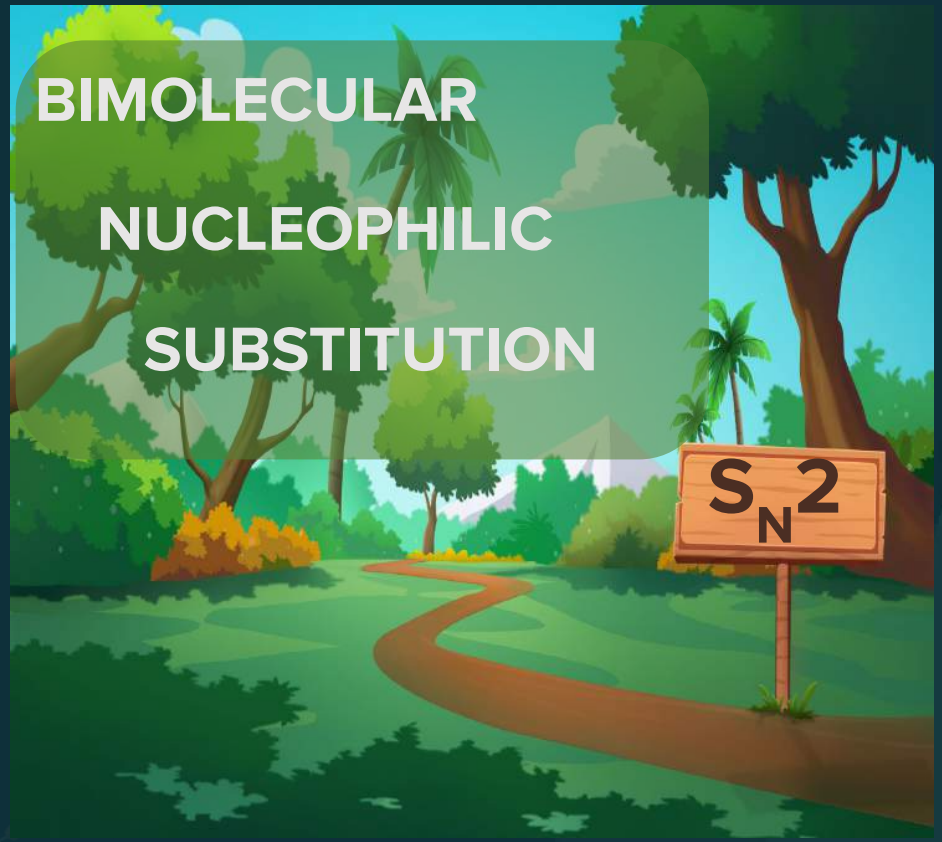
$F^- < Cl^- < Br^- < I^-$ — Bigger size, better lg.

$CH_3^- < NH_2^- < OH^- < F^-$ — Better stability of anion, better lg.

$R\text{-}COO^- > PhO^- > HO^- > RO^-$ — More stable by resonance, better lg.

Nucleophilic Substitution Reaction

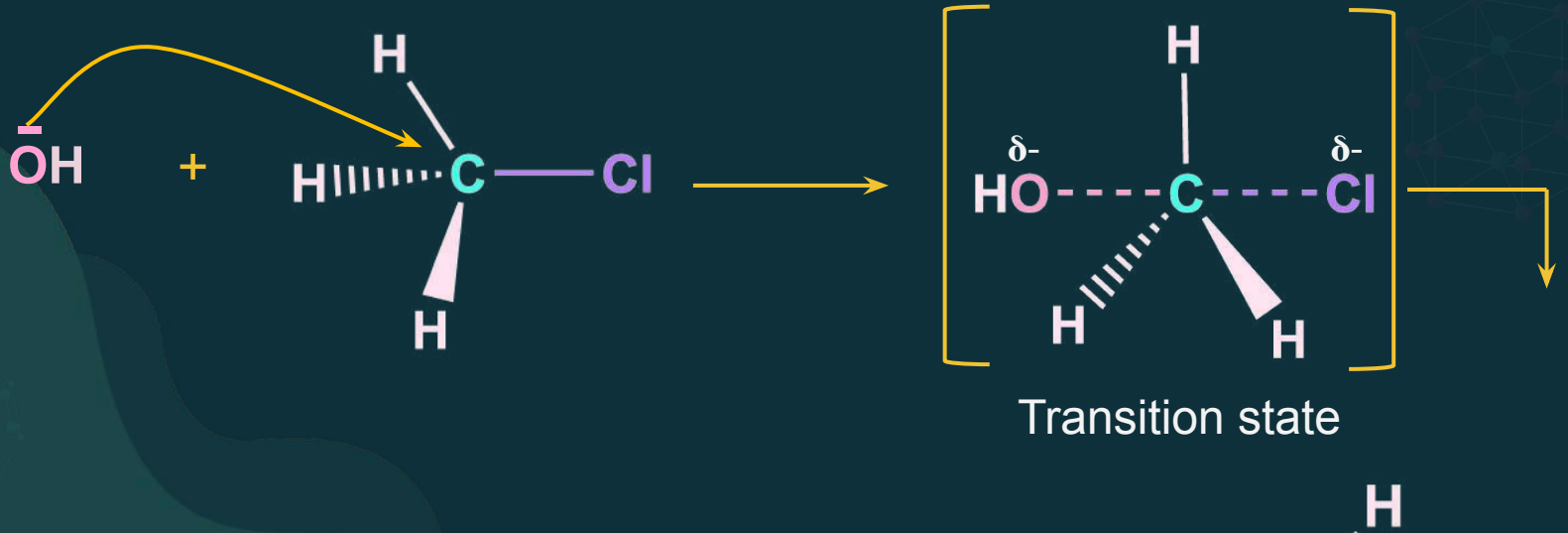




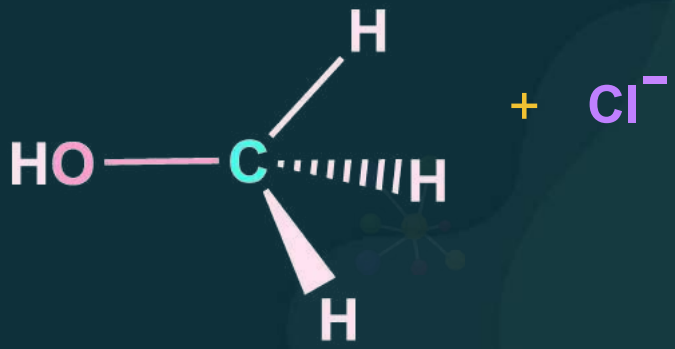
Substitution Nucleophilic Bimolecular

S_N2 reaction occurs in one step.

Mechanism of S_N2 Reaction

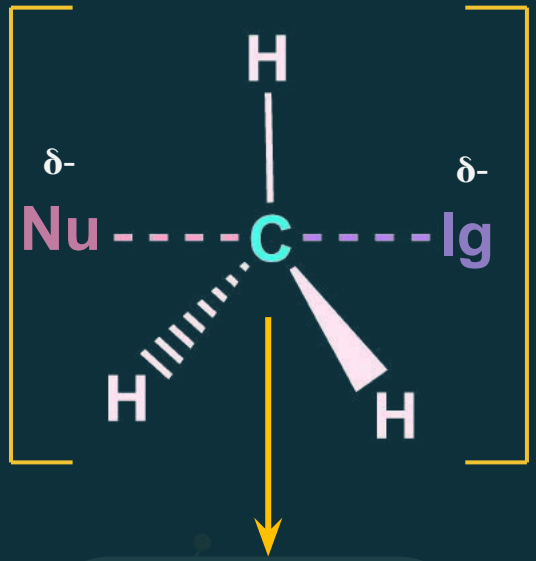


Transition state



Mechanism of S_N2 Reaction

In the **transition state**, a bond between nucleophile and carbon is **partially formed** and the bond between carbon and leaving group is **partially broken**.



Cannot be isolated

Pentavalent T.S. → Unstable

Stereochemistry of S_N2 Reaction

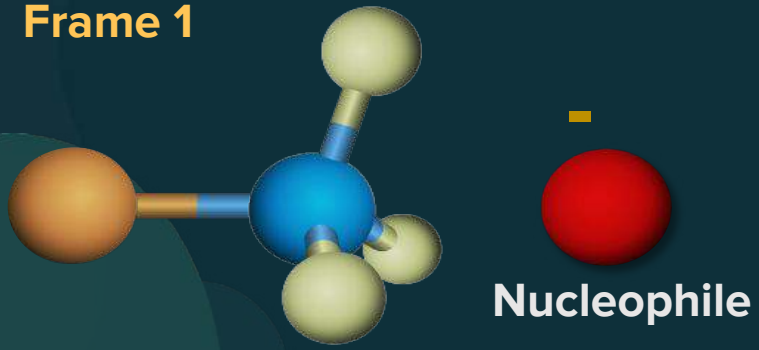
In an S_N2 mechanism, the nucleophile attacks from the **back side**, that is from the side exactly opposite to the leaving group.

This causes an **inversion of configuration** at the chiral carbon atom.

Also known as **Walden inversion.**

Stereochemistry of S_N2 Reaction

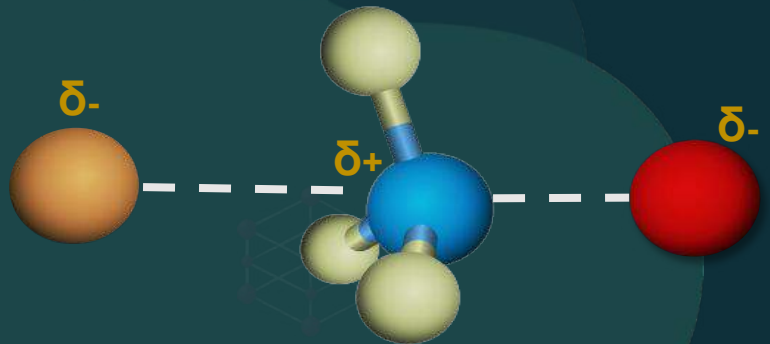
Frame 1



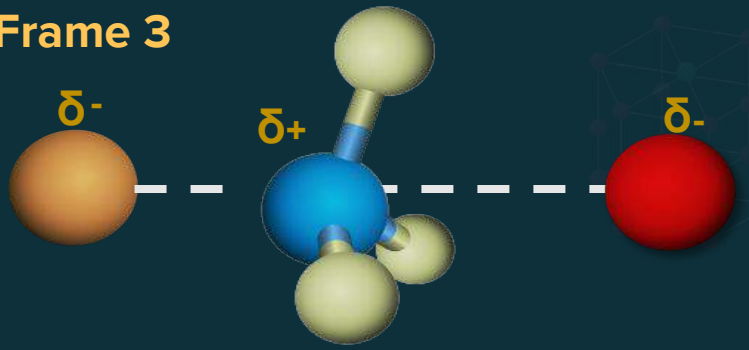
Haloalkane

Nucleophile

Frame 2



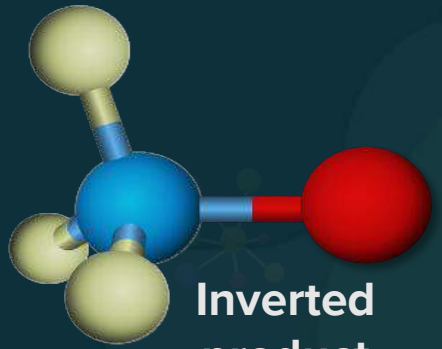
Frame 3



Transition state

Frame 4

Leaving group



Inverted product

Characteristics of S_N2 Reaction

01 It is **bimolecular**, **one step** process.

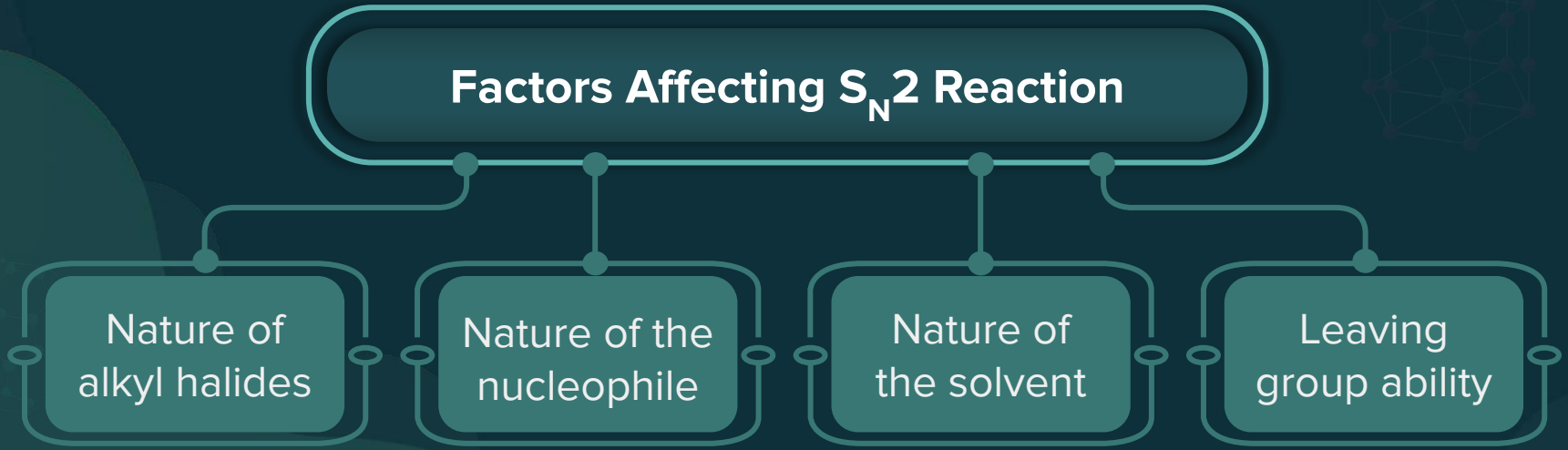
02 **Rate of S_N2** reaction depends on **concentration** of both alkyl halide & nucleophile

$$\text{Rate} \propto [\text{Alkyl halide}][\text{Nucleophile}]$$

01 **S_N2** reaction gives stereochemically inverted product

03 **S_N2** reaction proceeds via one transition state and no intermediate is observed.

Factors Affecting S_N2 Reaction



Factors Affecting S_N2 Reaction

Nature of alkyl halide

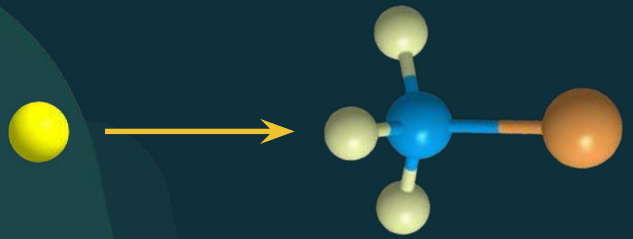
The important reason behind this order of reactivity is **steric effect**.

Very **large and bulky groups** can often **hinder** the formation of the required transition state. The crowding **raises the energy** of the transition state and **slows down the rate** of reaction.

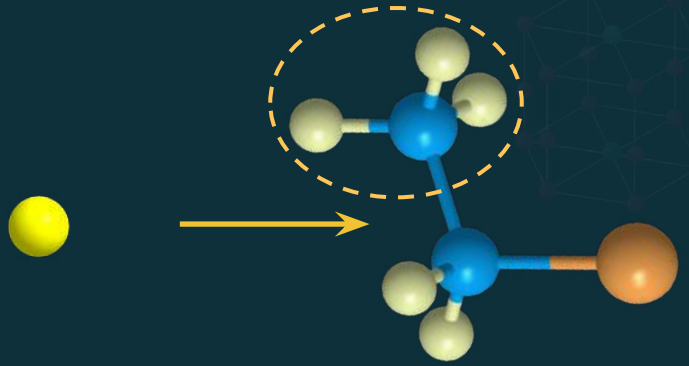
S_N2 reactivity

$CH_3—X$ > **1°** Alkyl halide > **2°** Alkyl halide > **3°** Alkyl halide

Factors Affecting S_N2 Reaction

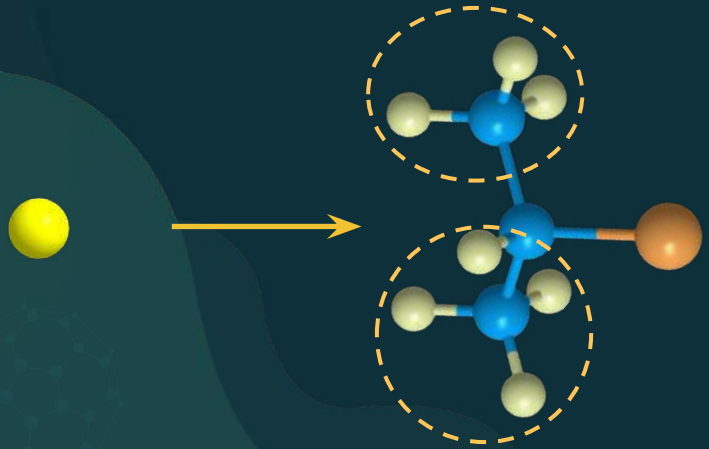


Nucleophile approaching methyl alkyl halide

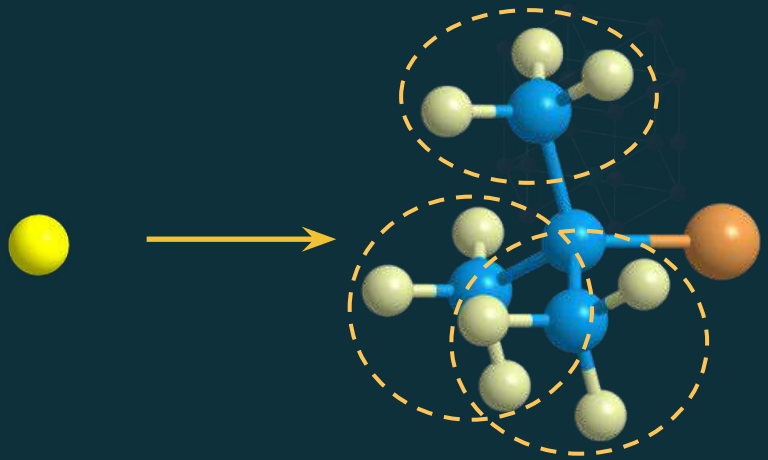


Nucleophile approaching to 1° alkyl halide

Factors Affecting S_N2 Reaction



Nucleophile approaching 2°
Alkyl halide



Nucleophile approaching 3°
Alkyl halide

Factors Affecting S_N2 Reaction

Substituent	Compound	Relative rate
Methyl	CH_3X	30
1°	CH_3CH_2X	1
2°	$(CH_3)_2CHX$	0.02
3°	$(CH_3)_3CX$	∞0

Factors Affecting S_N2 Reaction

Nature of nucleophile

Concentration of nucleophile ↑ → Rate of S_N2 ↑

Nucleophilicity ↑ → Rate of S_N2 ↑

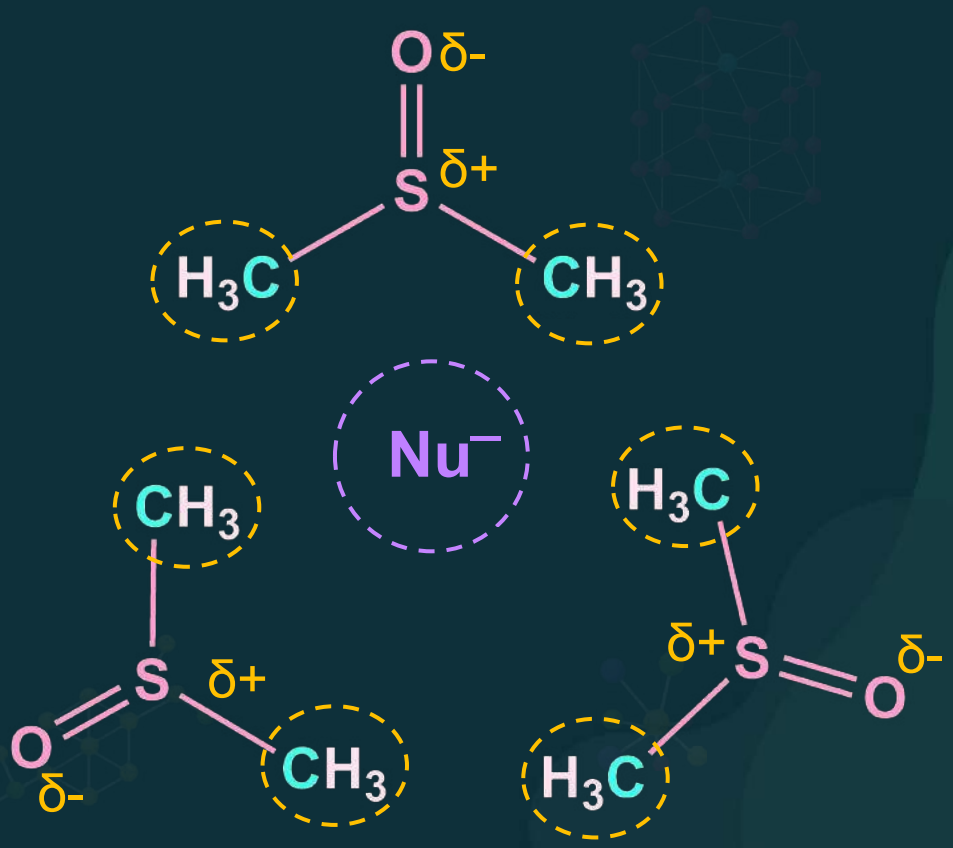
Anionic nucleophiles mostly give **S_N2** reaction

Factors Affecting S_N2 Reaction

Nature of solvent

Polar aprotic solvents have crowded **positive centre**, so they do not solvate the anion appreciably.

Hence, the rate of S_N2 reactions **increases** when they are carried out in polar aprotic solvent.



Factors Affecting S_N2 Reaction

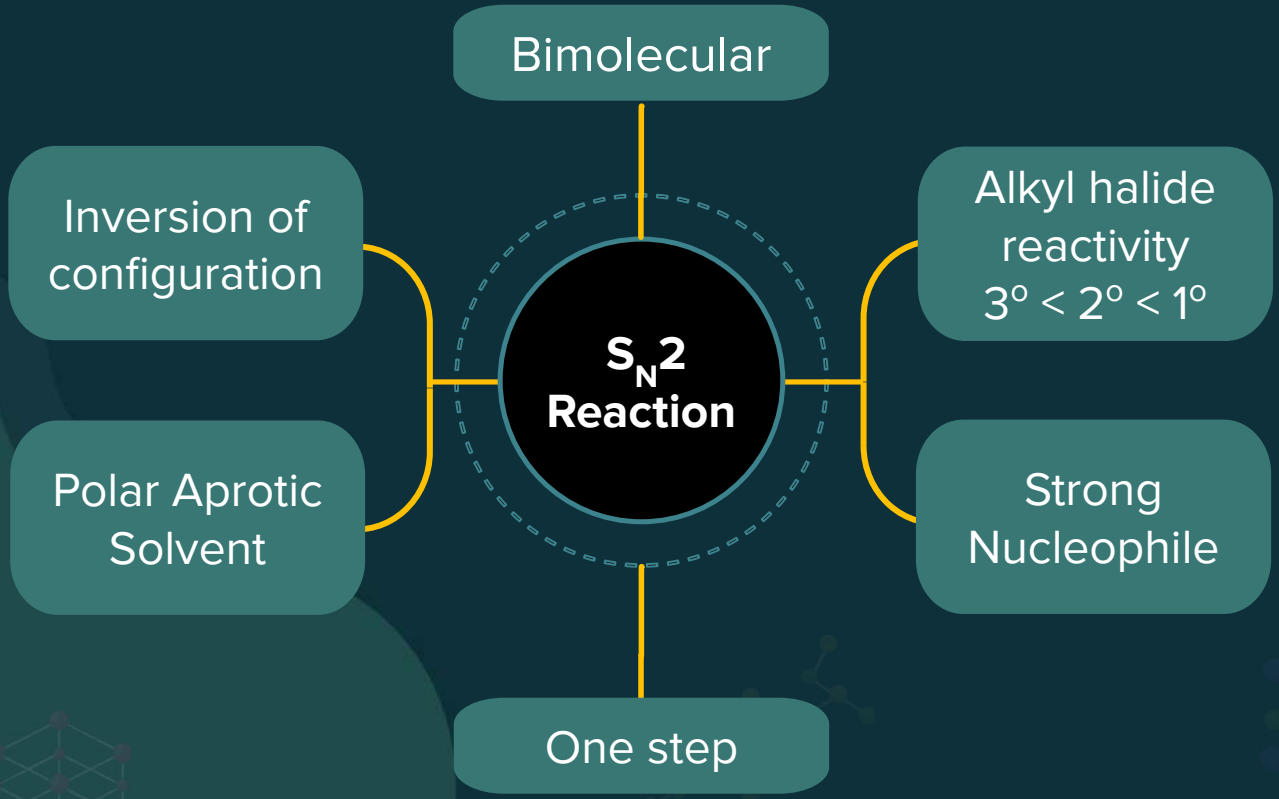
Leaving group ability

A good leaving group **stabilises the transition state** and thereby increases the rate of the reaction.

Relative reactivities of alkyl halides:

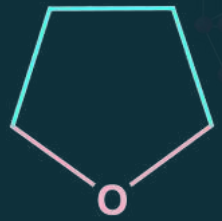
RF < RCl < RBr < RI

Quick Recap of S_N2 Reaction



Which of the following can be used as a solvent in S_N2 reaction?

(a) Acetic acid **(b)** Ethanol **(c)** Ammonia **(d)**



Solution

Polar aprotic solvent increases the rate of S_N2 reaction.
Solvents mentioned in a), b) and c) are polar protic solvent and d) is polar aprotic solvent, so solvent-(d) can be used as solvent in S_N2 reaction.

Hence, option (d) is the correct answer.

Arrange the compounds in order of reactivity towards S_N2 reaction.
1-Bromo-3-methylbutane, 2-Bromo-3-methylbutane and 2-Bromo-2-methylbutane.

Solution

1-Bromo-3-methylbutane : $CH_3CH(CH_3)CH_2CH_2(Br)$ is primary in nature.
2-Bromo-3-methylbutane : $CH_3CH(CH_3)CH(Br)CH_3$ is secondary in nature.
2-Bromo-2-methylbutane : $CH_3CH_2C(CH_3)(Br)CH_3$ is tertiary in nature.

The order of reactivity towards S_N2 reaction of Alkyl halide: $1^0 > 2^0 > 3^0$

Hence, correct order is given as follows:
1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane.

Which of the following is the correct order of decreasing S_N2 reactivity?

(a) $RCH_2X > R_3CX > R_2CHX$

(b) $RCH_2X > R_2CHX > R_3CX$

(c) $R_3CX > R_2CHX > RCH_2X$

(d) $R_2CHX > R_3CX > RCH_2X$

Solution

The order of reactivity towards S_N2 reaction of alkyl halide is $1^0 > 2^0 > 3^0$.

Hence, option (b) is the correct answer.

The major products A and B of the following reactions are:

$$RX + KCN \longrightarrow A$$

$$RX + AgCN \longrightarrow B$$

Solution

$KCN \longrightarrow K^+ + CN^-$

$RX + CN^- \longrightarrow RCN + X^-$

The KCN will dissociate as K^+ and CN^-; So CN^- will attack the R group as it has a partial positive charge because of the electronegative nature of halogen so we get RCN and X^-.

$AgCN + RX \longrightarrow RNC + X^-$

In case of AgCN, there is covalent bond between Ag and C, this CN^- is no longer available for attack on alkyl group.

So lone pair of nitrogen will attack, although the nucleophilicity of nitrogen is poor in comparison to carbon as the former is more electronegative in nature. The attack from lone pair of nitrogen on alkyl group will generate the alkyl isocyanide.

Hence, A is RCN (alkyl cyanide) , B is RNC (alkyl isocyanide).

The major products A and B of the following reactions are:

$$RX + KNO_2 \longrightarrow A$$

$$RX + AgNO_2 \longrightarrow B$$

Solution

The KNO_2 will dissociate as K^+ and ONO^-; So, ONO^-, the oxygen which is having a negative charge will attack the R group as it has a partial positive charge because of the electronegative nature of halogen so we get RONO and X^-.

$$KNO_2 \longrightarrow K^+ + ONO^-$$
$$RX + ONO^- \longrightarrow RONO + X^-$$

In case of $AgNO_2$, there is covalent bond between Ag and N, this ONO^- is no longer available for attack on alkyl group..

So lone pair of nitrogen will attack.

The attack from lone pair of nitrogen on alkyl group will generate the nitro alkane.

$$AgNO_2 + RX \longrightarrow RNO_2 + X^-$$

Hence, A is RONO (Alkyl nitrite) , B is RNO_2 (Nitro Alkane).

Consider the reaction,

$$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$$

This reaction will be the fastest in:

(a) Ethanol

(b) Methanol

(c) *N*,*N*-Dimethylformamide (DMF)

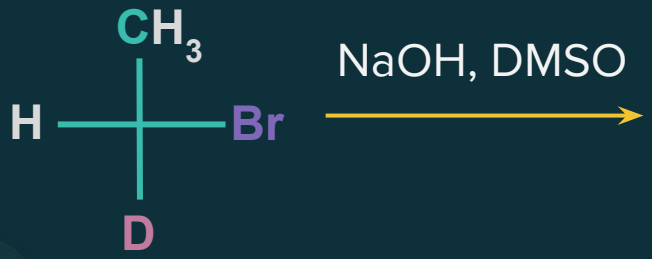
(d) Water

Solution

The reaction $CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$ being a S_N2 reaction, will be fastest in a polar aprotic solvent.
So correct choice is DMF.

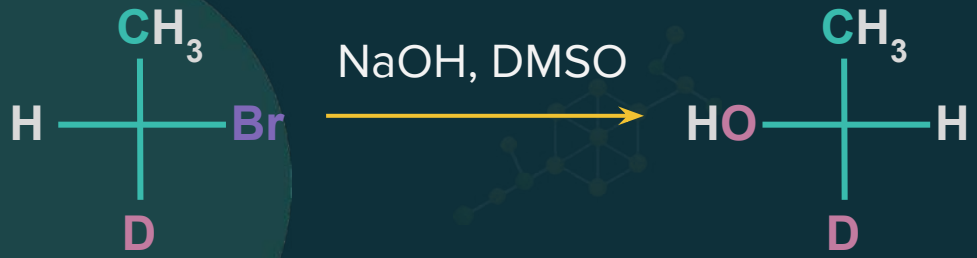
Hence, the correct answer is option(c).

The product of given reaction is:



Solution

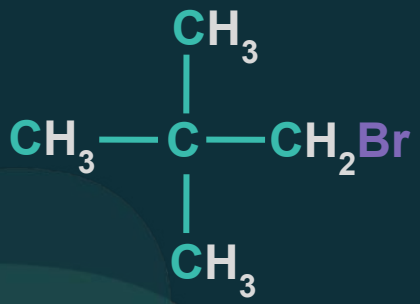
The reaction will proceed via the S_N2 mechanism and there will be inversion of configuration. So we get the product as mentioned below.



In a S_N2 substitution reaction of the type

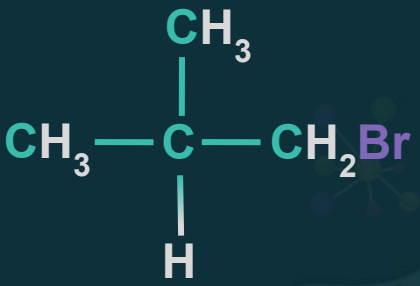
$$R{-}Br + Cl^- \xrightarrow{DMF} R{-}Cl + Br^-$$

Which one of the following has the highest relative rate?

(a) 

(b) $CH_3{-}CH_2Br$

(c) $CH_3{-}CH_2{-}CH_2Br$

(d) 

Solution

The alpha carbon of all the options are primary so to decide the rate we need to study the beta carbon.

Option (a) CH_3-$C(CH_3)_2$-CH_2-Br : The beta carbon in this case is quaternary so steric hindrance is there that is why it is not having the fastest rate.

Option (b) CH_3-CH_2-Br : The beta carbon in this case is primary and, it is methyl, the smallest alkyl group so steric hindrance is least. That is why it is having the **fastest rate.**

Option (c) $CH_3–CH_2-CH_2-Br$: The beta carbon in this case is primary and, it is ethyl alkyl group. So more steric hindrance is there compared to methyl group. That is why it is not having the fastest rate.

Option (d) $CH_3-CH(CH_3)-CH_2-Br$: The beta carbon in this case is secondary so steric hindrance is there. That is why it is not having the fastest rate.

So, the increasing order of rate is: a) < d) < c) < b).

Hence, option (b) is the correct answer.

Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of:

(a) Steric hindrance

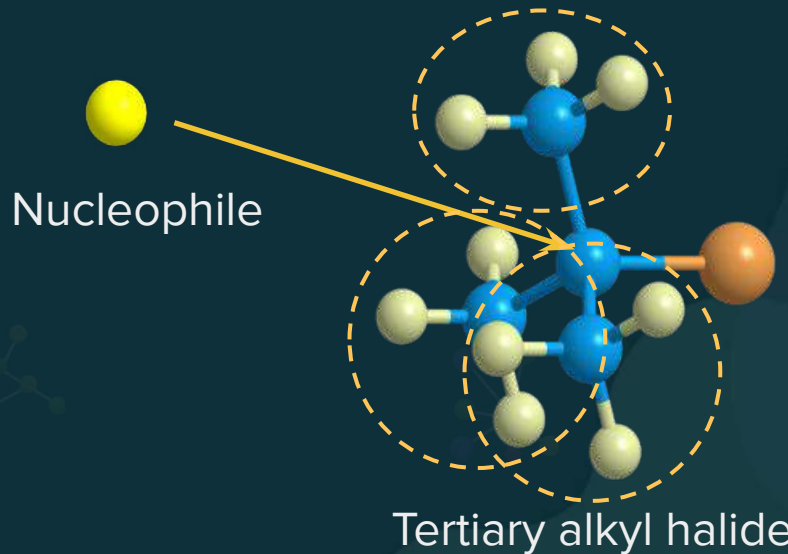
(b) Inductive effect

(c) Instability

(d) Insolubility

Solution

Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of steric hindrance only.



Hence, option (a) is the correct answer.

Out of the following the best leaving group is:

(a) F^-

(b) Br^-

(c) Cl^-

(d) I^-

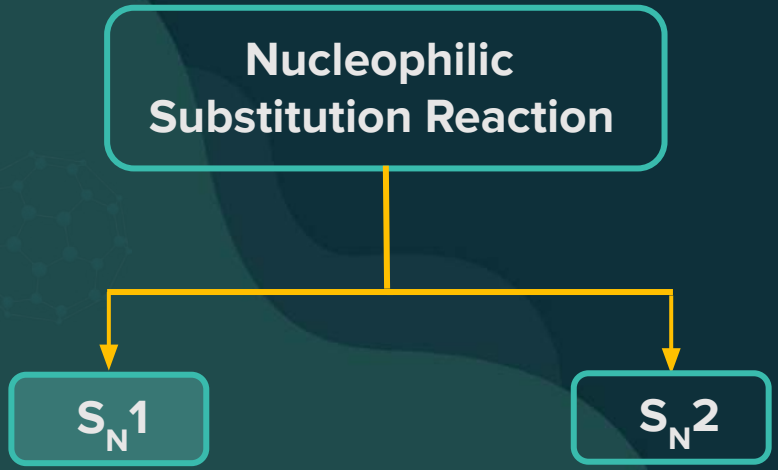
Solution

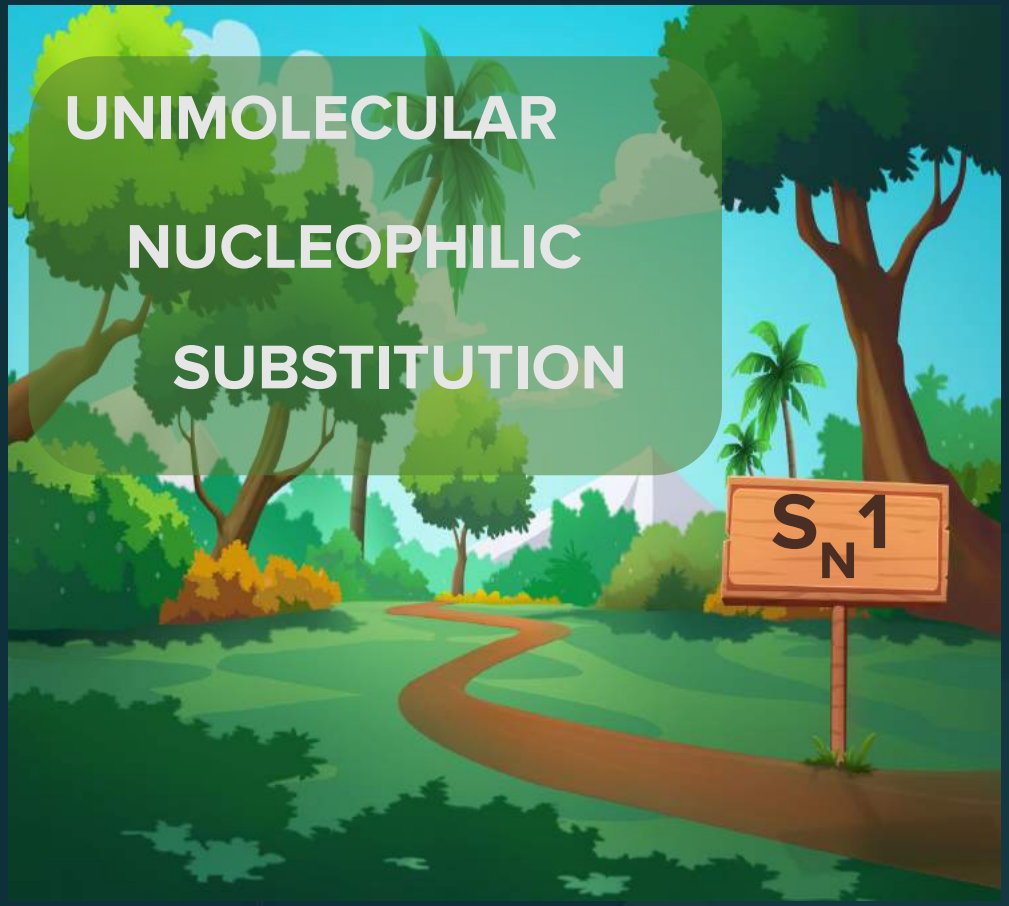
Down the group, basic character decreases and the leaving capacity increases. So, iodide ion is the best choice.

Hence, option (d) is the correct answer.

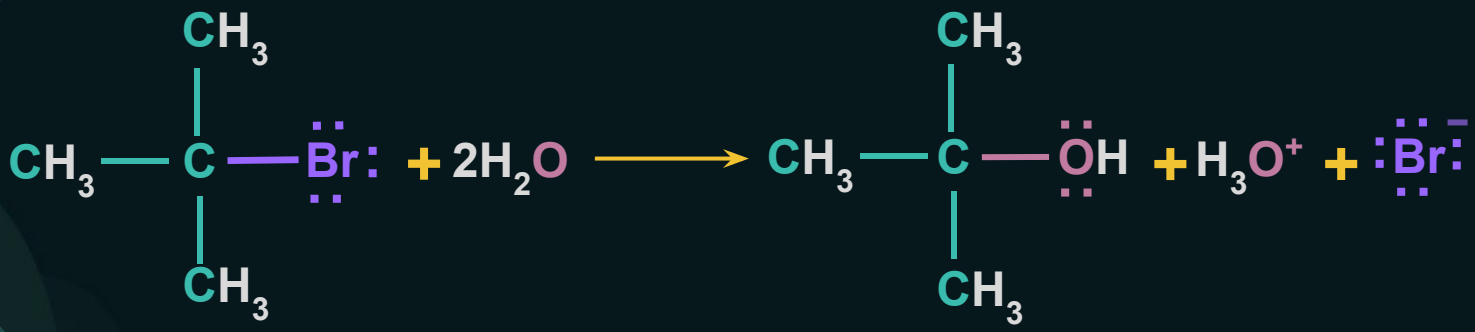
The order follows: (a) < (c) < (b) < (d).

Substitution Nucleophilic Unimolecular





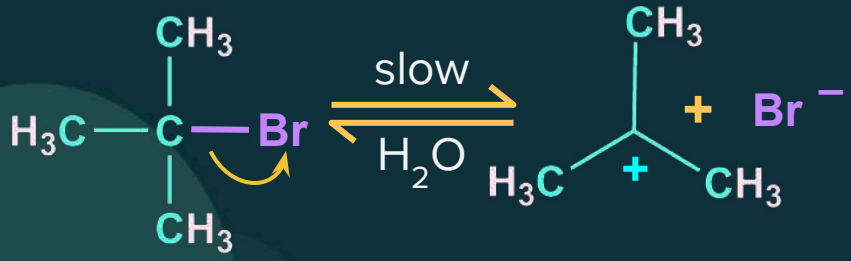
Substitution Nucleophilic Unimolecular

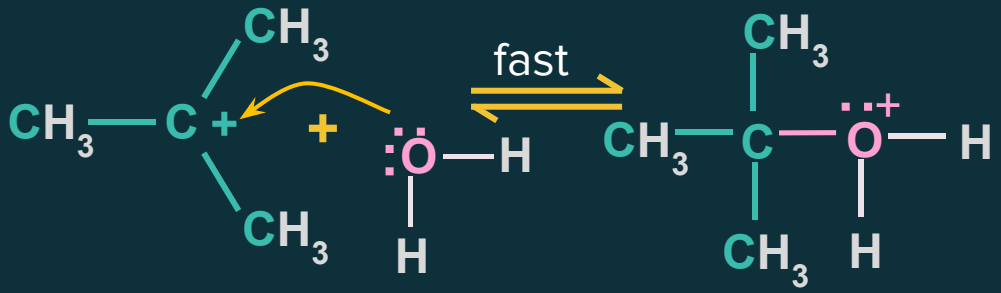


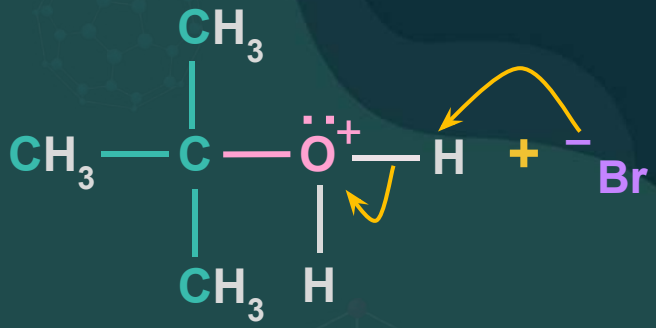
Step 1 — Formation of carbocation

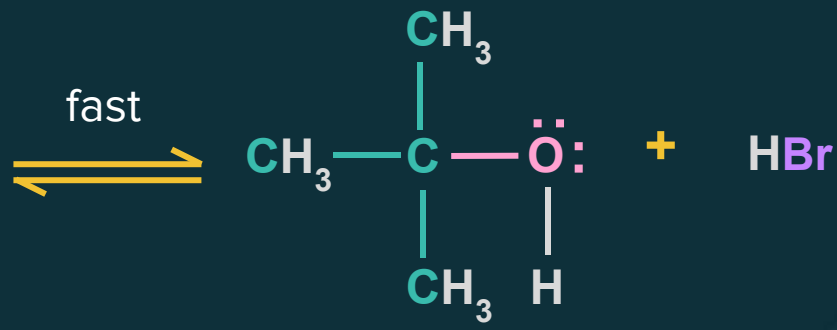
Step 2 — Attack of nucleophile

Mechanism of S_N1 Reaction





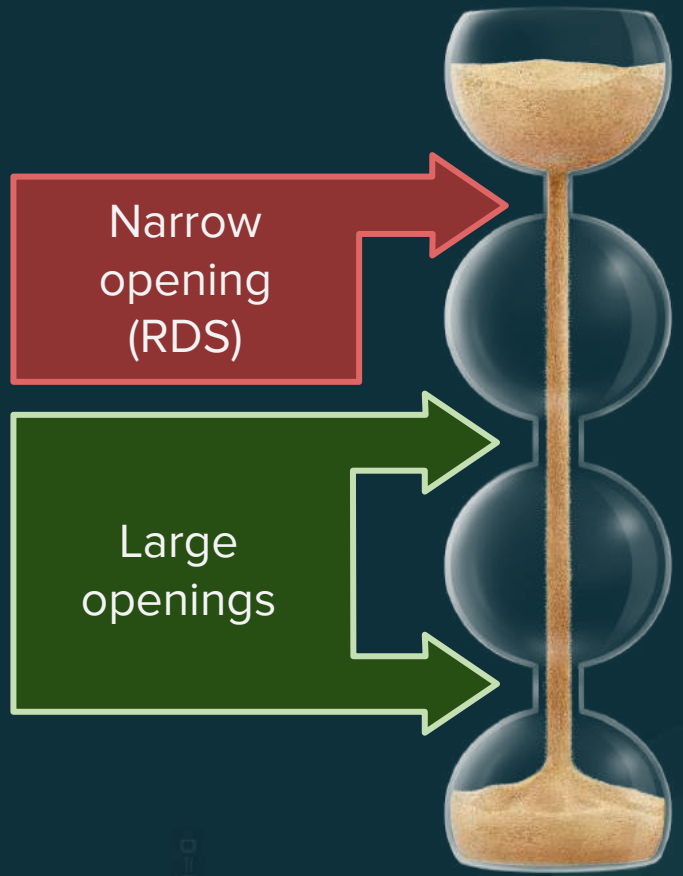




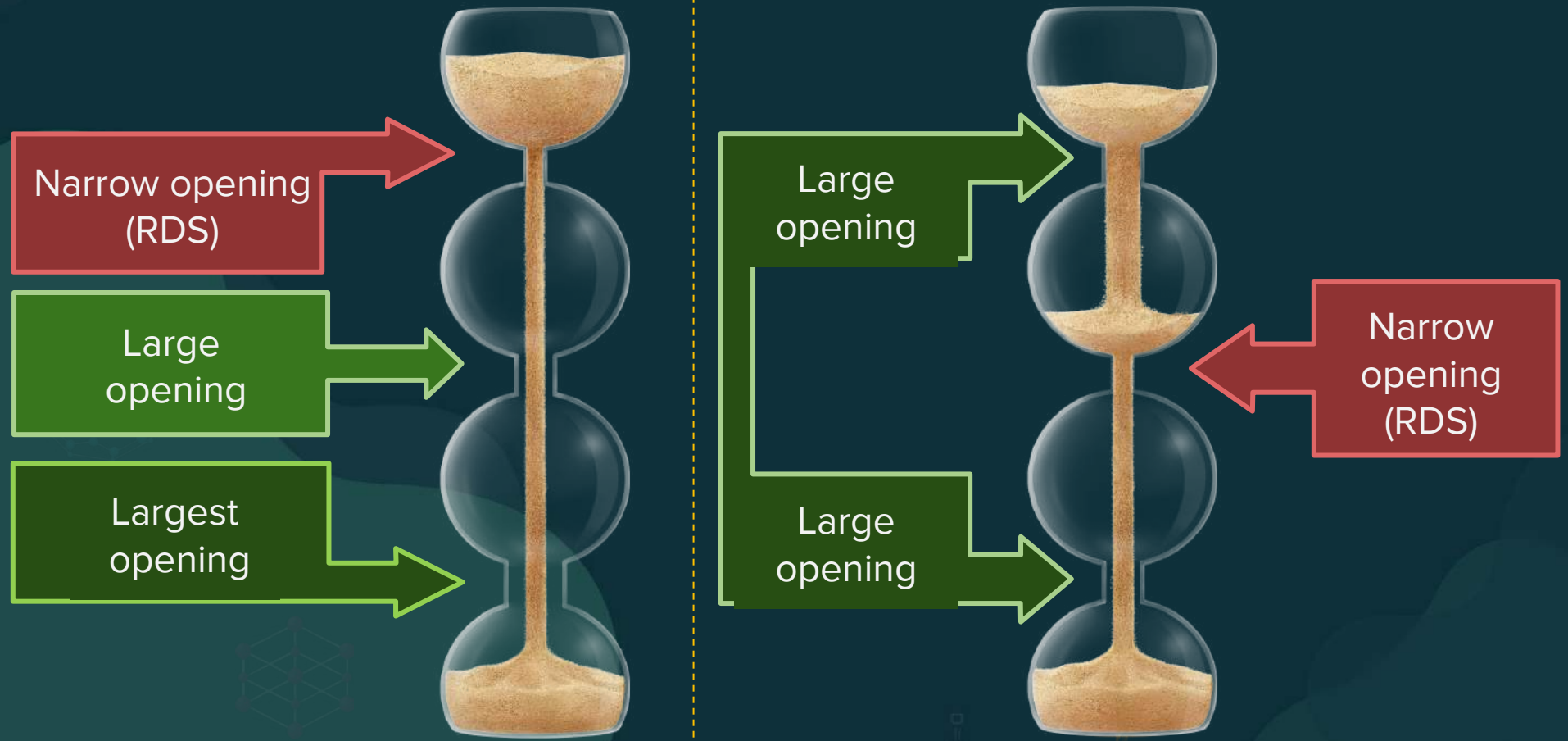
Rate Determining Step (RDS)

If one step in a multistep reaction is **intrinsically slower** than all the others, then the rate of the overall reaction will be essentially the same as the rate of this slowest step.

This slowest step is called the **rate-limiting** step
or
the **rate determining step.**



Rate Determining Step (RDS)



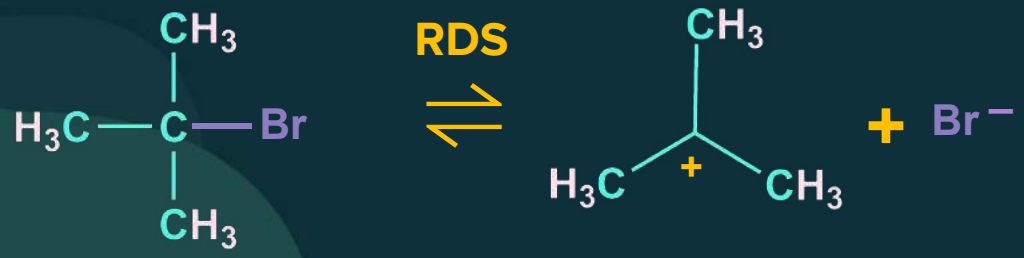
Characteristics of S_N1 Reactions

1. It is **unimolecular**, two step process.
2. **Carbocation** intermediate is formed, so **rearrangement** is possible in S_N1 reaction.

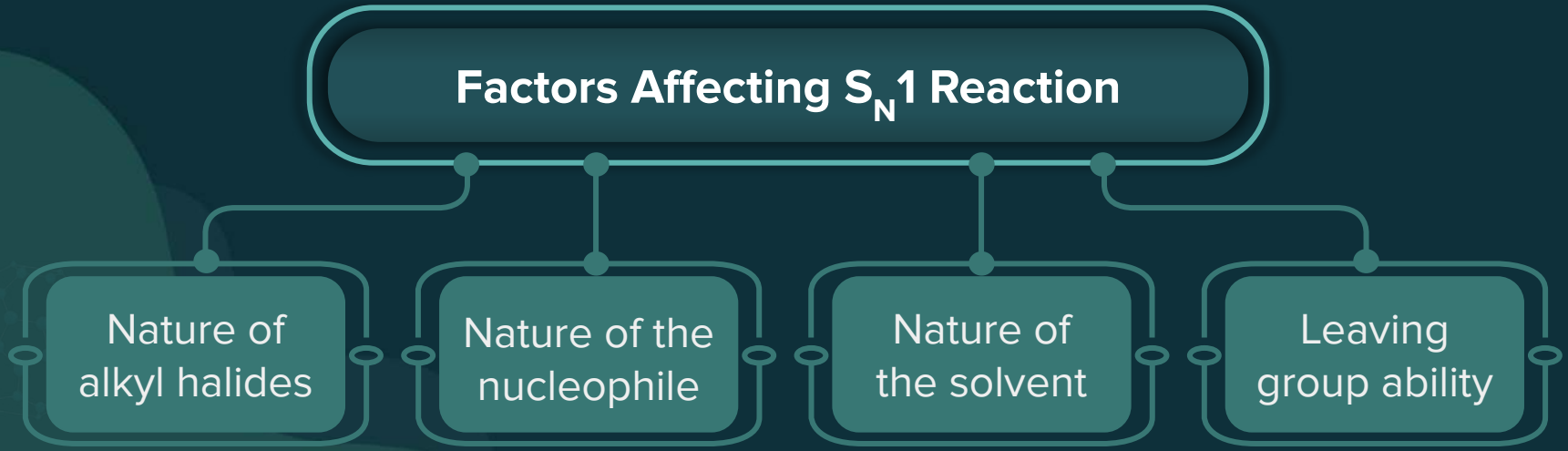
Rate of S_N1 reaction is **independent** of concentration and nature of **nucleophile.**

Characteristics of S_N1 Reactions

Rate ∝ [Alkyl Halide] → First step must be the slow and rate-determining step.



Factors Affecting S_N1 Reaction

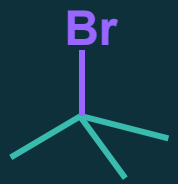
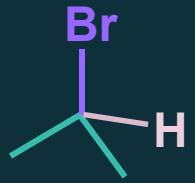
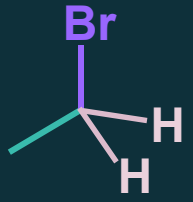


Factors Affecting S_N1 Reaction

Nature of alkyl halide

S_N1 reactivity

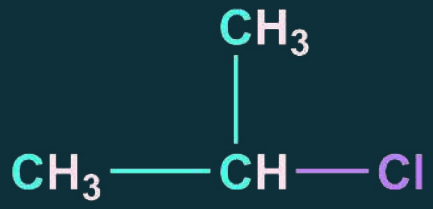
$CH_3 - X$ < 1° Alkyl halide < 2° Alkyl halide < 3° Alkyl halide

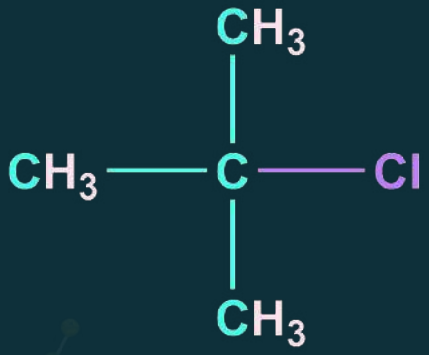
Alkyl bromide	Class of alkyl bromide	Relative rate
	Tertiary	12,00,000
	Secondary	11.6
	Primary	≃ 0

Which of the following gives the fastest S_N1 reaction?

(a) CH_3-Cl

(b) CH_3-CH_2-Cl

(c) 

(d) 

Solution

Option (a) CH_3-Cl **:** The alkyl halide is primary in nature.
Option (b) CH_3–CH_2-Cl **:** The alkyl halide is primary in nature.
Option (c) CH_3-$CH(CH_3)$-Cl **:** The alkyl halide is secondary in nature.
Option (d) CH_3-$C(CH_3)_2$-Cl **:**The alkyl halide is tertiary in nature.

S_N1 reactivity

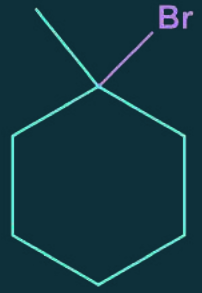
CH_3 - X < 1° Alkyl halide < 2° Alkyl halide < 3° Alkyl halide

Hence, option (d) is the correct answer.

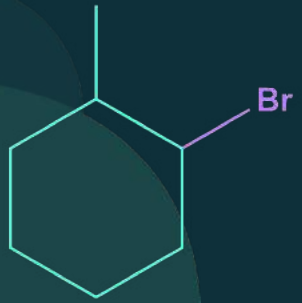
Which of the following gives the fastest S_N1 reaction?

(a)

(b)



(c)



(d)

Solution

Option (a) CH_3-Cl **:** The alkyl halide is primary in nature.
Option (b) CH_3–CH_2-Cl **:** The alkyl halide is tertiary in nature.
Option (c) CH_3-$CH(CH_3)$-Cl **:** The alkyl halide is secondary in nature.
Option (d) CH_3-$C(CH_3)_2$-Cl **:**The alkyl halide is secondary in nature.

S_N1 reactivity

CH_3 - X < 1° Alkyl halide < 2° Alkyl halide < 3° Alkyl halide

Hence, option (b) is the correct answer.

Factors Affecting S_N1 Reaction

Nature of nucleophile

Rate of S_N1 reaction is **unaffected** by the **concentration** of the nucleophile.

Weak and neutral nucleophile favours S_N1 reaction.

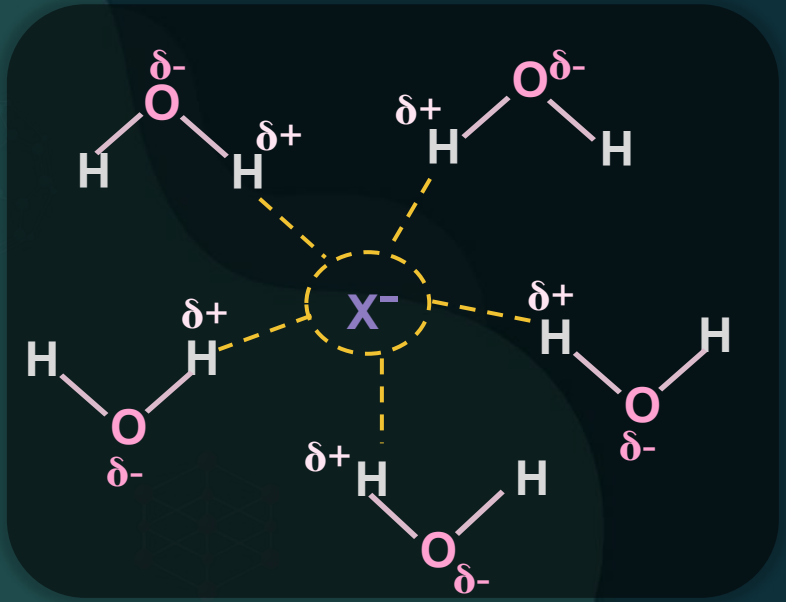
Mostly, solvents (protic) itself function as nucleophiles in S_N1 reaction, so S_N1 reaction is termed as **solvolysis reaction**.

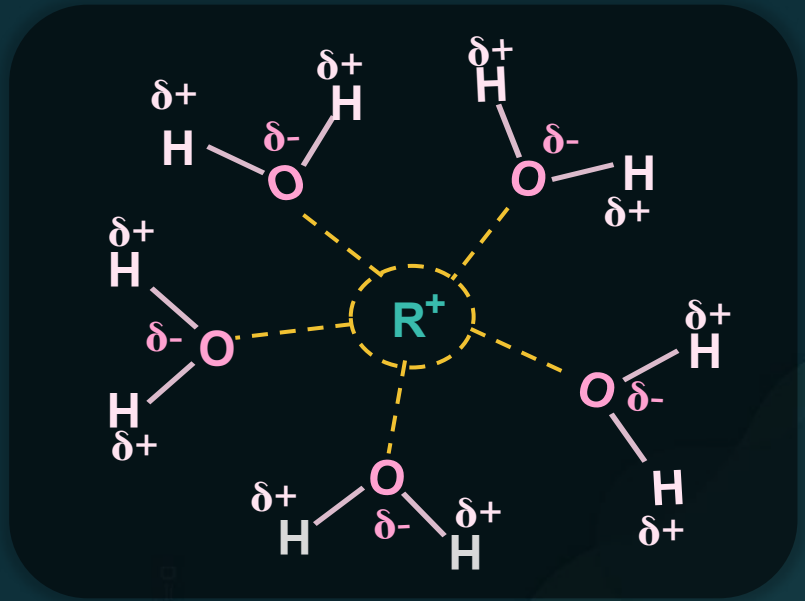
Water	**Hydrolysis**
Ethanol	**Ethanolysis**

Factors Affecting S_N1 Reaction

Nature of solvent

Using a **polar protic solvent** will greatly **increase** the rate of carbocation formation of an alkyl halide in any S_N1 reaction because of its ability to **solvate cations and anions** effectively.





Factors Affecting S_N1 Reaction

Leaving group Ability

In the S_N1 reaction, the leaving group begins to acquire a **negative charge**.

↓

Stabilisation of this developing negative charge on the leaving group **increases** the rate of reaction.

Relative reactivities of alkyl halides

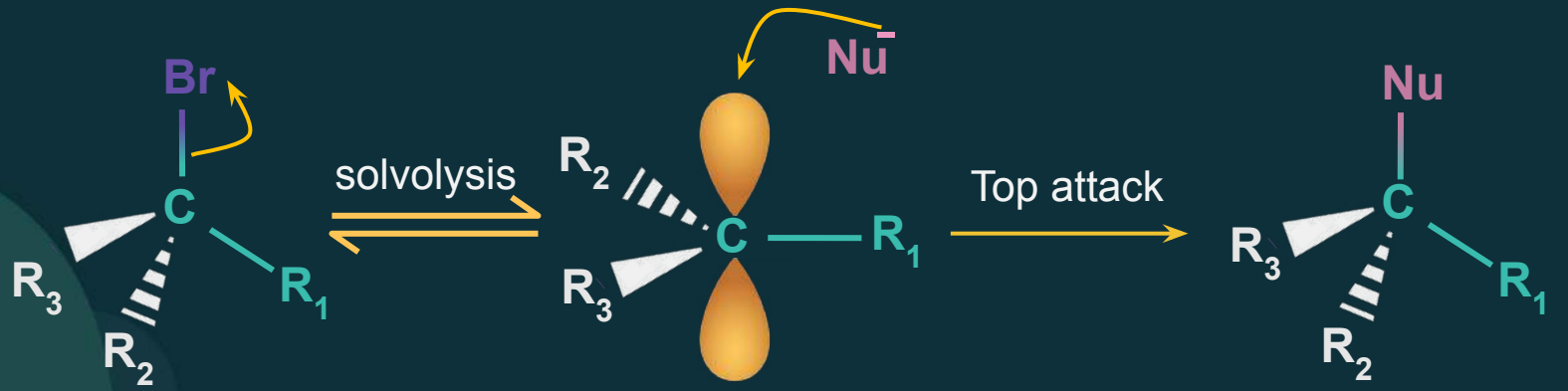
RF < **RCl** < **RBr** < **RI**

Stereochemistry of S_N1 Reaction

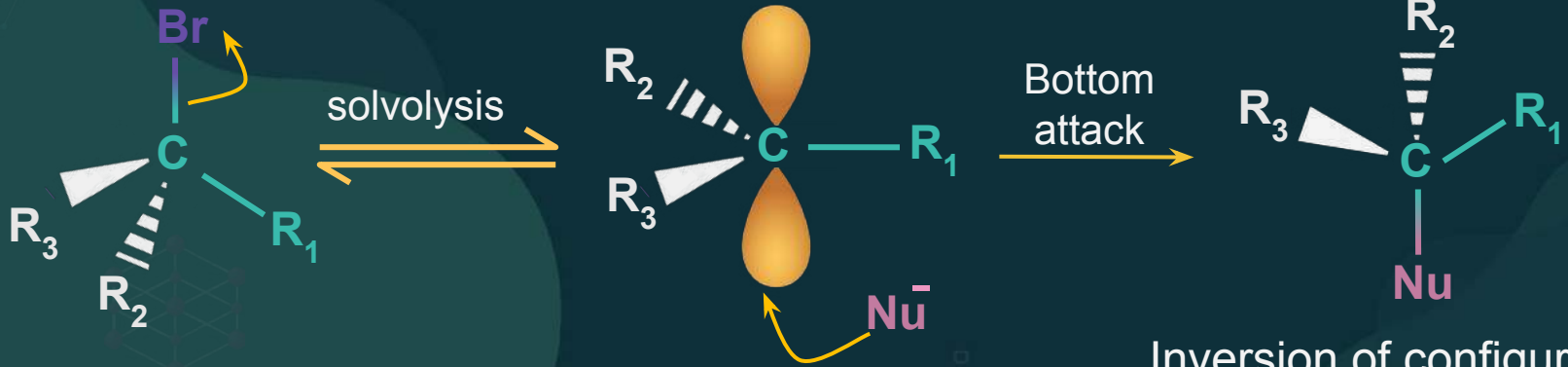
In the **S_N1** mechanism, the carbocation intermediate is **sp^2** hybridised and planar.

A **nucleophile** can attack on the **carbocation** from either face. If reactant is **chiral,** then attack of nucleophile from both faces gives enantiomers as the product, which is called **racemisation**.

Stereochemistry of S_N1 Reaction

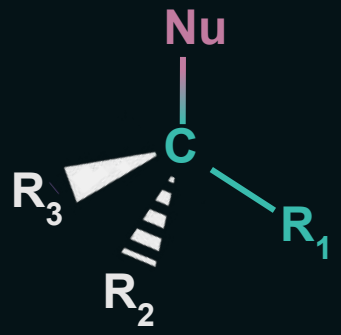


Retention of configuration

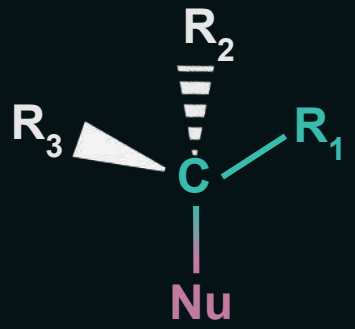


Inversion of configuration

Stereochemistry of S_N1 Reaction



Retention of configuration

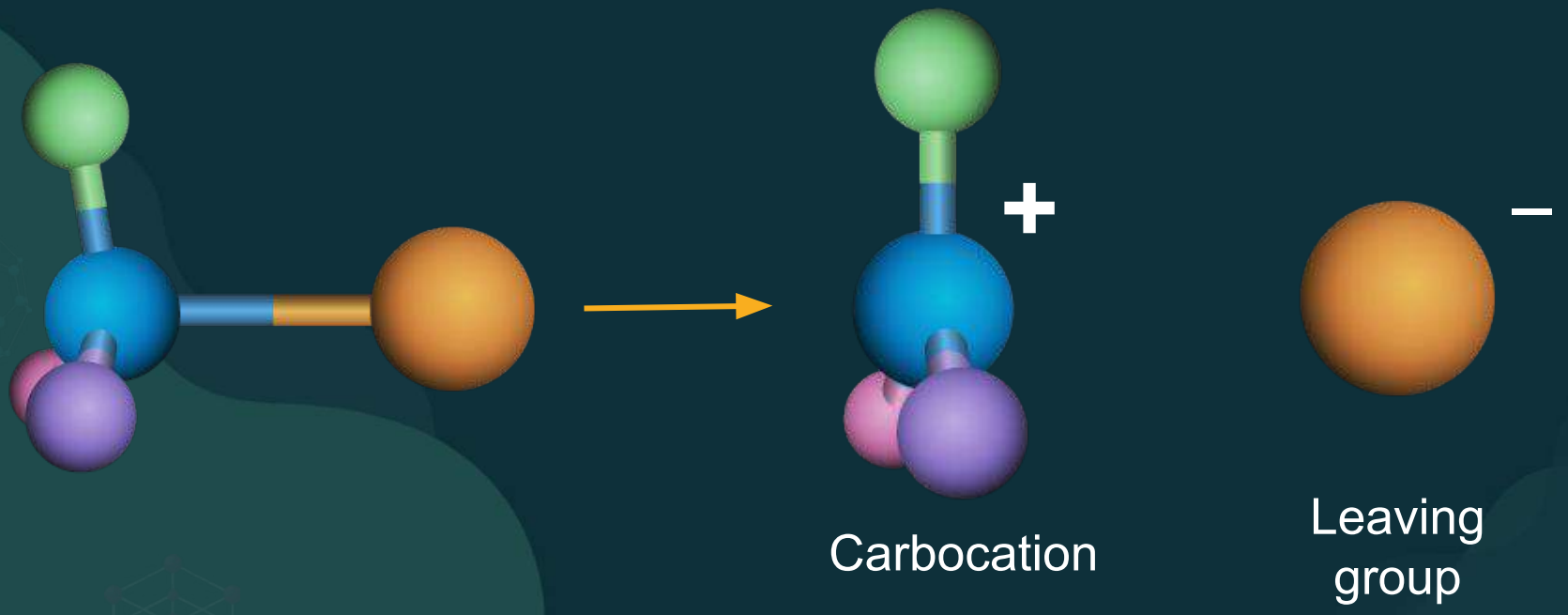


Inversion of configuration

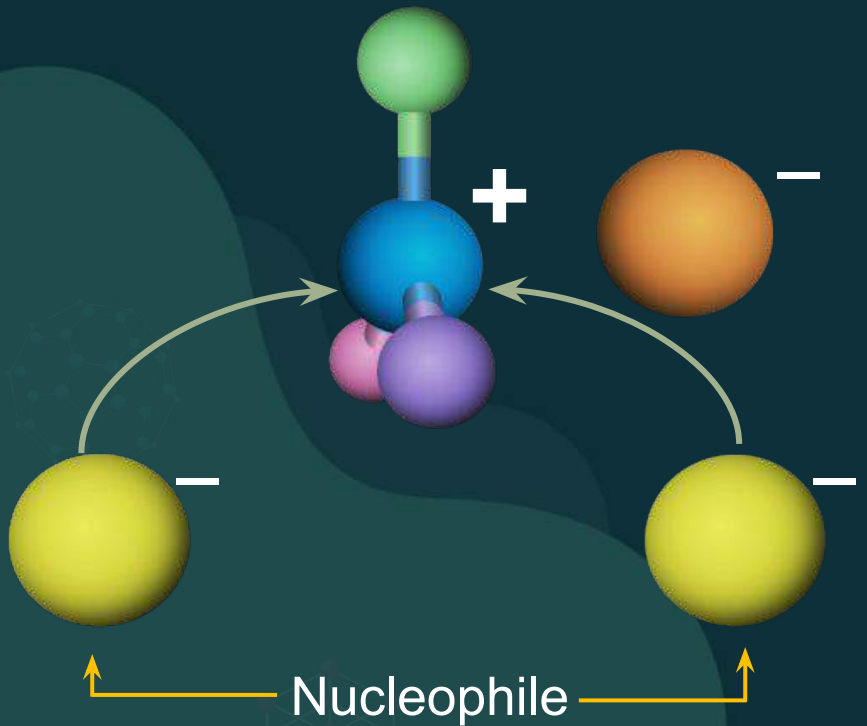
Racemic mixture

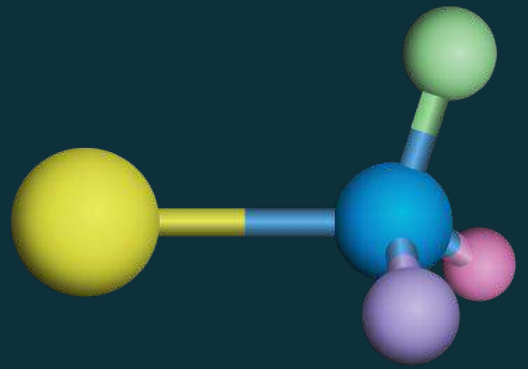
But practically, we get slightly higher proportion of inverted product in S_N1 reaction.

Stereochemistry of S_N1 Reaction

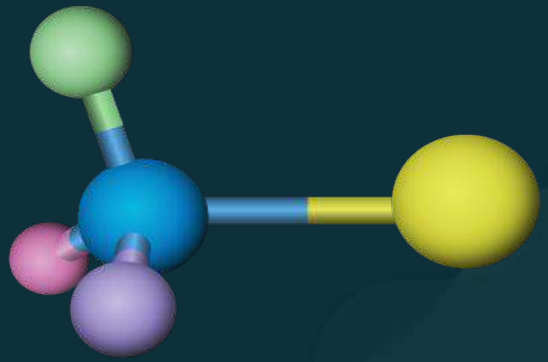


Stereochemistry of S_N1 Reaction





Inversion of configuration (>50%)



Retention of configuration (< 50%)

In a S_N1 reaction, on a chiral centre, there is:

(a) CH_3O^-

(b) Inversion more than retention leading to partial racemisation

(c) 100% inversion

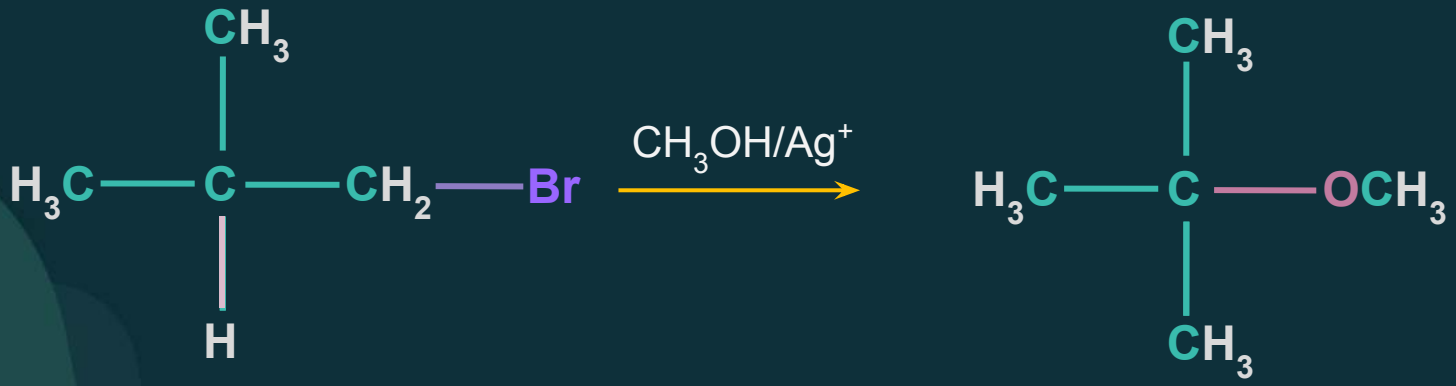
(d) 100% retention

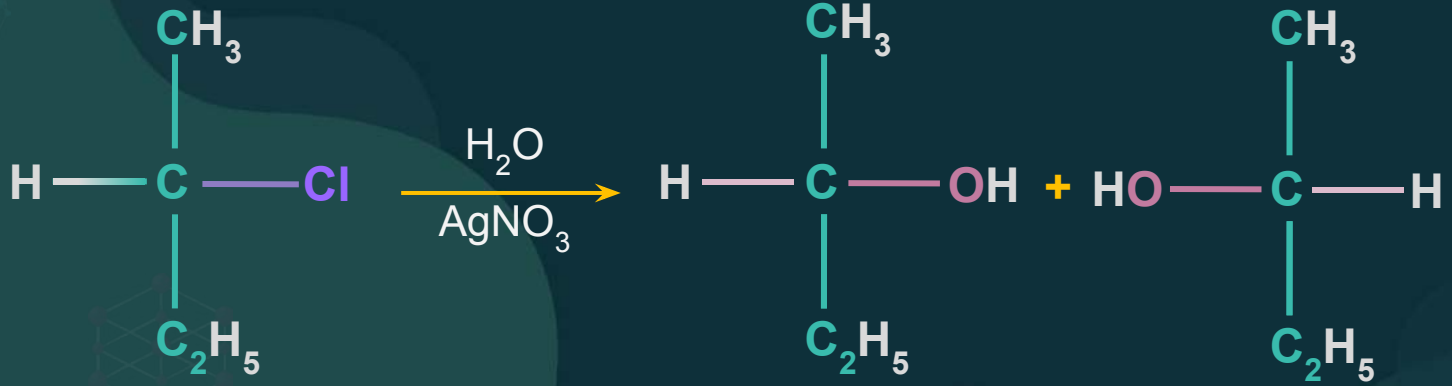
Solution

Practically, we get a slightly higher proportion of inverted product in S_N1 reaction because of formation of intimate ion pair and resistance offered by leaving group to the incoming nucleophile.

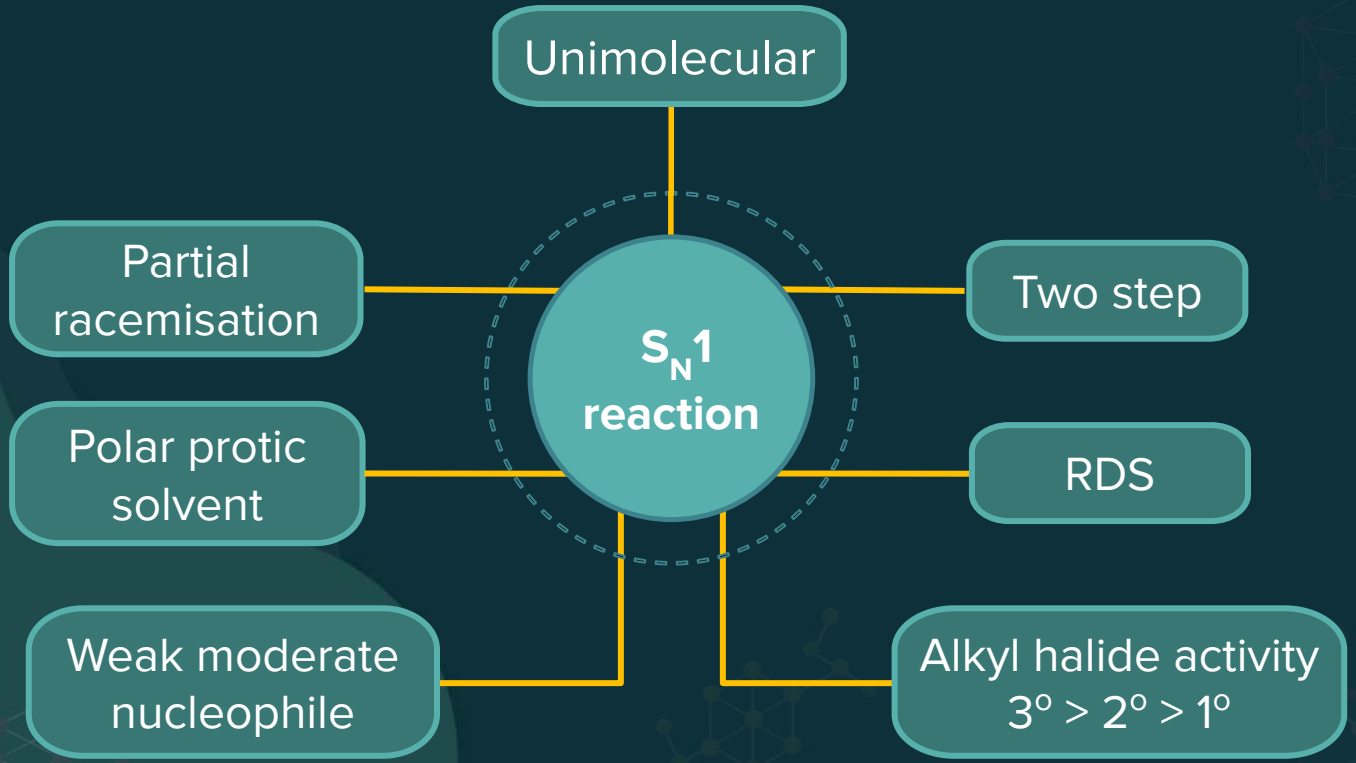
Hence, option (b) is the correct answer.

Example of S_N1 Reaction

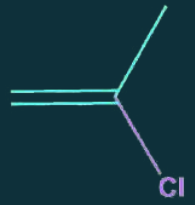


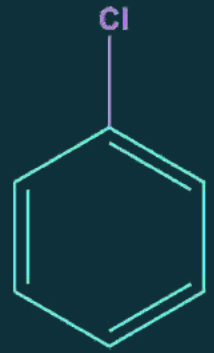


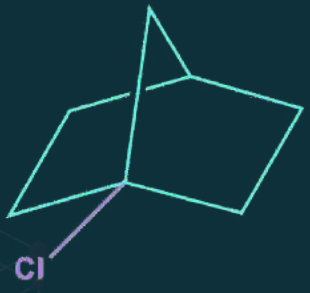
Quick Recap of S_N1 Reaction

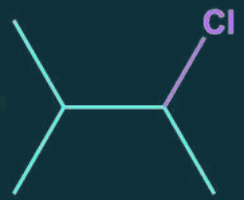


Which of the following compounds can show S_N1 reaction?

(a) 

(b) 

(c) 

(d) 

Solution

Option (a) Cation formation occurs at vinyl position which is not stable so this reaction will not proceed by S_N1.

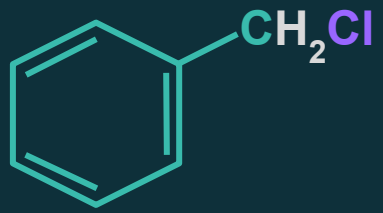
Option (b) Cation formation occurs at phenyl position which is not stable so this reaction will not proceed by S_N1.

Option (c) Cation formation occurs at Bridge head position which is not stable according to Bredt's rule so this reaction will not proceed by S_N1.

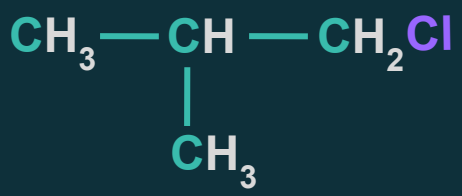
Option (d) Cation formation occurs at secondary carbon which is stable so this reaction will proceed by S_N1.

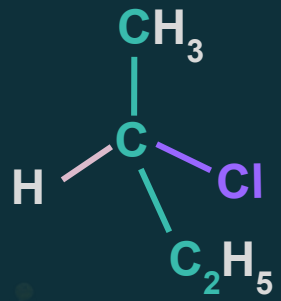
Hence, option (d) is the correct answer.

Which of the following compounds will undergo racemisation when they undergo hydrolysis?

(I) 

(II) $CH_3-CH_2-CH_2Cl$

(III) 

(IV) 

(a) (I) and (II)

(b) (II) and (IV)

(c) (III) and (IV)

(d) Only (IV)

Solution

Compound containing chiral carbon can undergo racemisation.
Hence, due to chirality only compound (iv) will undergo racemisation.

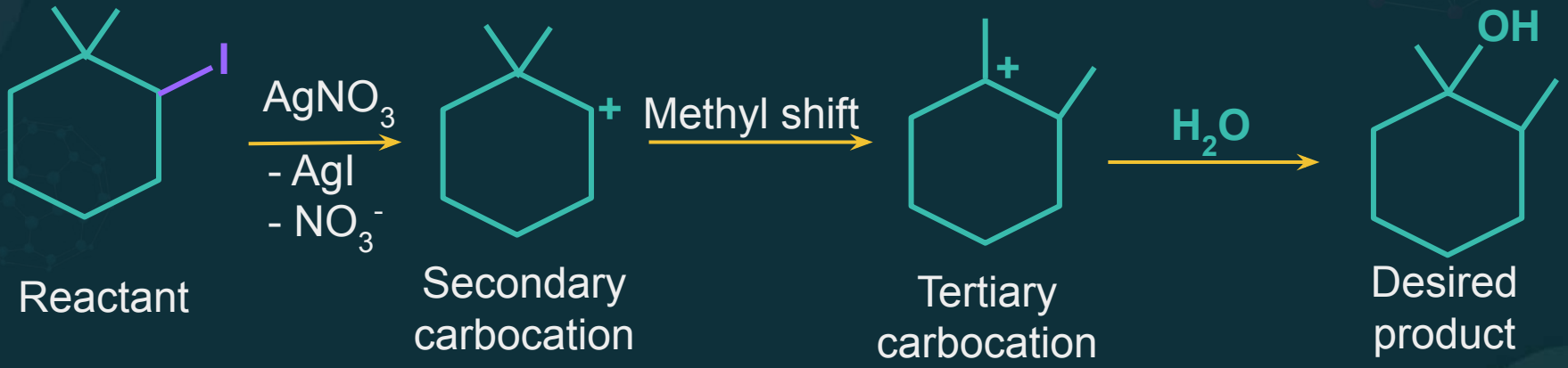
Hence, option (d) is the correct answer.

Major product for the following reaction:

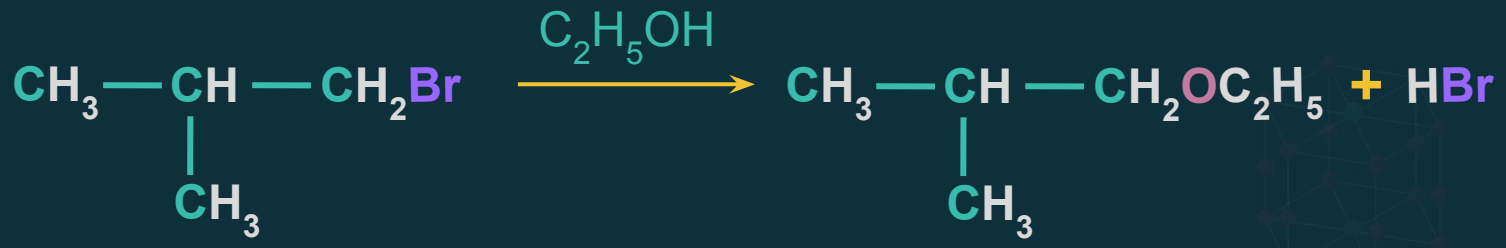
Solution

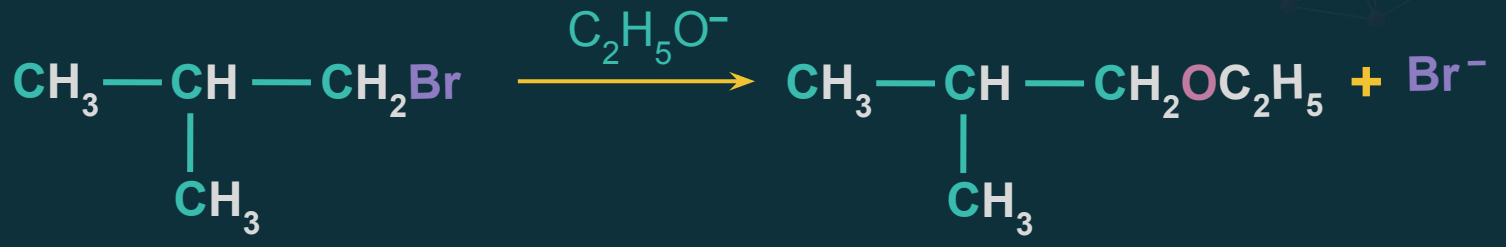
This reaction is very slow, if we add $AgNO_3$ then the rate of reaction will increase; iodide ion will form the compound AgI with $AgNO_3$ and secondary carbocation will be formed, the formed carbocation will stabilize by methyl shift.

After methyl shift we will get the tertiary carbocation (Most stable);
H_2O will attack on the carbocation and we will get the final desired product.



Consider the reaction:

(i) 

(ii) 

The mechanisms of reactions (i) and (ii) are respectively:

(a) S_N1 and S_N2

(b) S_N1 and S_N1

(c) S_N2 and S_N2

(d) S_N2 and S_N1

Solution

In reaction (i) if mechanism will S_N1 then product will form after the formation of carbocation and definitely hydride will shift and product obtained will be different from given;
So, the product formation will be favoured by S_N2 mechanism.

In Reaction (ii) $C_2H_5O^-$ [Strong nucleophile] will directly attack the reactant and product will be formed via S_N2 mechanism.

S_N1 reactions nearly always involve weak nucleophiles, because strong nucleophiles are too reactive to allow a carbocation to form.

Because the nucleophile is involved in the rate-determining step of S_N2 reactions, stronger nucleophiles react faster.

Hence, option (c) is the correct answer.

Which of the following is least reactive in S_N1 reaction?

(a) $(CH_3)_3CCl$

(b) $H_2C=CHCl$

(c) H_3C-CH_2Cl

(d) $H_2C=CHCH_2Cl$

Solution

Here, in S_N1 reaction carbocation will be formed.
So, less stable is the carbocation, less will be the reactivity towards S_N1 reaction.

Vinyl carbocation will be the least stable, so vinyl chloride will be the least reactive towards S_N1 reaction.
Hence, option (b) is the correct answer.

Which of the following can undergo reaction via S_N1 mechanism?

(a) Benzyl chloride

(b) Allyl chloride

(c) tert-Butyl chloride

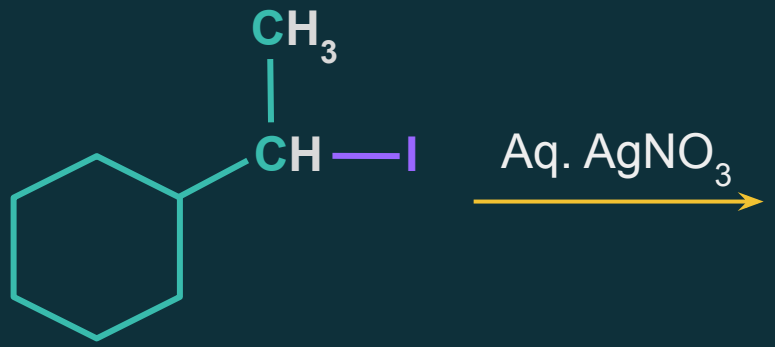
(d) All of these

Solution

The reactant which will form stable carbocation can undergo reaction via S_N1 mechanism.
Here all the given compounds will form the stable carbocation.
So, all of these can undergo reaction via S_N1 mechanism.

Hence, option (d) is the correct answer.

For the following solvolysis reaction, give the major products:

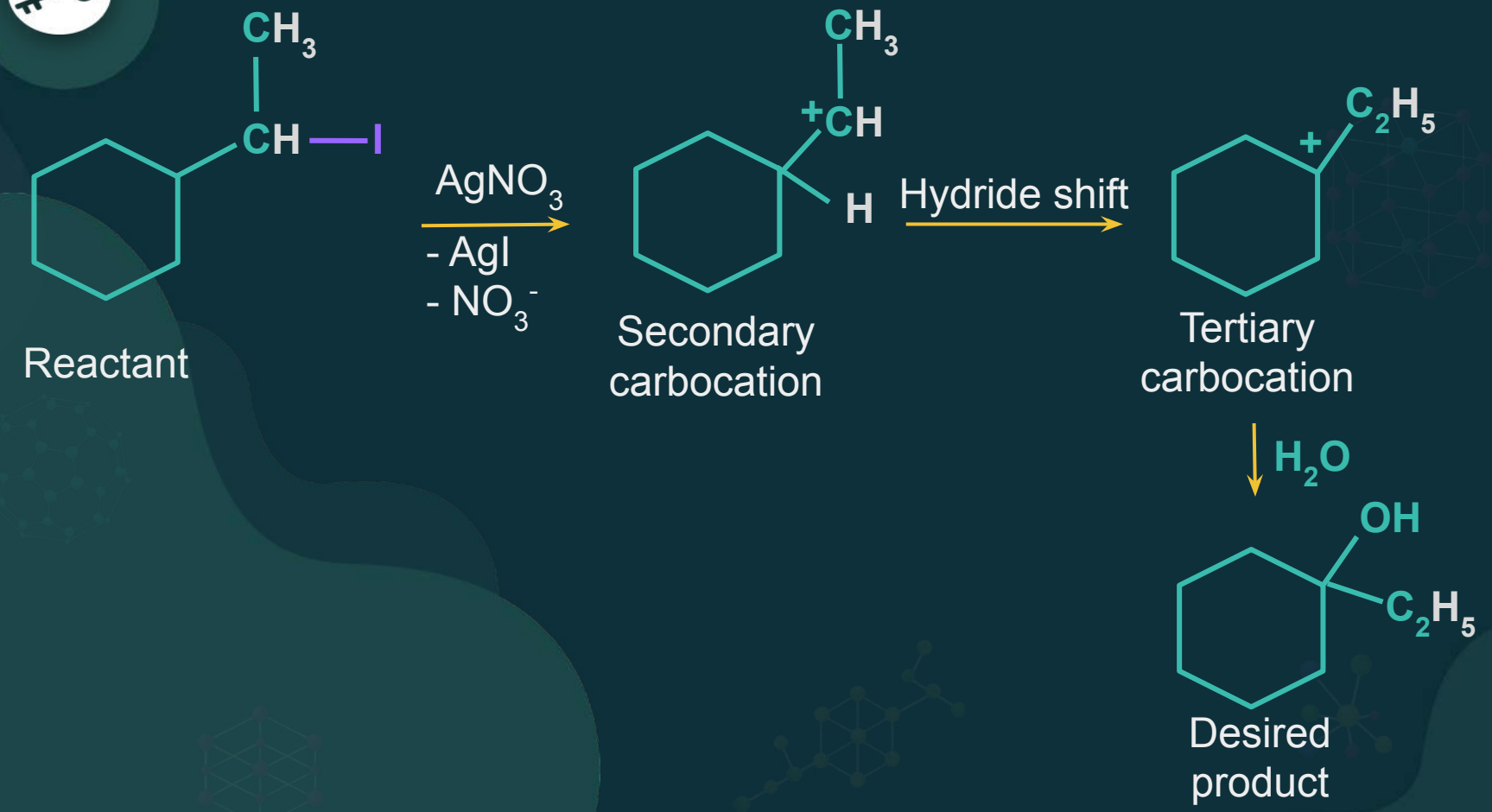


Solution

Iodide ion will form the compound AgI with $AgNO_3$ and secondary carbocation will be formed, and secondary carbocation will stabilised by the hydride shift.

After hydride shift we will get the tertiary carbocation (Most stable);

H_2O will attack on the carbocation and we will get the final major product.



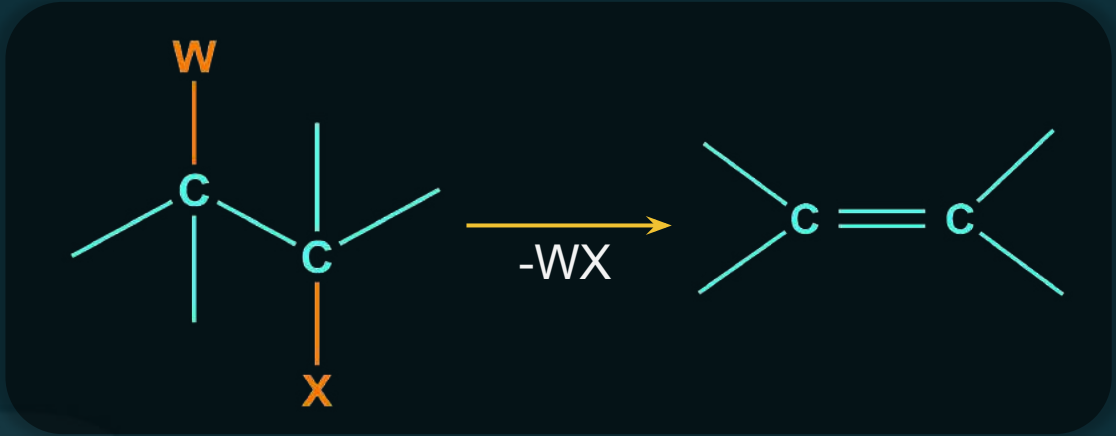
Reactant

Secondary carbocation

Tertiary carbocation

Desired product

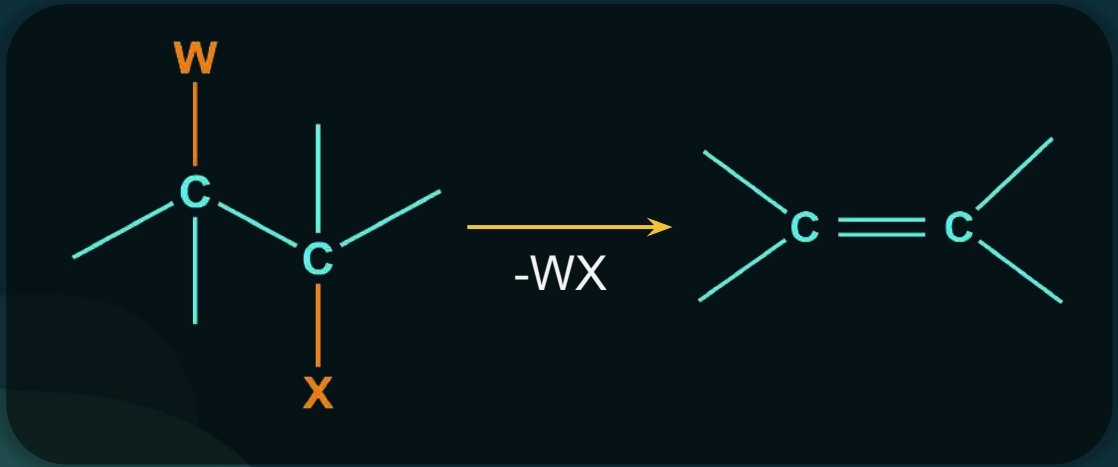
Elimination Reaction



In an elimination reaction, two atoms or groups (WX) are removed from the substrate, generally resulting into formation of **π bond**.

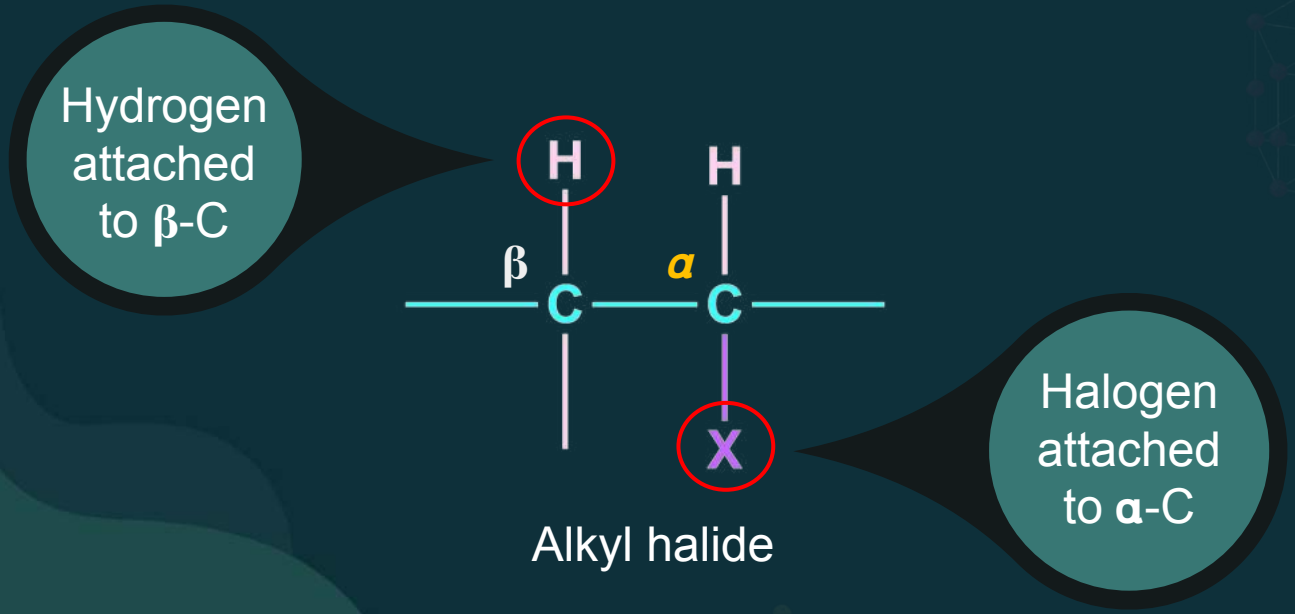
β-Elimination Reaction

Also known as **1,2-elimination**



When two groups are removed from adjacent atoms so that a **new π bond** is formed

β-Elimination Reaction in Mono Haloalkanes



E2 Reaction

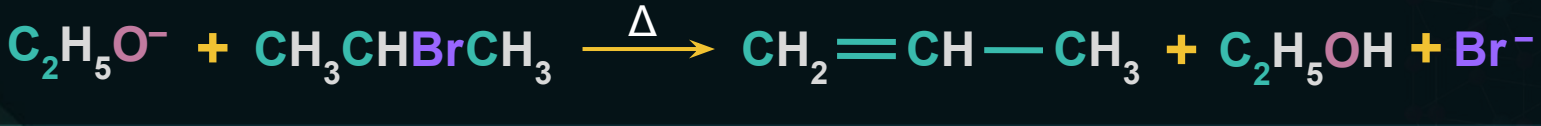
In the E2 mechanism, two groups **depart simultaneously**, with the proton being pulled off by a base.

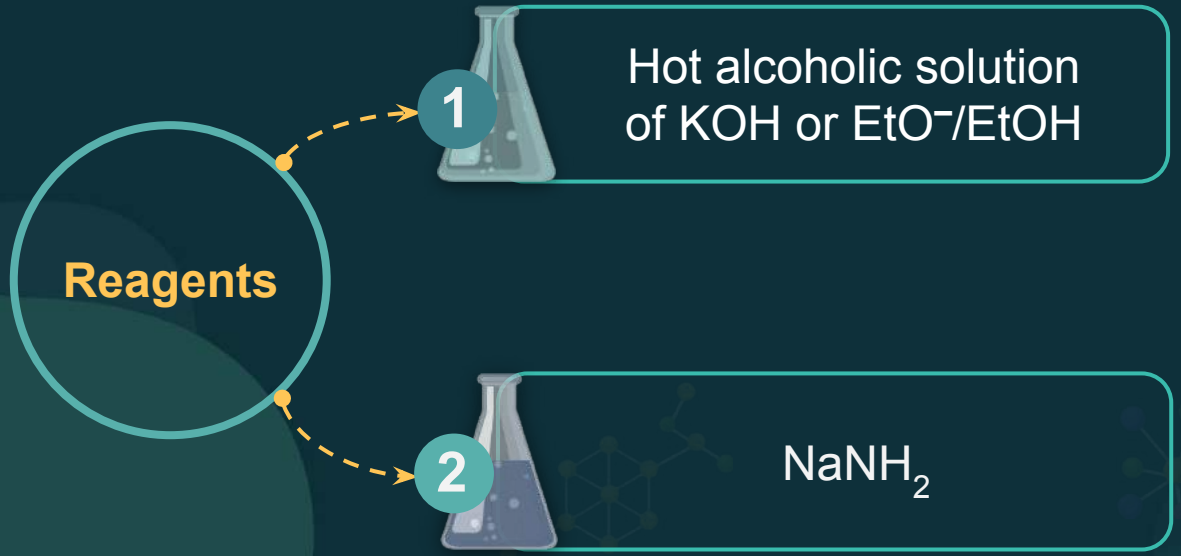
Dehydrohalogenation

1. Elimination of a **hydrogen and halogen** from an alkyl halide to form an alkene

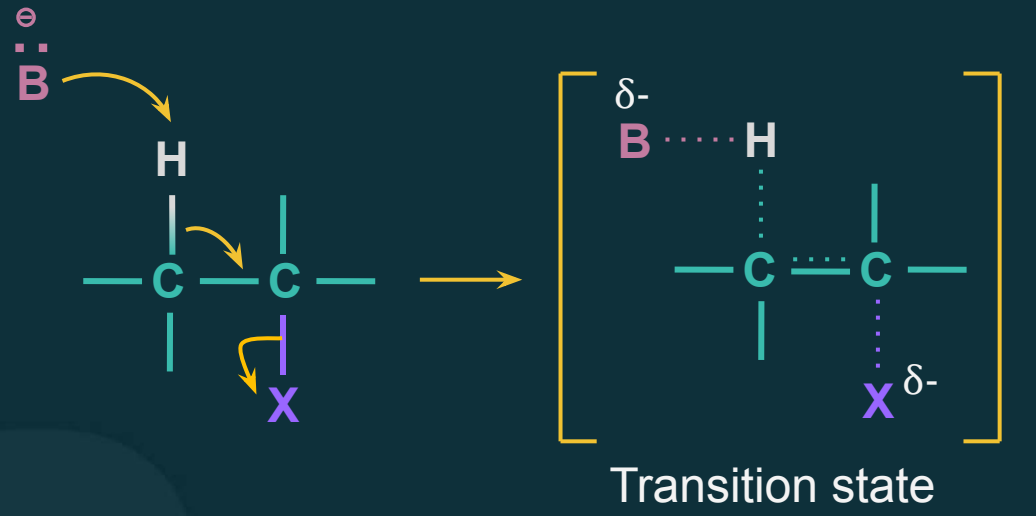
2. Can take place by **E2 mechanism**

E2 Reaction

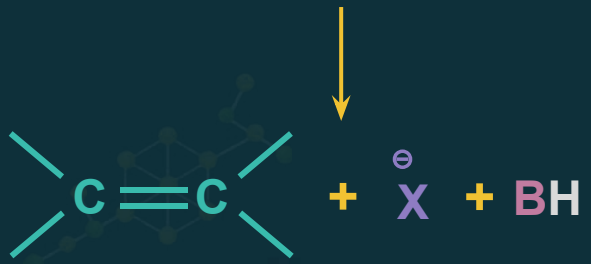

$C_2H_5O^-$ + $CH_3CHBrCH_3$ $\xrightarrow{\Delta}$ $CH_2=CH-CH_3$ + C_2H_5OH + Br^-


Reagents
1
Hot alcoholic solution of KOH or EtO^-/EtOH
2
$NaNH_2$

Mechanism



Transition state



Characteristics of E2 Reaction

01 It is a **single-step bimolecular** reaction.

02 It is a **second order** reaction.

03 **Rate ∝ [R-X] [Base]**

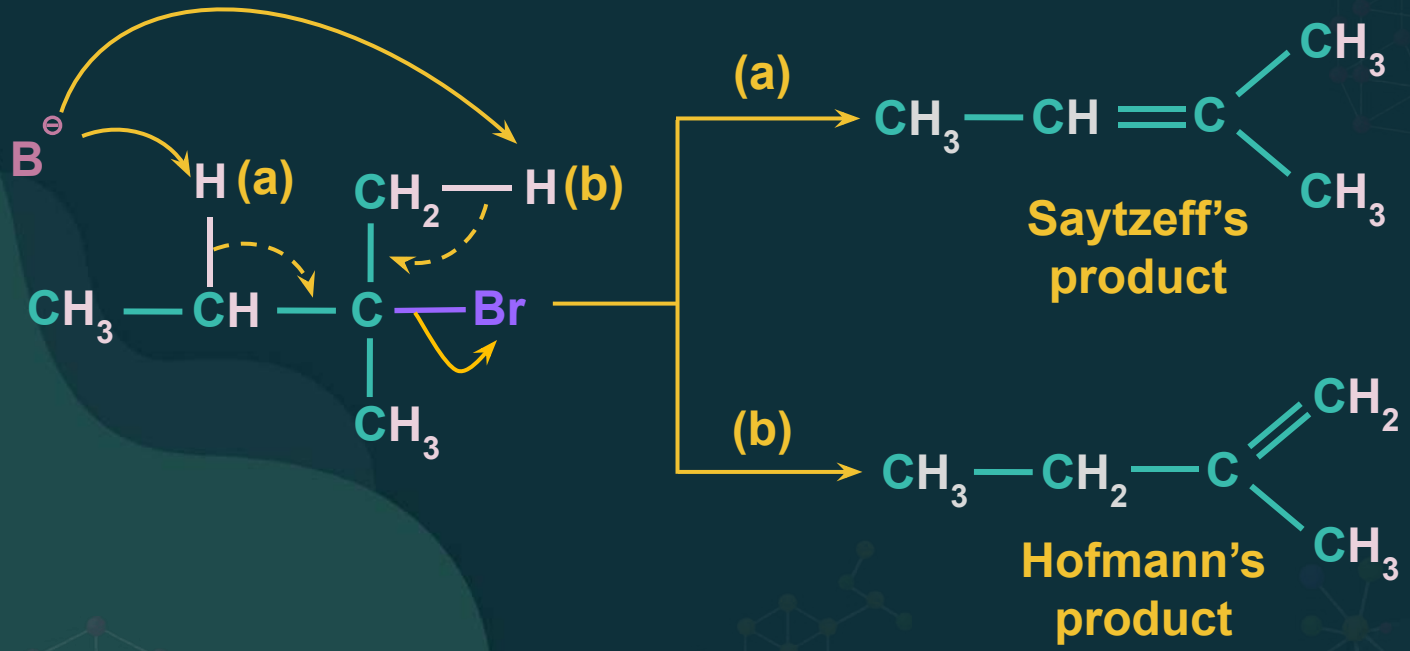
04 Rearrangement is **not possible**.

05 The orientation of the proton and the leaving group should be **anti.**

06 Here, **β-H is eliminated** by the base. Hence it is known as **β-elimination.**

07 If two or more elimination products are possible, the product with the most **highly substituted double bond** will predominate (**Saytzeff's rule**).

Dehydrohalogenation



Characteristics of E2 Reaction

Reactivity towards E2

R-I > R-Br > R-Cl > R-F

Rate of E2 reaction

3° Alkyl halide > 2° Alkyl halide > 1° Alkyl halide

Factors Affecting E2 Reaction

- Nature of alkyl halides
- Nature of the base
- Nature of the solvent
- Leaving group ability

Stability of Alkenes Governs the Rate of E2 Reaction

Nature of Alkyl Halide and Nature of Base

Rate of E2 reaction

3° alkyl halide > **2°** alkyl halide > **1°** alkyl halide

Rate of E2 reaction depends on the **concentration** of the base.

A strong base favours E2 reaction.

Nature of the Solvent and Leaving Group Ability of Alkyl halides

Choice of solvent depends on **reagent** taken.

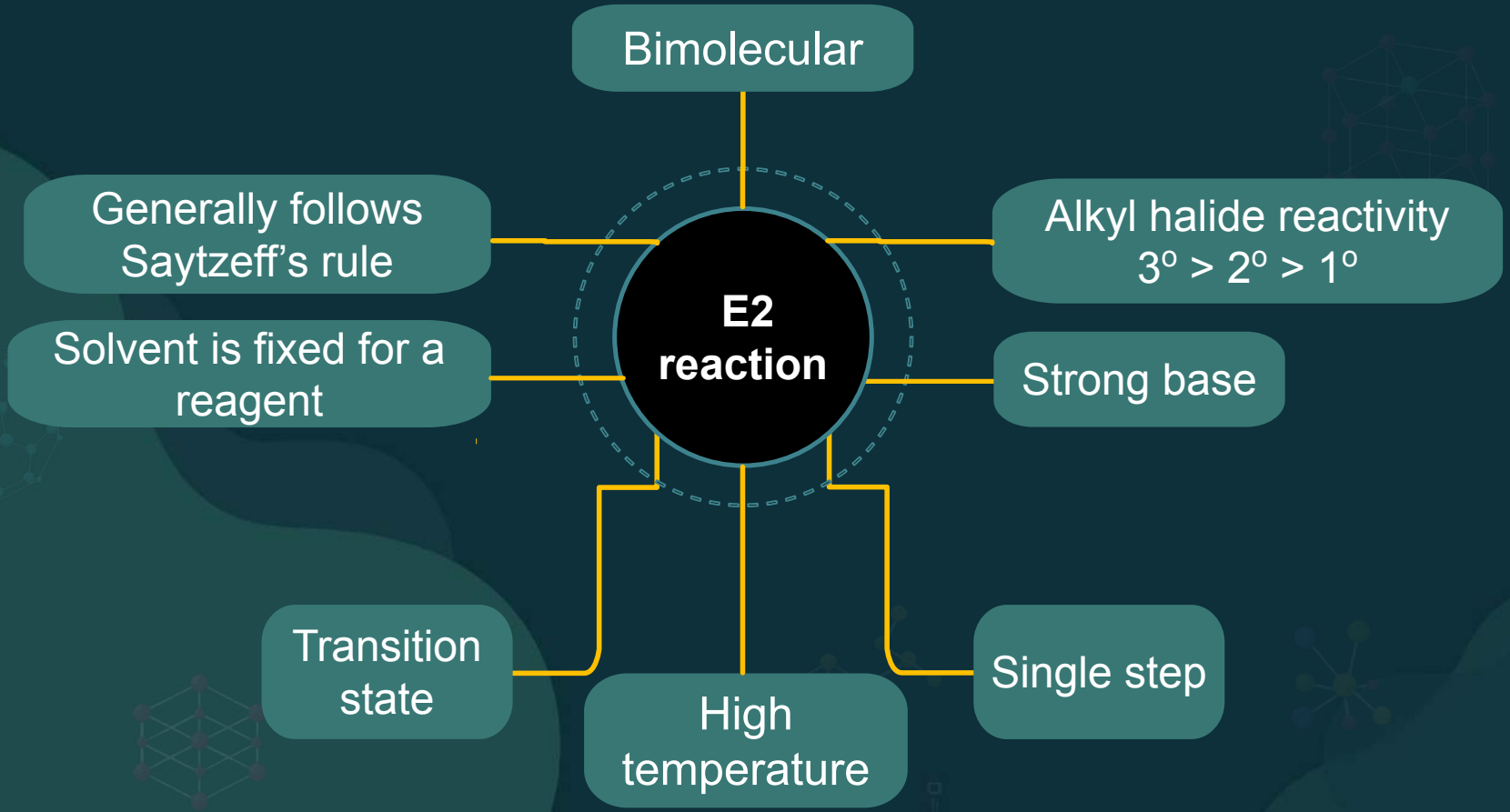
Example:
EtO^- is taken in EtOH

Weaker bases are **good leaving group**

Relative **reactivities** of alkyl halides

R-I > R-Br > R-Cl > R-F

Quick Recap of E2 Reaction



Which among the following is the most reactive towards alcoholic KOH?

(a) $H_2C=CHBr$

(b) CH_3CH_2Br

(c) $CH_3COCH_2CH_2Br$

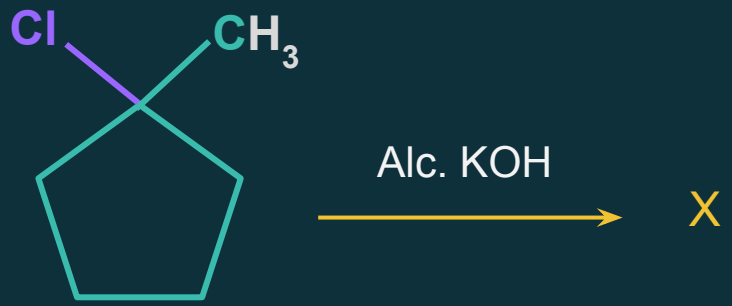
(d) $CH_2CH_2CH_2Br$

Solution

Option (a) vinylic carbocation is unstable so option a is ruled out.
Option (b) on reaction with alcoholic KOH gives ethene.
Option (d) on reaction with alcoholic KOH gives propene.
Option (c) on reaction with alcoholic KOH gives α,β - unsaturated ketone which is conjugated in nature and hence becomes more stable.

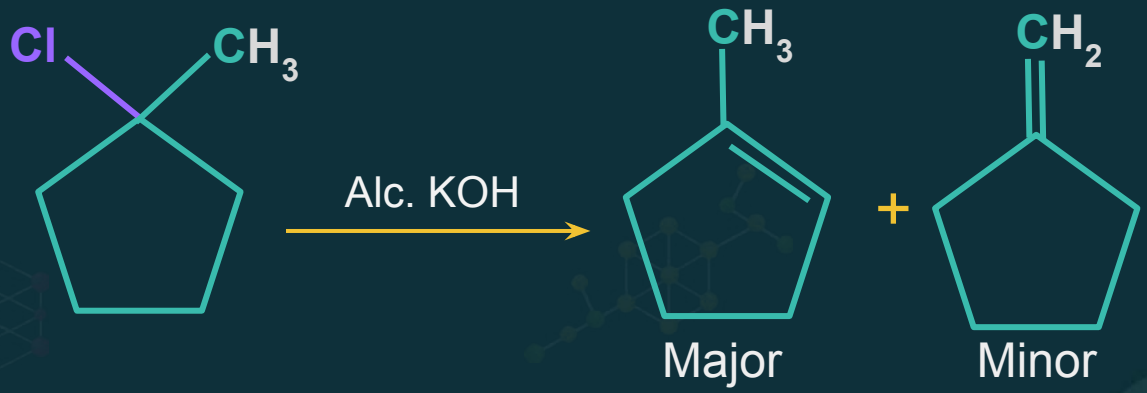
Hence, option (c) is the correct answer.

Major product (X) for the following reaction is:



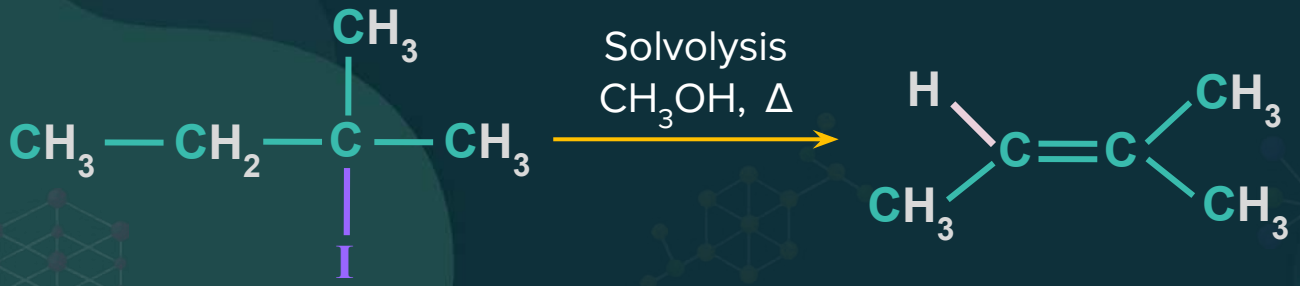
Solution

1-Methylcyclopentene is the major product and 1-methylenecyclopentane is the minor product. This is an example of an E2 elimination reaction.



Unimolecular Reaction

E1 reaction is a two step process. The **rate-determining step (RDS)** is ionisation of the substrate to give a **carbocation** that rapidly loses a β-proton to a base, usually the solvent.



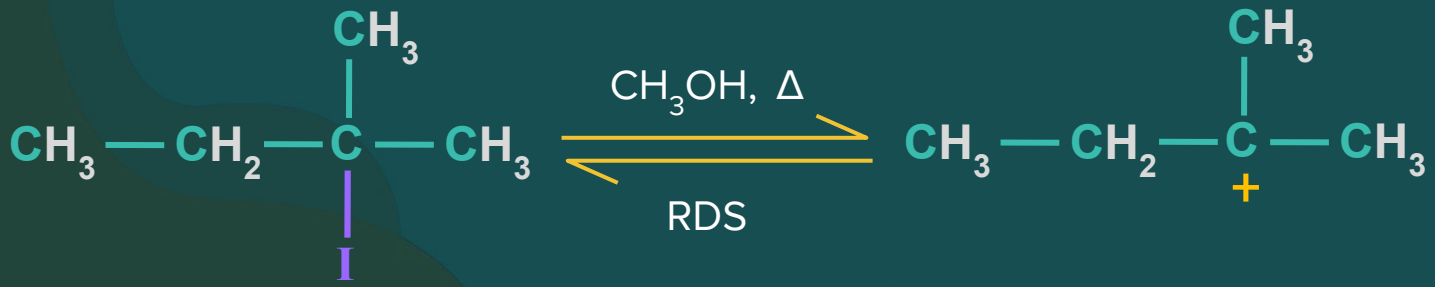
Mechanism of E1 Reaction

Step 1 Formation of carbocation

Step 2 Attack of base

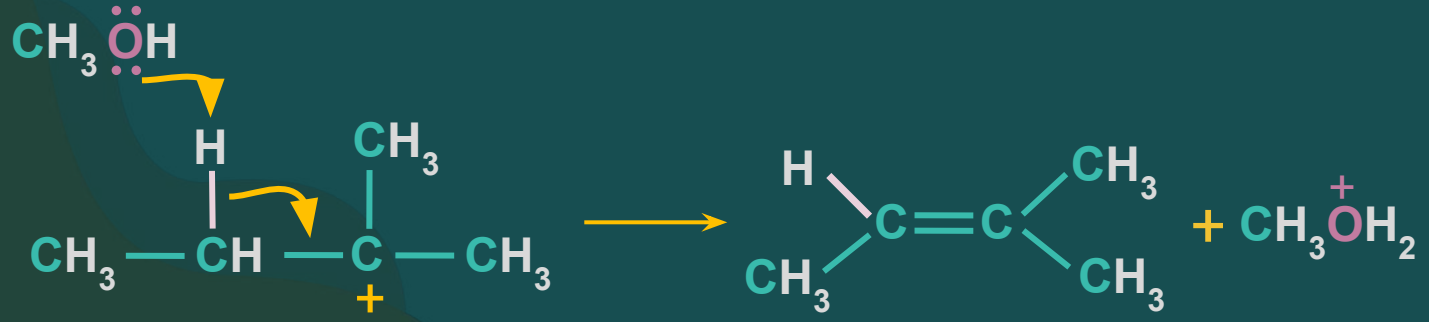
Mechanism of E1 Reaction

Step 1: Formation of carbocation



Mechanism of E1 Reaction

Step 2: Attack of base



Characteristics of E1 Reaction

01

It is **unimolecular**, **two-step** process.

02

The reaction intermediate is carbocation, so **rearrangement** is possible.

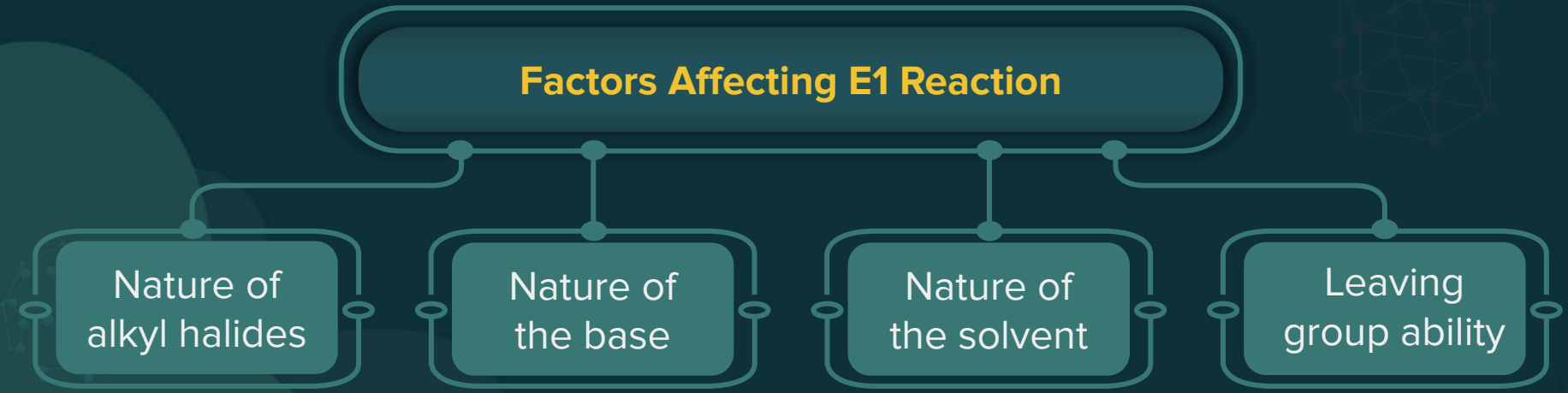
03

Rate of reaction $\propto$ Stability of **carbocation**

04

Rate $\propto$ [Alkyl halide]

Factors Affecting E1 Reaction



Factors Affecting E1 Reaction

Nature of alkyl halide

E1 reactivity

1° Alkyl halide < 2° Alkyl halide < 3° Alkyl halide

Nature of base

Rate of E1 reaction is **unaffected** by the **concentration** of the base.

Weak base favours **E1** reaction.

Factors Affecting E1 Reaction

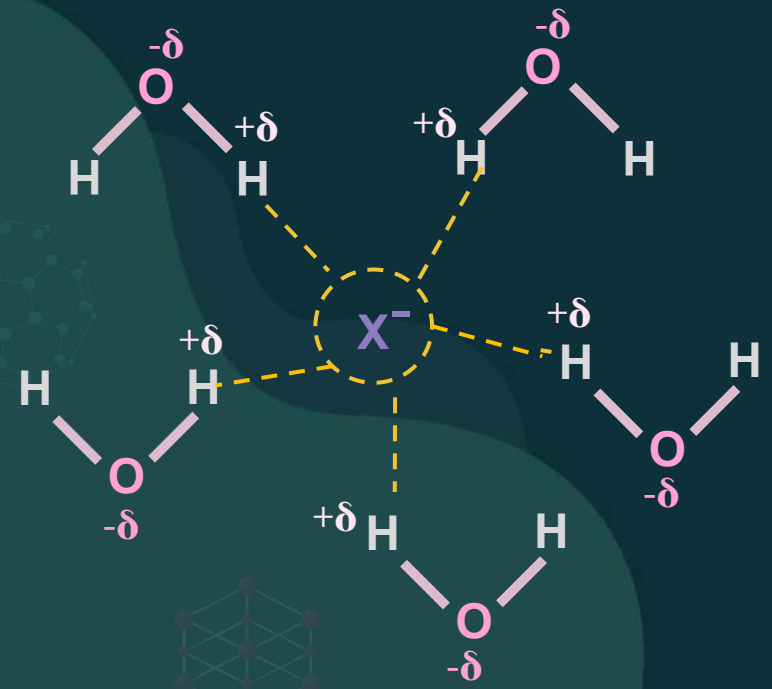
Nature of solvent

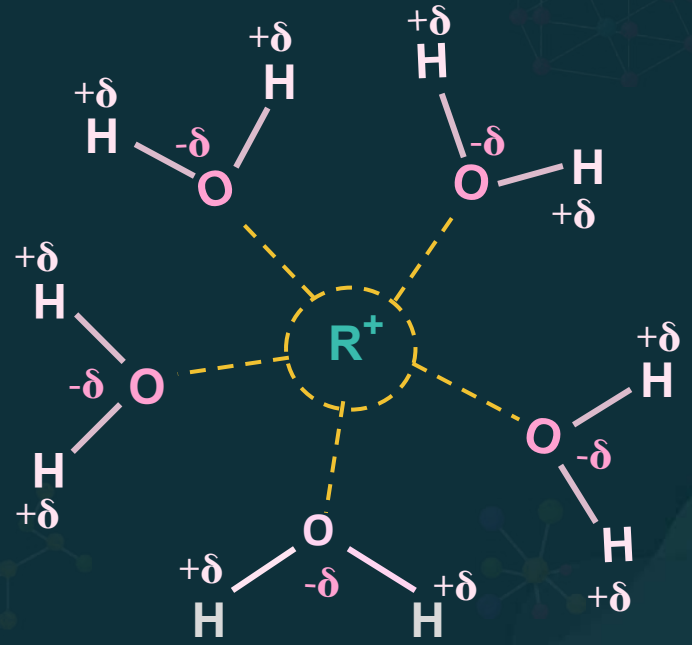
The use of a **polar protic solvent** will greatly **increase** the rate of carbocation formation of an alkyl halide in any E1 reaction because of its ability to **solvate cations and anions** effectively.

$$R{-}X \rightleftharpoons R^{+} + X^{-}$$

Factors Affecting E1 Reaction

Nature of solvent





Factors Affecting E1 Reaction

Leaving group ability

In an E1 reaction, the leaving group begins to acquire a **negative charge**.

The stabilisation of this developing negative charge on the leaving group **increases** the rate of reaction.

Relative **reactivities** of alkyl halides

R-I > R-Br > R-Cl > R-F

E1 vs S_N1 Reaction

E1 and **S_N1** respond in **similar ways** to the factors affecting reactivities because both the reactions proceed through the formation of a **carbocation**.

Increasing the **temperature** of the reaction favours reaction by the **E1 mechanism** at the expense of the **S_N1 mechanism**.

Select the correct statement for an E1 reaction.

a) It is a two-step process

b) Rearrangement is possible

c) Good leaving groups are favoured

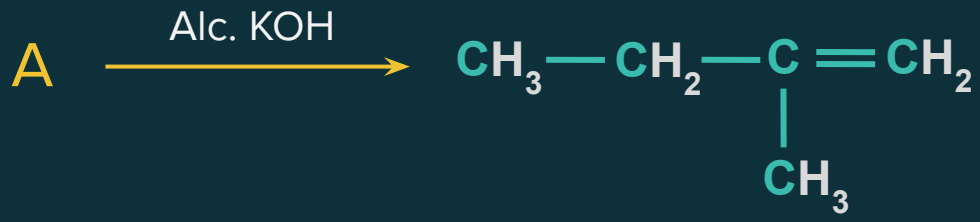
d) All of these

Solution

E1 reaction is a two-step process and here rearrangement is possible and also good leaving groups are favoured.

Therefore, option (d) is the correct answer.

Which alkyl chloride (A) would yield the following pure alkene on reaction with alcoholic KOH?



Solution

CH_3-CH_2-$CH(CH_3)$-CH_2Cl on reaction with alc. KOH will produce CH_3-CH_2-$C(CH_3)$=CH_2 as the product.

The intermediate of E2 reaction is:

a) Carbocation

b) Carbanion

c) Free radical

d) Intermediate is not formed

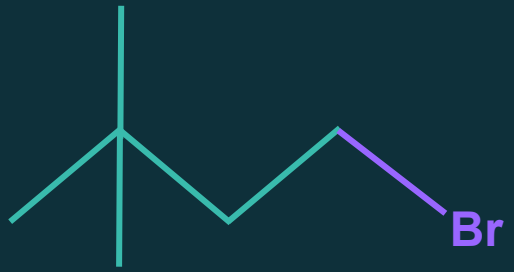
Solution

E2 mechanism is a single step process, so only transition state is formed in E2 reaction but no intermediate is there.

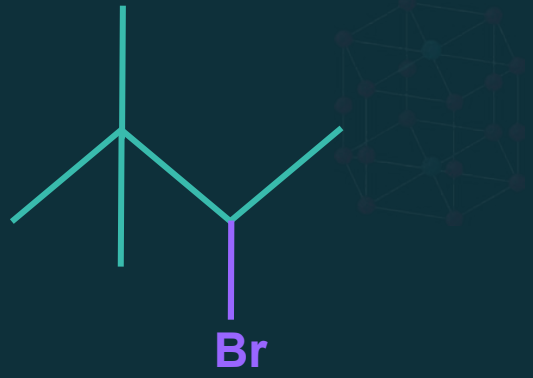
Thus, option (d) is the correct answer.

Which of the following cannot undergo E2 reaction?

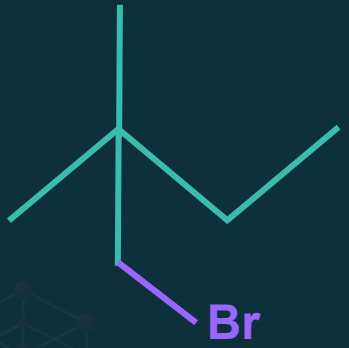
a)



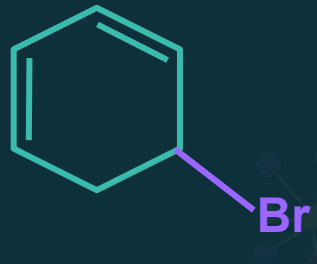
b)



c)



d)



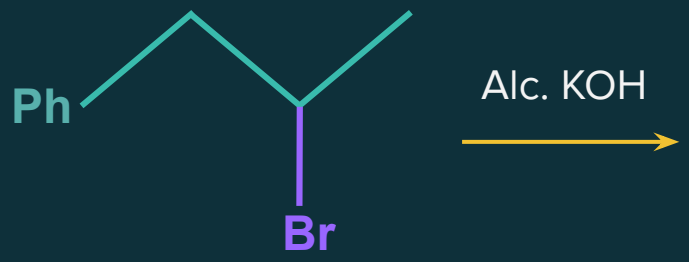
Solution

For E2 reaction to be followed there must be β-hydrogen present with respect to the halide in the molecule.

Option a) It has 2 β-hydrogens and hence E2 reaction is possible.
Option b) It also has β-hydrogen and hence E2 reaction is possible.
Option c) It do not have any β-hydrogen and hence no E2 reaction is possible.
Option d) E2 reaction is possible due to presence of β-hydrogen.

Thus option (c) is the correct answer.

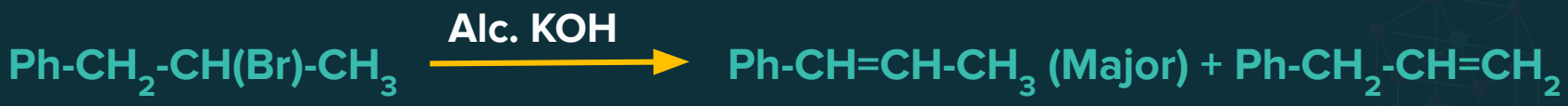
The total number of possible alkenes in the given elimination reaction is:



Solution

E2 reaction takes place when there are **β-hydrogens** present in the reactant, Here there are two type of beta hydrogens.

Two products are possible by removal of either hydrogen atom.



Major product is **Ph-CH=CH-CH$_3$** due to increased stability by conjugation of double bond with benzene ring.

Ph-CH$_2$-CH=CH$_2$ is a minor product.

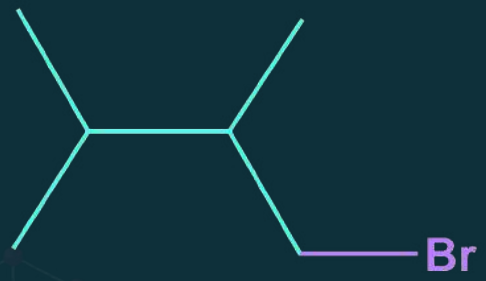
Ph-CH=CH-CH$_3$ can be **trans as well as cis** alkene showing geometrical isomerism. Hence, **3 possible alkenes** can be formed in the given elimination reaction.

Which of the following gives the fastest reaction with EtOH?

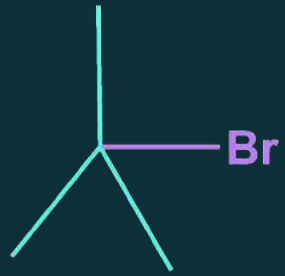
a)

b)

c)



d)



Solution

EtOH is neither a strong nucleophile, nor a strong base and hence **S_N2 or E2** is not possible. So, **S_N1 or E1** can be followed. In both cases, first step is formation of carbocation.

The one which can give the most **stable carbocation** will give fastest reaction. In options **(a), (b) and (c), primary carbocation** is formed while **tertiary carbocation is formed in option (d)** which is most stable and hence will give the fastest reaction.

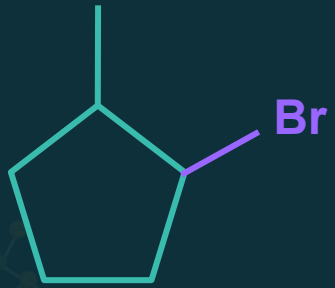
Thus, option (d) is the correct answer.

Major final product (Z) is:

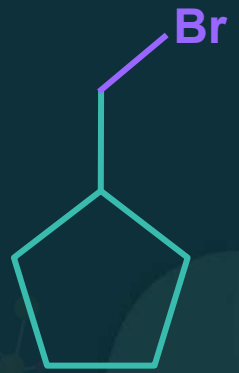
a)

b)

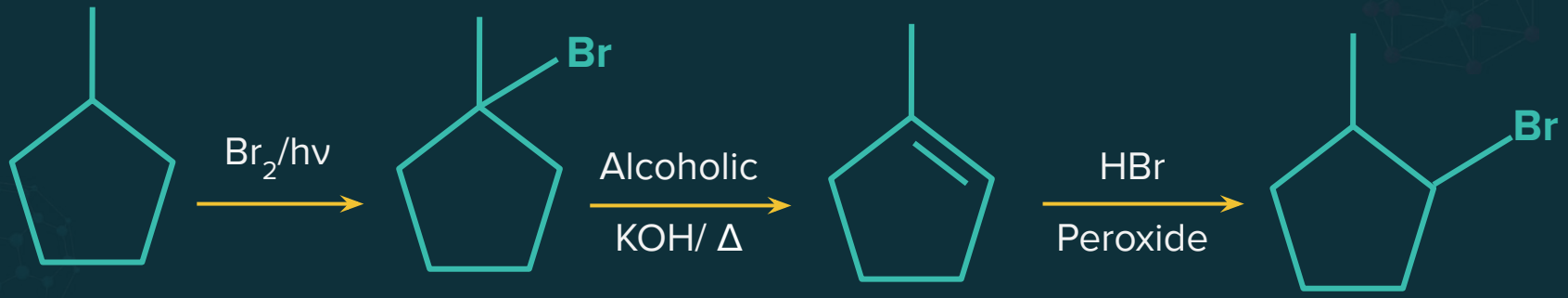
c)



d)



Solution



Anti-Markovnikov product

Thus, option (c) is the correct answer.

Reactivity order of halides for dehydrohalogenation is:

a) R-F > R-Cl > R-Br > R-I

b) R-I > R-Br > R-Cl > R-F

c) R-I > R-Cl > R-Br > R-F

d) R-F > R-I > R-Br > R-Cl

Solution

In dehydrohalogenation reaction, RI is most reactive as iodide is the best leaving group among the given halides. Order of leaving group is: $\mathbf{I^- > Br^- > Cl^- > F^-}$. Hence the order of reactivity of halides is: **R–I > R–Br > R–Cl > R–F**.

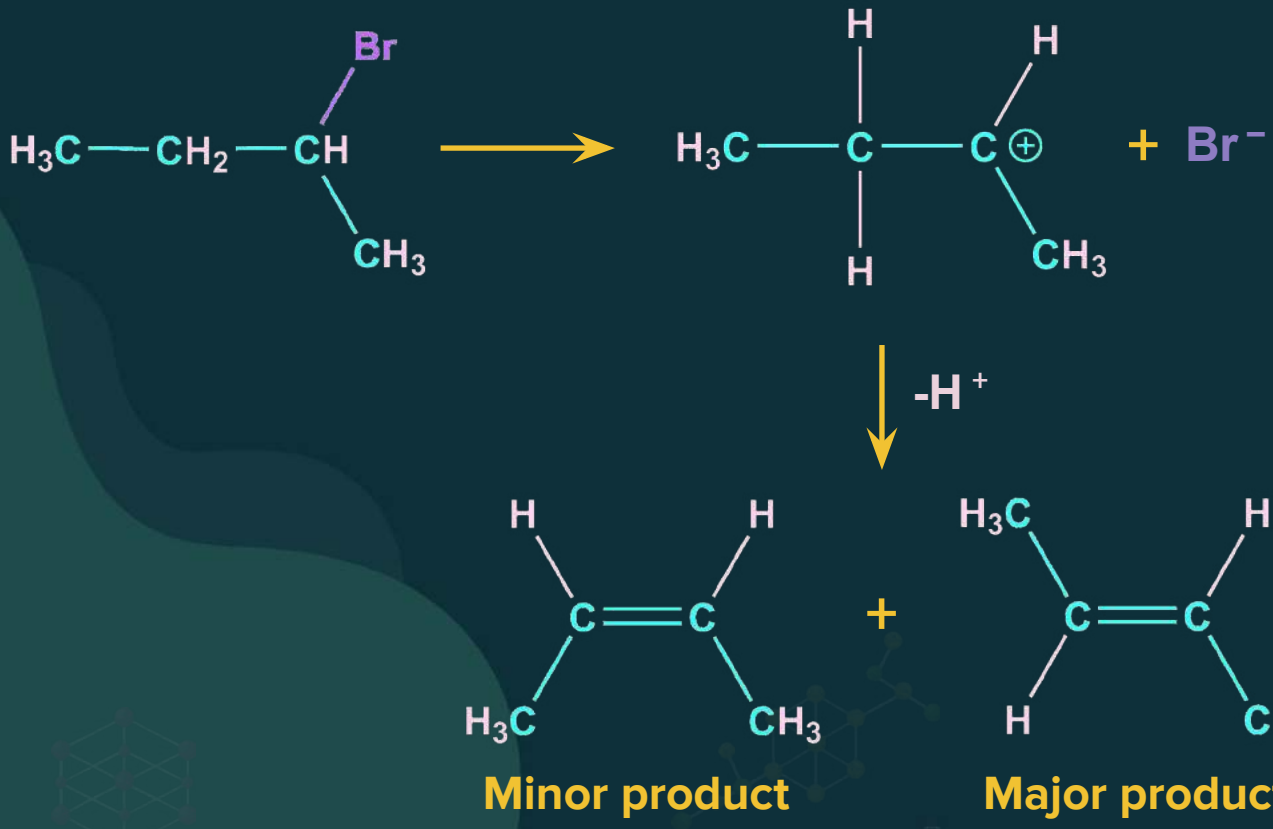
Thus, option (b) is the correct answer.

Stereochemistry of E1 Reaction

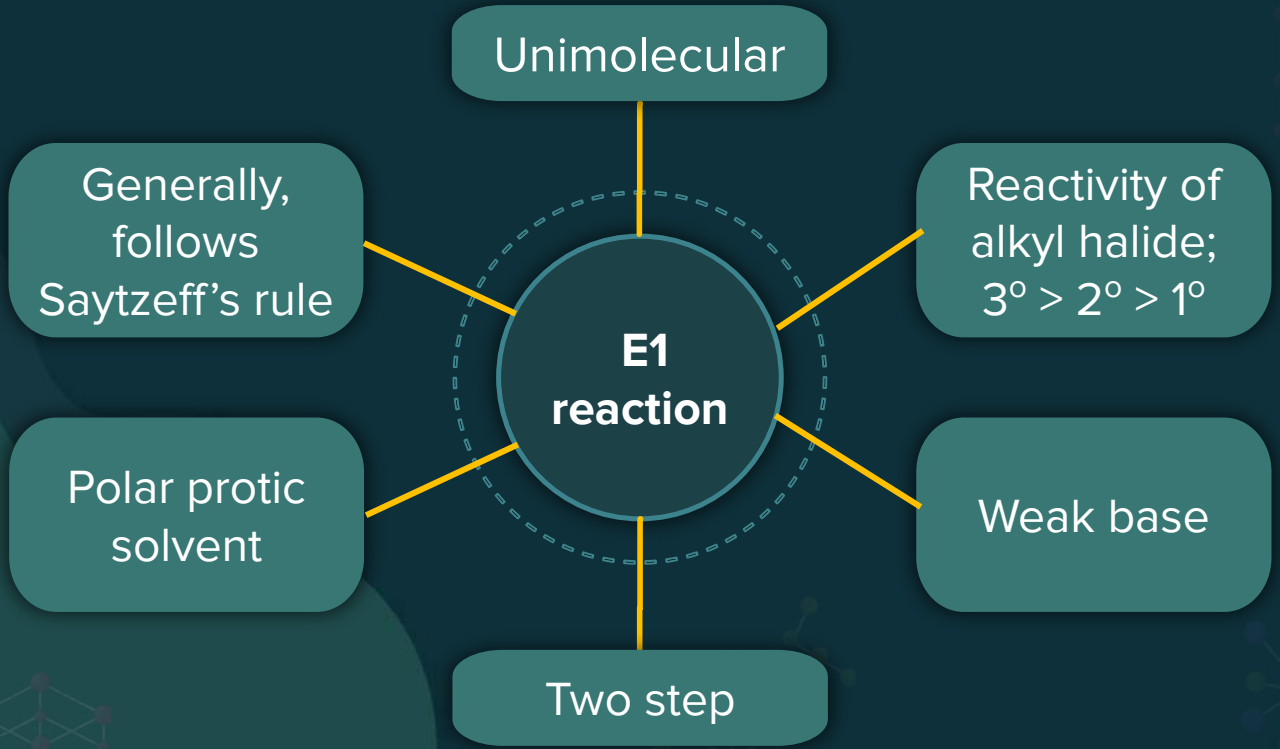
For steric reasons, **trans-alkenes** are usually **lower in energy** than cis-alkenes because the substituents are far apart from one another.

E1 reactions **favour** the formation of trans-alkenes.

Stereochemistry of E1 Reaction



Quick Recap of E1 Reaction



Elimination reaction of 2-bromopentane to form pent-2-ene is:

(A) ***β***-Elimination reaction

(B) Follows Saytzeff's rule

(C) Dehydrohalogenation

(D) Dehydration reaction

a) (A), (B), (C)

b) (A), (C), (D)

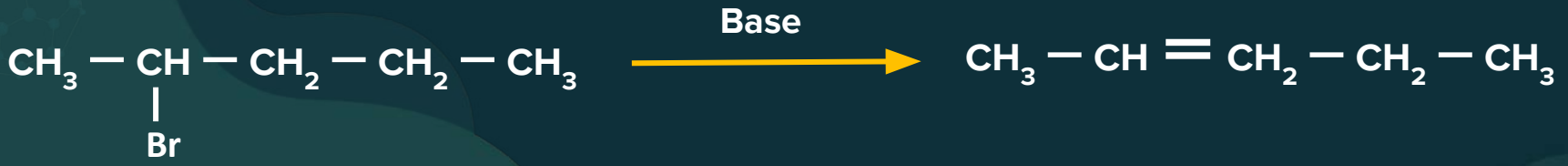
c) (B), (C) ,(D)

d) (A), (B), (D)

Solution

We have two type of β-hydrogens in 2-bromopentane. The one which leads to more substituted alkene is removed. So, it is a ***β*-elimination reaction and is forming Saytzeff's product**.

This is result of **dehydrohalogenation (removal of HX)** and not **dehydration (removal of water molecule).**



Thus, option (a) is the correct answer.

Intermediate of E1 reaction is:

a) Carbocation

b) Carbanion

c) Free radical

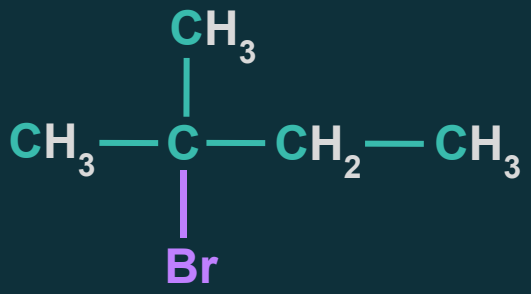
d) Intermediate is not formed

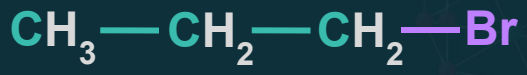
Solution

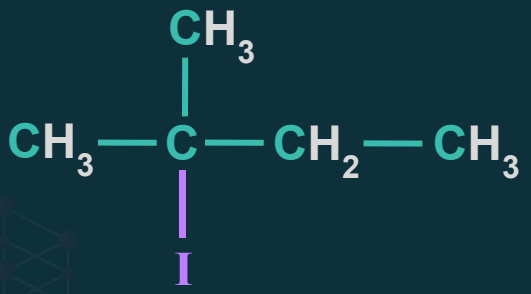
The intermediate formed in E1 reactions is carbocation and hence rearrangement is possible.

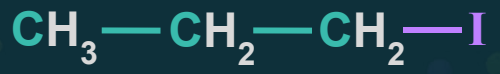
Thus, option (a) is the correct answer.

Which one of the following compounds most readily undergoes E1 reaction?

a) 

b) 

c) 

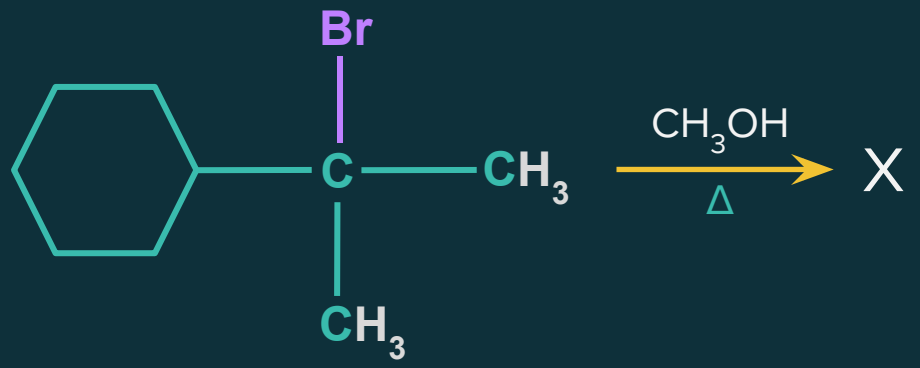
d) 

Solution

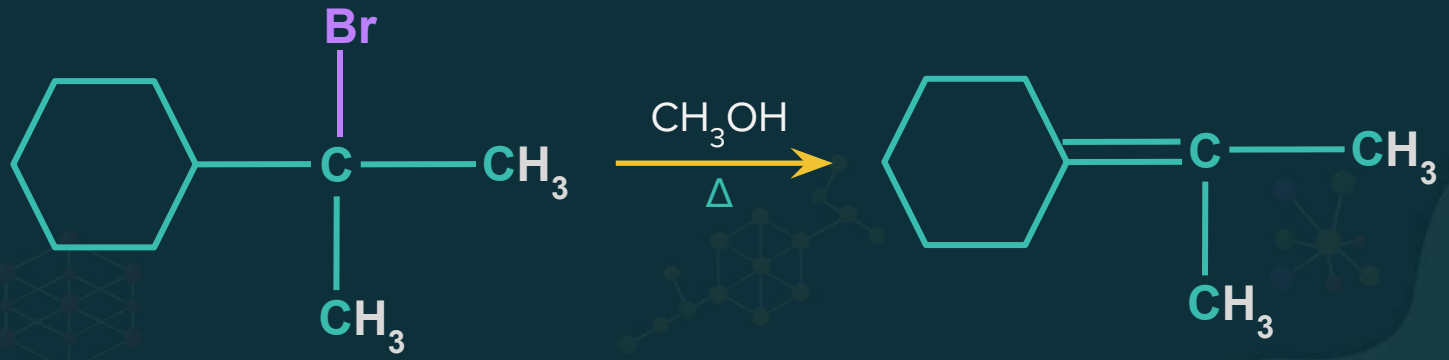
Option (a) is **tertiary bromide** compound which has bromine as leaving group.
Option (b) will lead to **primary carbocation** which is not favoured in E1.
Option (c) gives **tertiary carbocation** with iodine as leaving group.
Option (d) will lead to **primary carbocation** which is not favoured in E1 (less stable).
As iodine is the better leaving group and tertiary is more stabilised carbocation, so option (c) will most readily undergoes to E1 reaction.

Thus, option (c) is the correct answer.

In the given reaction, the major product [X] is:



Solution

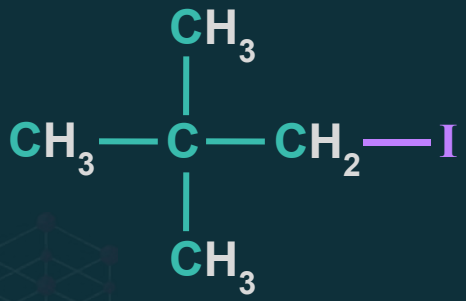


Which of the following substrates shows E1 reaction?

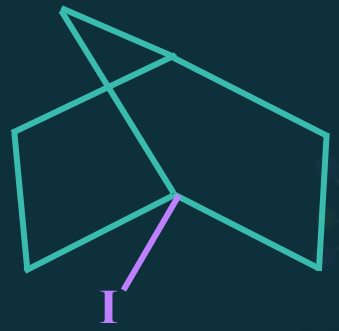
a) CH_3CH_2I

b)

c)



d)



Solution

Compound in option (a) will lead to primary carbocation. Hence not favoured for E1.
Compound in option (b) is benzylic halide and no E1 elimination will be possible.
In option (c), the carbocation formed is primary which can be rearranged to a more stable tertiary carbocation.
In option (d), there will be no formation of double bond at bridgehead carbon due to higher instability (Bredt's rule).

Thus, option (c) is the correct answer.

Elimination vs Substitution

All **nucleophiles** are potential bases and all **bases** are potential nucleophiles.

The reactive part of both nucleophiles and bases is an **unshared electron** pair.

Nucleophilic substitution reactions and **elimination** reactions often **compete with each other.**

Elimination vs Substitution

At first, we must decide whether the reaction conditions favour **S_N2/ E2** or **S_N1/ E1** reactions.

The conditions that favour **S_N2** reaction also favour an **E2 reaction,** and the conditions that favour **S_N1** reaction also favour an **E1 reaction**.

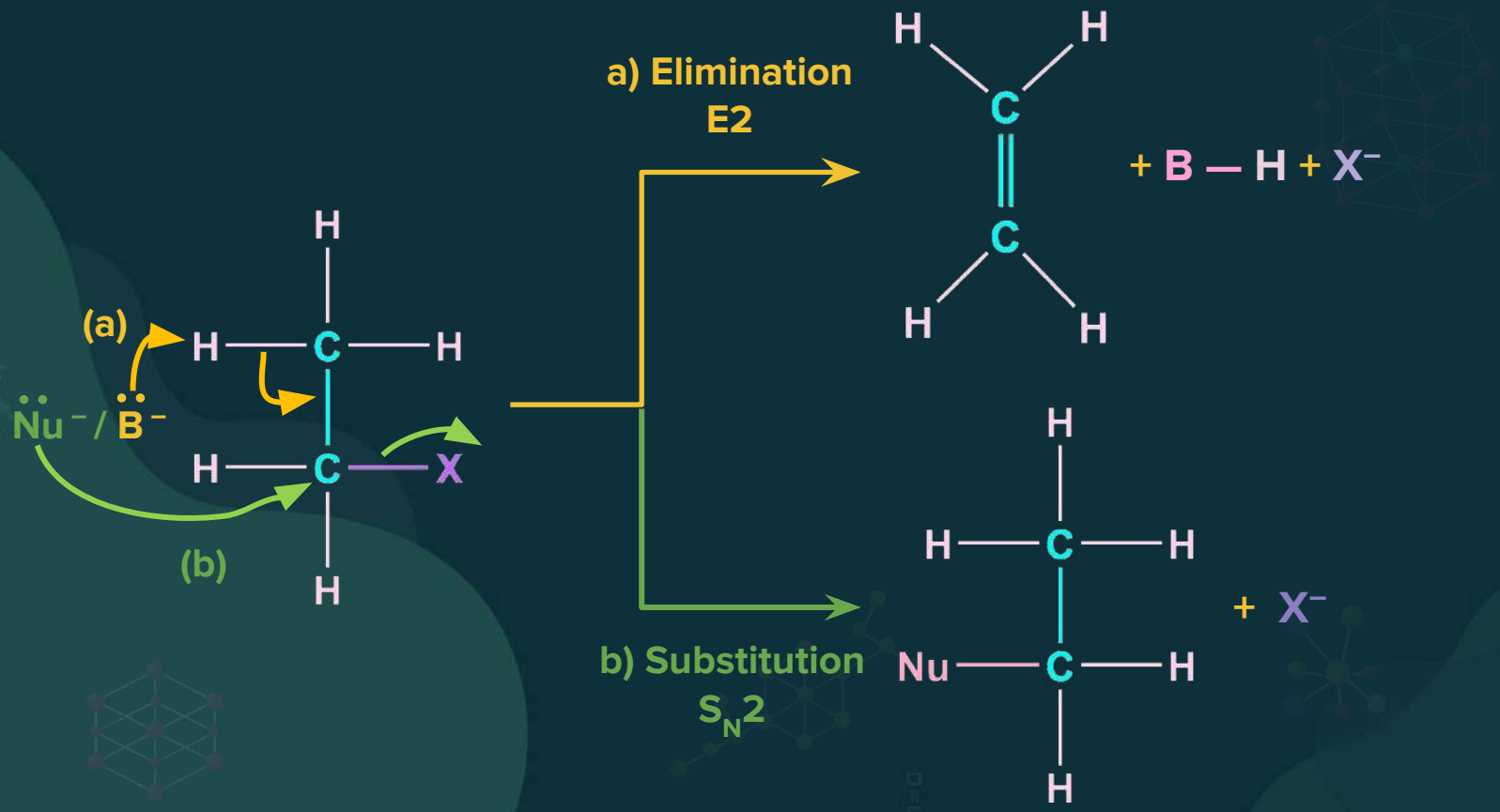
Elimination vs Substitution

Both **S_N2** and **E2** reactions are both favoured by a **high concentration** of a strong nucleophile or a base.

The base attacks a **β-hydrogen atom** and leads to **elimination**.

The nucleophile attacks the **C atom** bearing the leaving group, and leads to **substitution.**

Elimination vs Substitution



Factors Affecting Elimination & Substitution

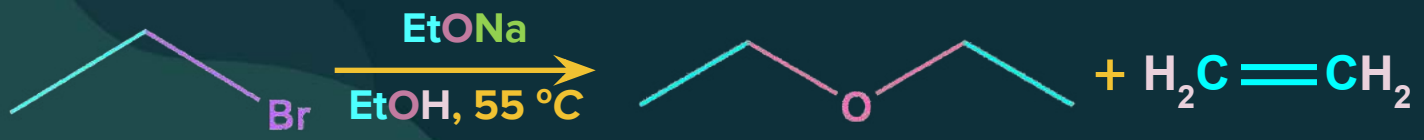
1. Relative **steric hindrance** of the substrate
2. Temperature
3. **Size** of the base/nucleophile

Factors Affecting Elimination & Substitution

Primary alkyl halide

The substrate is a **primary unhindered alkyl halide** and the **base** is strong and unhindered like **ethoxide ion.**

Substitution is highly favoured because the base can easily approach the carbon bearing the leaving group.



S_N2 major (90%)

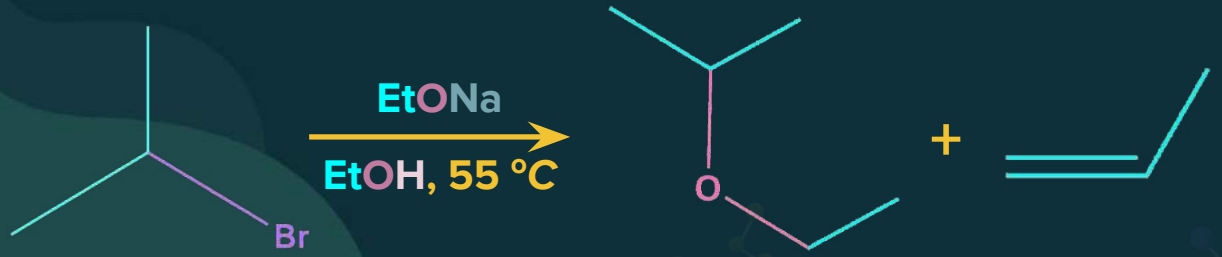
E2 minor (10%)

Factors Affecting Elimination & Substitution

Secondary alkyl halide

Secondary alkyl halides with a strong base favours **elimination.**

Steric hindrance in the substrate makes substitution **more difficult.**



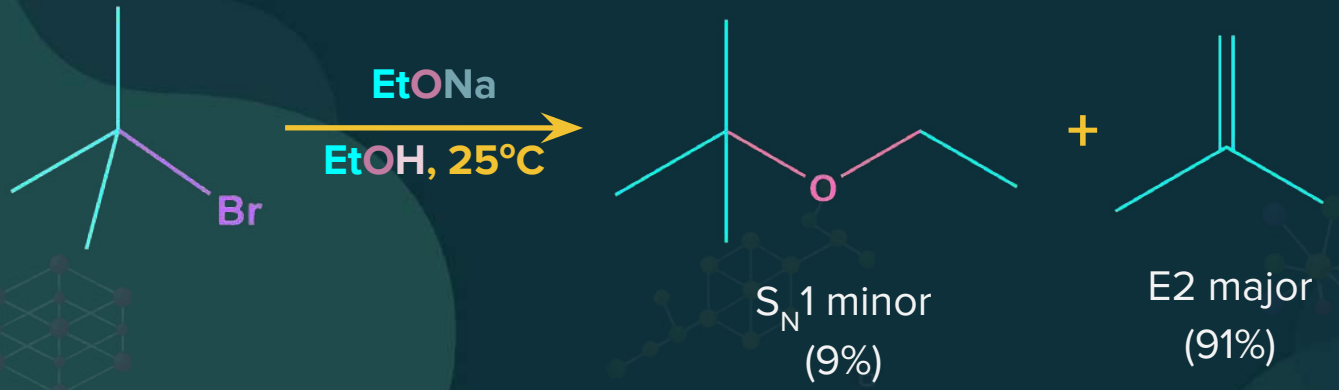
S_N2 minor (21%)

E2 major (79%)

Factors Affecting Elimination & Substitution

Tertiary alkyl halide

With tertiary alkyl halides, **steric hindrance** in the substrate is severe, therefore **elimination** is highly **favoured**.



Factors Affecting Elimination & Substitution

Effect of temperature

Increasing the temperature of the reaction favours elimination over substitution.

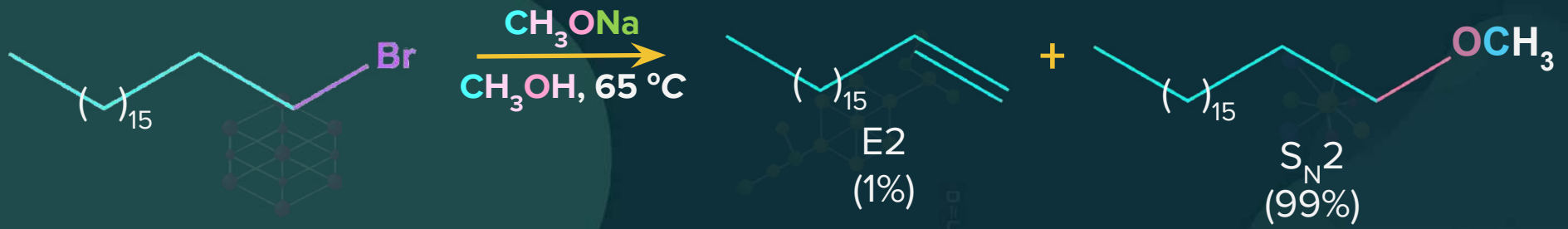
Factors Affecting Elimination & Substitution

Size of the base/nucleophile

Strong sterically hindered base/nucleophile such as the tert-butoxide ion

Favours **elimination reaction**

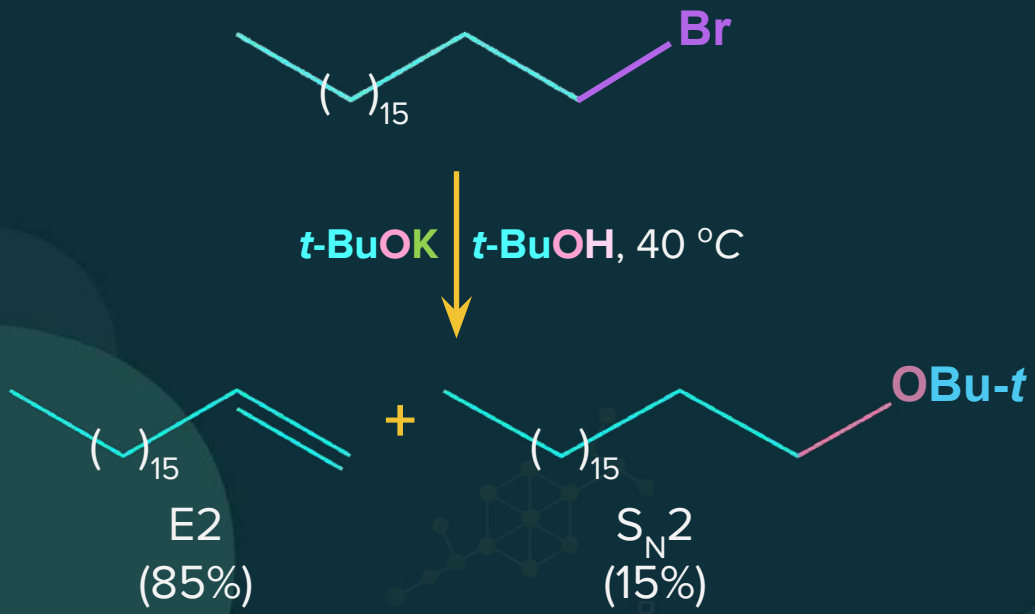
Unhindered (small) base/nucleophile



Factors Affecting Elimination & Substitution

Size of the base/nucleophile

Hindered base/nucleophile



S_N1 vs E1

E1 and **S_N1** reactions proceed through the formation of a common intermediate (carbocation).

Therefore, both the types of reactions **respond** to the factors affecting reactivity **in a similar way**.

S_N1 vs E1

Both E1 and S_N1 are favoured with:

Substrates that can form **stable carbocations** (E.g., tertiary halides)

The use of **poor nucleophiles** (weak bases) and **polar protic solvents**.

Increasing the temperature of the reaction **favours reaction by E1** mechanism at the expense of S_N1 mechanism.

Elimination vs Substitution

Methyl	1° Alkyl halide
Gives **S_N2** reactions **only**	Gives **mainly S_N2** except with a hindered strong base [E.g., *t*-BuO^-], and then gives E2.

Elimination vs Substitution

2° Alkyl halide	3° Alkyl halide
Gives mainly **S_N2** with **weak basic nucleophiles** (E.g., I^-,CN^-, RCO_2^-) and mainly **E2** with **strong bases** (E.g., RO^-)	**No S_N2** reaction. In solvolysis, it gives **S_N1/E1**, and at lower temperatures, it favours S_N1. When a strong base (E.g., RO^-) is used, E2 predominates.

Which of the following statements is correct?

a) E2 elimination are favoured by weak base.

b) The first step in both S_N1 and E2 reactions is the same.

c) S_N2 reaction proceeds with total retention of configuration.

d) Bridgehead halide are inert for both S_N1 and S_N2 reactions.

Solution

Option a) E2 elimination are favoured by weak base is incorrect as E2 elimination is favoured by strong base.

Option b) The first step in both S_N1 and E2 reactions is the same is incorrect because the first step in both S_N1 and E1 reactions is the same not E2.

Option c) S_N2 reaction proceeds with total retention of configuration is incorrect as we get inversion of configuration.

Option d) Bridgehead halides are inert for both S_N1 and S_N2 reactions: On bridge head carbon formation of carbocation is not possible due to instability (Bredt's rule) so no S_N1 reaction and also as the ring is closed so no backside attack is possible i.e. no S_N2 reaction.

Thus, option (d) is the correct answer.

Which of the following statements is incorrect for alkyl halide?

a) E1 reactions are favoured by the use of weak bases and polar protic solvents.

b) Both E1 and S_N1 are favoured with substrates that can form stable carbocations.

c) In an unimolecular reaction, increasing the temperature favours E1 mechanism.

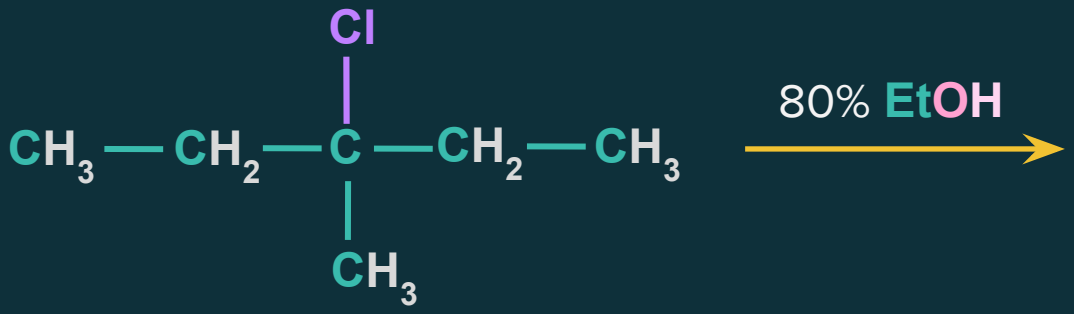
d) A strong sterically hindered base such as tert-butoxide ion favours substitution reaction.

Solution

A strong sterically hindered base such as tert-butoxide ion favours elimination reaction. So, option (d) is incorrect statement for alkyl halide.

Thus, option (d) is the correct answer.

What is correct regarding the following reaction?



a) The major product is given by S_N1 reaction.

b) Three alkenes are formed through E1 mechanism.

c) 3-Methylpentan-3-ol is also formed as one of the product.

d) All of these

Solution

Option a): The Alkyl halide is tertiary and poor nucleophile i.e. ROH so S_N1 reaction is favoured, Option a) is correct.

Option b): When we proceed via elimination mechanism there is a formation of carbocation, we get three alkenes: 2-ethylbut-1-ene, cis 3-methylpent-2-ene, trans 3-methylpent-2-ene. so option b) is correct.

Option c): We have 20% water in this so 3-methylpentan-3-ol will be formed as water is also a nucleophile, So option c) is also correct.

Thus, option (d) is the correct answer.

Which mechanism has a different reactivity order of alkyl halides (1^o, 2^o, 3^o) than others?

a) S_N1 b) S_N2 c) E1 d) E2

Solution

S_N1 reactivity: 1^0 Alkyl halide < 2^0 Alkyl halide < 3^0 Alkyl halide

S_N2 reactivity: 3^0 Alkyl halide < 2^0 Alkyl halide < 1^0 Alkyl halide

E1 reactivity: 1^0 Alkyl halide < 2^0 Alkyl halide < 3^0 Alkyl halide

E2 reactivity: 1^0 Alkyl halide < 2^0 Alkyl halide < 3^0 Alkyl halide

Thus, option (b) is the correct answer.

Which of the following is an example of S_N2 reaction?

a) $CH_3—Br + OH^- \longrightarrow CH_3—OH + Br^-$

b) $(CH_3)_3C—Br + OH^- \longrightarrow (CH_3)_3COH + Br^-$

c) $HO—CH_2—CH_3 \xrightarrow{-H_2O} CH_2=CH_2$

d) None of these

Solution

Option a) CH_3-Br + OH^- $\longrightarrow$ CH_3-OH + Br^- : It will follow S_N2 mechanism.

Option b) $(CH_3)_3$C-Br + OH^- $\longrightarrow$ $(CH_3)_3$ C-OH + Br^-: It will follow S_N1 mechanism as the halide is tertiary.

Option c) OH-CH_2-CH_3 $\longrightarrow$ CH_2=CH_2 + H_2O : This proceed via elimination.

Thus, option (a) is the correct answer.

Reaction of t-butyl bromide with sodium methoxide produces:

a) Sodium t-butoxide

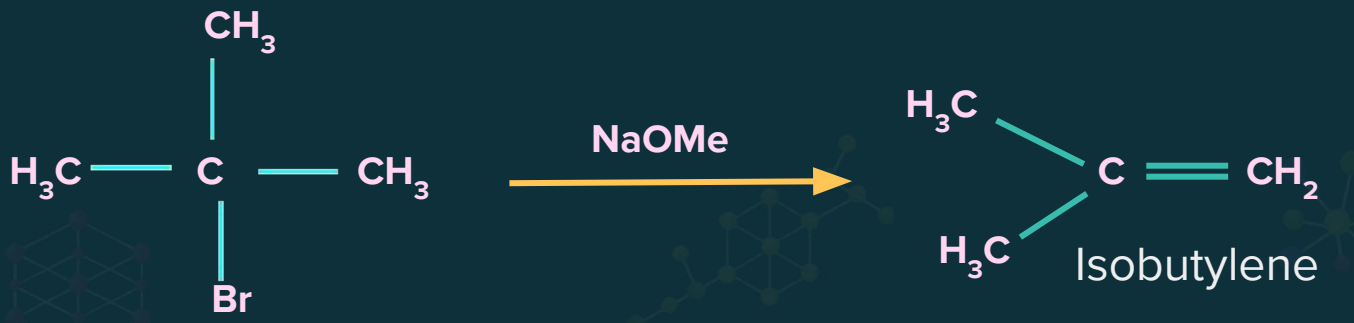
b) t-Butyl methyl ether

c) Isobutane

d) Isobutylene

Solution

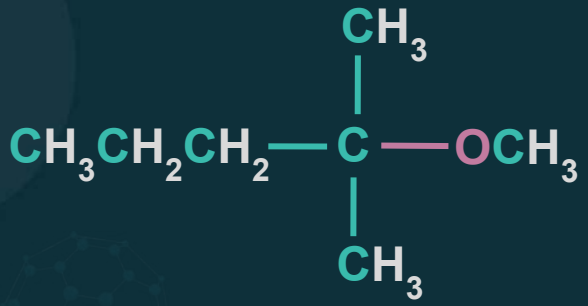
Reaction of t-butyl bromide with sodium methoxide produces isobutylene.



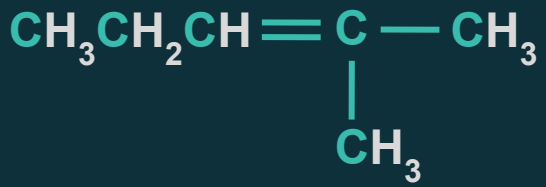
t-Butyl bromide is a tertiary halide, when it reacts with sodium methoxide which is a strong base we get isobutylene as the elimination reaction is favoured.

Thus, option (d) is the correct answer.

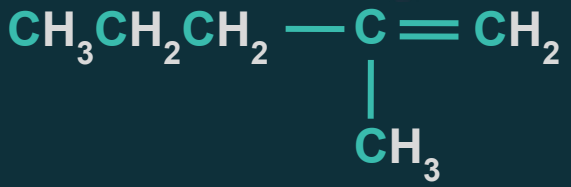
2-Chloro-2-methylpentane on reaction with sodium methoxide in methanol yields:



(1)



(2)



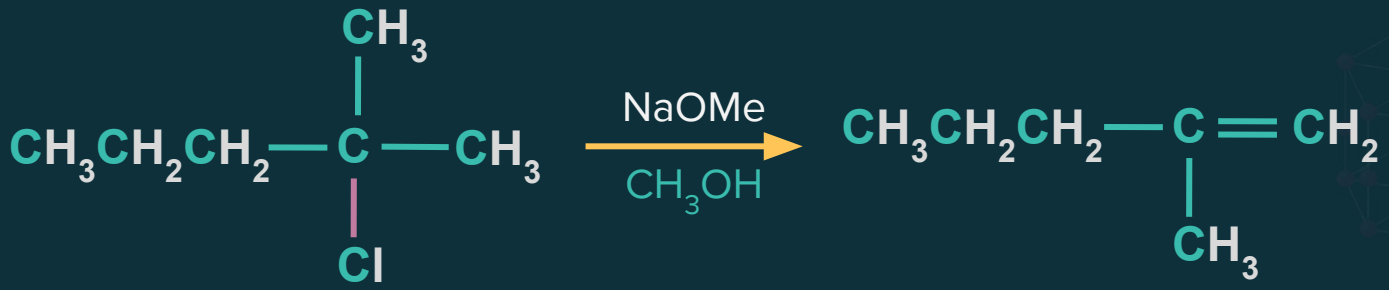
(3)

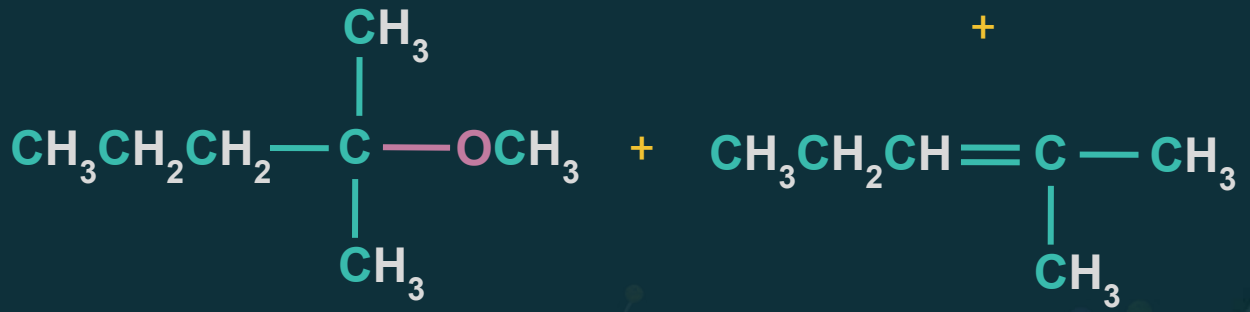
a) (1) and (3)

b) (3) only

c) (1) and (2)

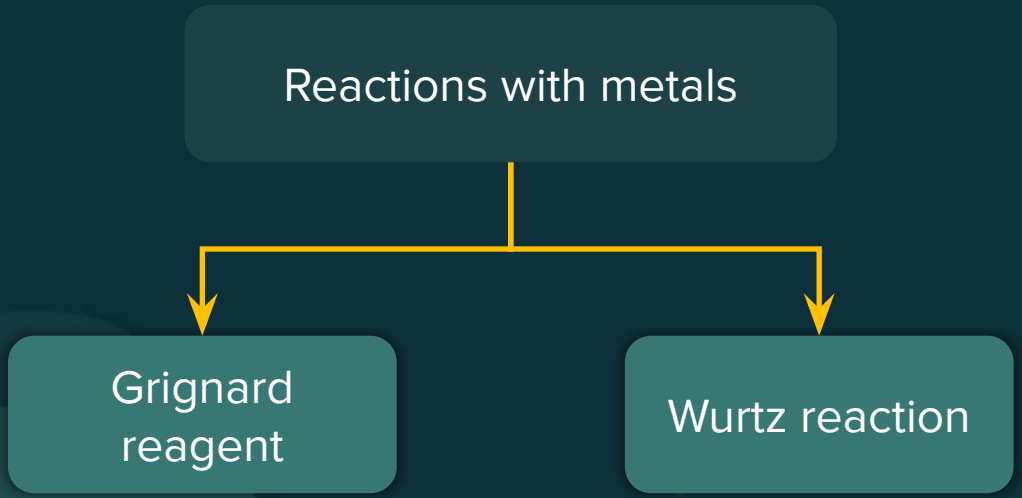
d) All of these





Thus, option (d) is the correct answer.

Reactions with Metal



Organometallic Compounds

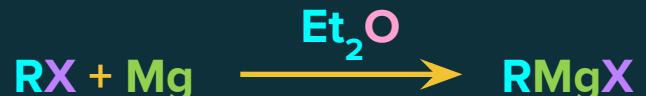
Compounds that contain **carbon–metal** bonds

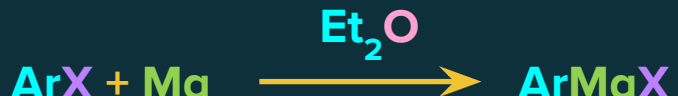
Organomagnesium halides were discovered by the French chemist **Victor Grignard** in **1900**.

Organometallic Compounds

Preparation

Grignard reagents are prepared by the reaction of an **organic halide with magnesium metal** in an anhydrous ether solvent.



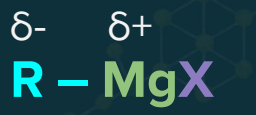


Grignard reagent → **RMgX**

Organometallic Compounds

Structure

The **C-Mg bond** in Grignard reagents is predominantly **covalent** and less ionic.



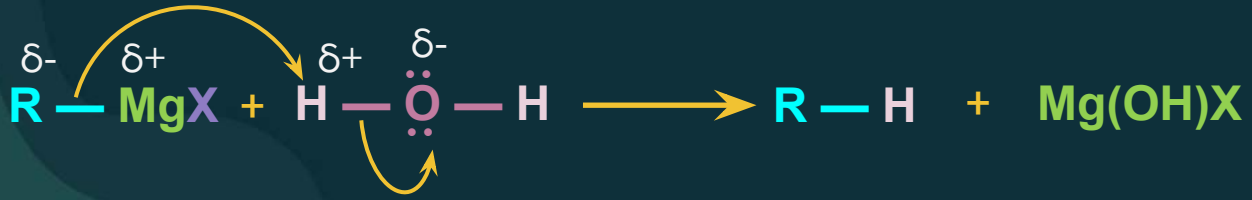
Reaction of Grignard Reagent

Grignard reagents are **very strong bases**.

They react with any compound that has a **hydrogen atom** attached to an electronegative atom such as oxygen, nitrogen, or sulphur.

Reaction of Grignard Reagent

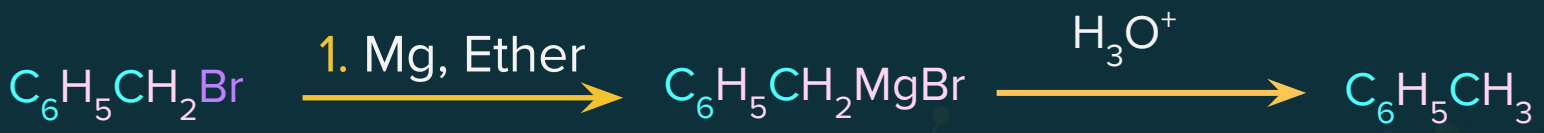
The reactions of Grignard reagents with water and alcohols are **acid–base reactions**.



In the following reaction, the product 'X' is:

a) $C_6H_5CH_2OCH_2C_6H_5$ b) $C_6H_5CH_2OH$ c) $C_6H_5CH_3$ d) $C_6H_5CH_2CH_2C_6H_5$

Solution



Thus, option (c) is the correct answer.

Grignard reagent is prepared by the reaction between:

a) Magnesium and alkane

b) Magnesium and aromatic hydrocarbon

c) Zinc and alkyl halide

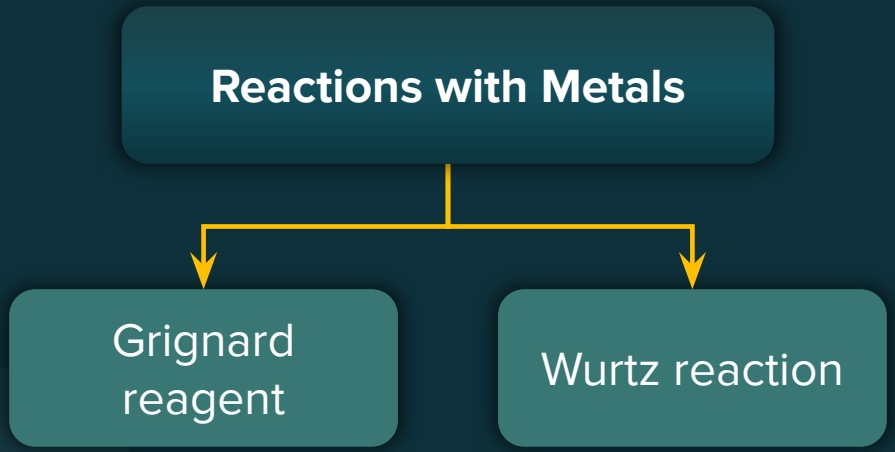
d) Magnesium and alkyl halide

Solution

Grignard reagents are prepared by the reaction of an organic halide with magnesium metal in an anhydrous ether solvent.

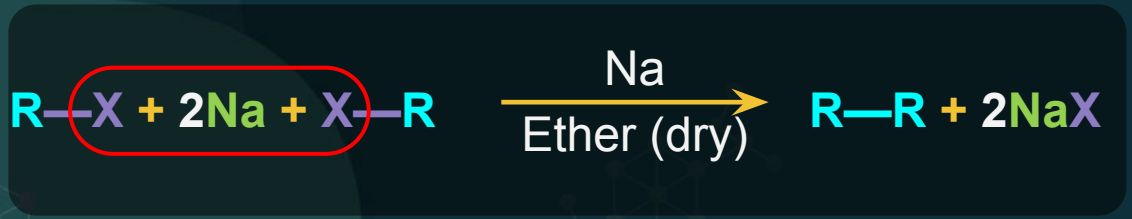
Thus, option (d) is the correct answer.

Reactions with Metal



Wurtz Reaction

In this method **two moles** of alkyl halides are treated with '**Na**' metal in dry ether for preparation of higher alkanes from **1° or 2° alkyl halides**.



Which of the following alkane cannot be made in good yield by Wurtz reaction?

a) 2,3-Dimethylbutane

b) Heptane

c) Isobutyl chloride

d) Butyl chloride

Solution

Wurtz reaction cannot be used for the preparation of unsymmetrical alkanes because if two dissimilar alkyl halides are taken as the reactants, then a mixture of alkanes is obtained as the products. Therefore heptane cannot be made in good yield by Wurtz reaction.

Hence, option (b) is the correct answer.

An organic compound A (C_4H_9Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative, then A is:

a) tert-Butyl chloride

c) Isobutyl chloride

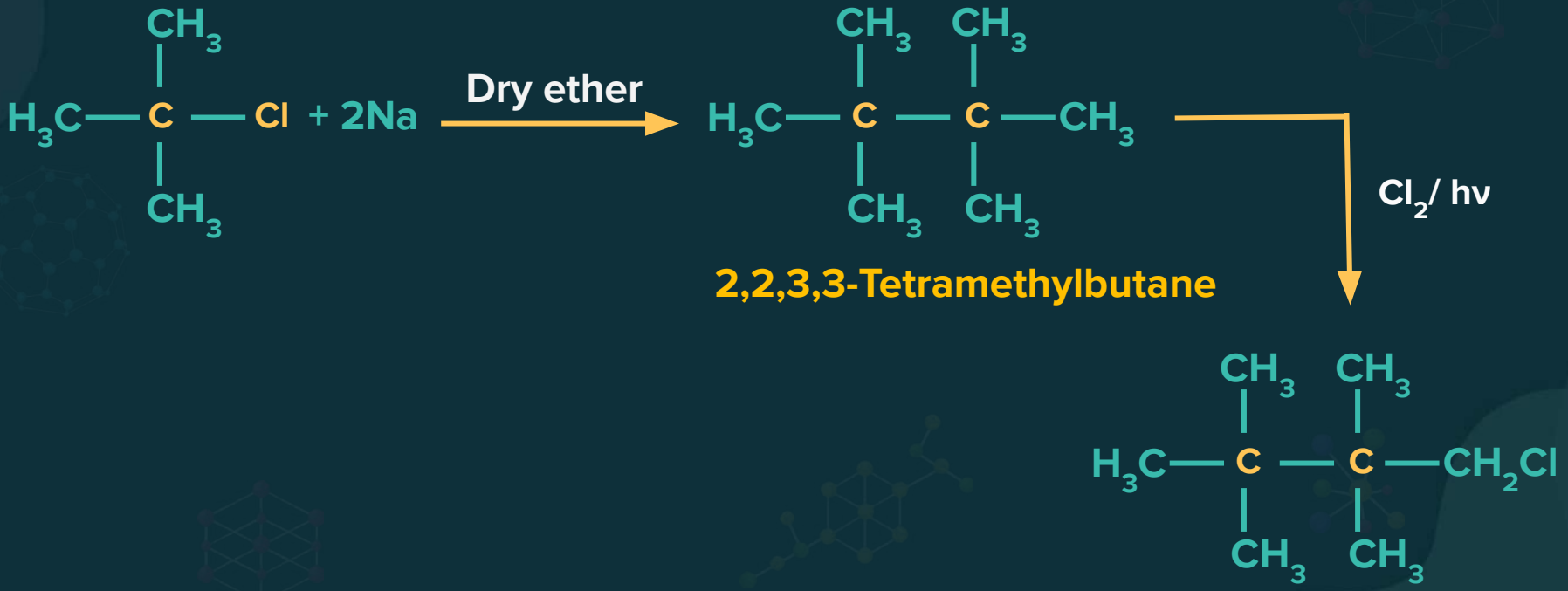
b) sec-Butyl chloride

d) Butyl chloride

Solution

A is tertiary butyl chloride because the reaction of tertiary butyl chloride with Na/diethyl ether gives 2,2,3,3-tetramethylbutane (Wurtz Reaction)

which has only one type of H atom that is replaced with chlorine to give only one monochloro derivative.



2,2,3,3-Tetramethylbutane

Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to a gaseous hydrocarbon containing less than four carbon atoms. (A) is:

a) $CH \equiv CH$

b) $CH_2 = CH_2$

c) $CH_3 - CH_3$

d) CH_4

Solution

Step 1: Hydrocarbon (A) is methane (CH_4), It reacts with bromine to form methyl bromide $CH_3 - Br$.

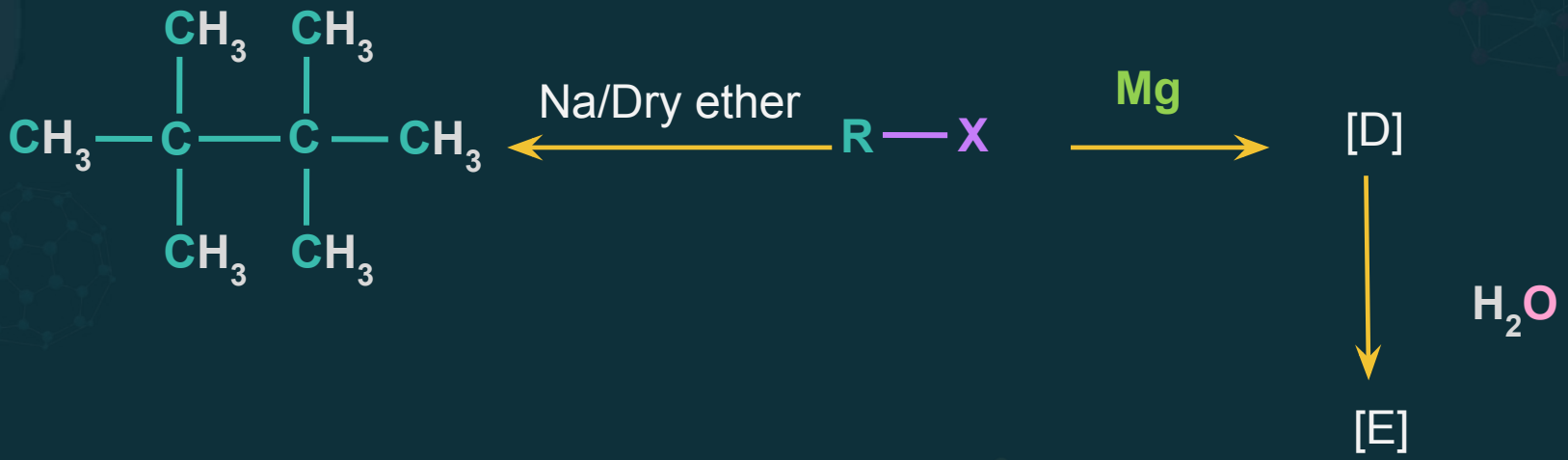
$$CH_4 + Br_2 \xrightarrow{h\nu} CH_3Br + HBr$$

Step 2 : Methyl bromide by Wurtz reaction is converted to a gaseous hydrocarbon containing less than four carbon atoms.

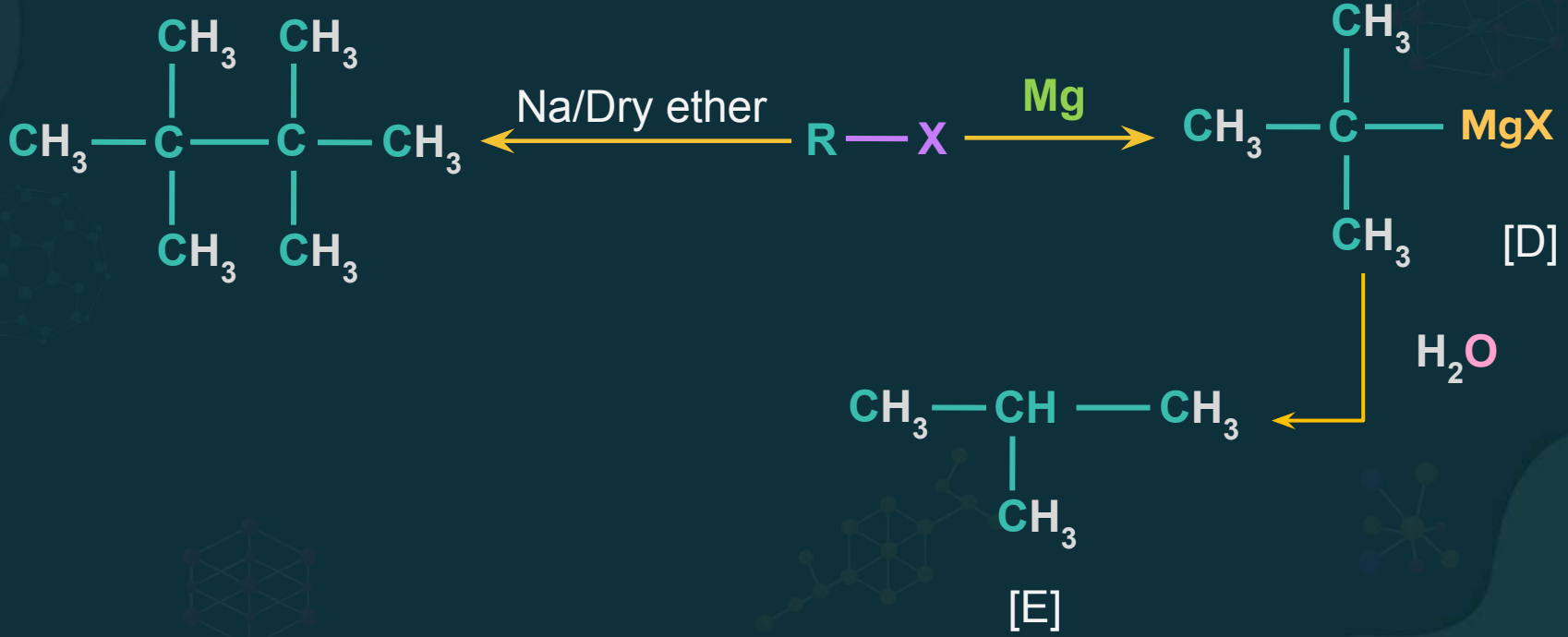
$$2CH_3Br + 2Na + \text{dry ether} \rightarrow CH_3\text{-}CH_3 + 2NaBr$$

Hence, option (d) is the correct answer.

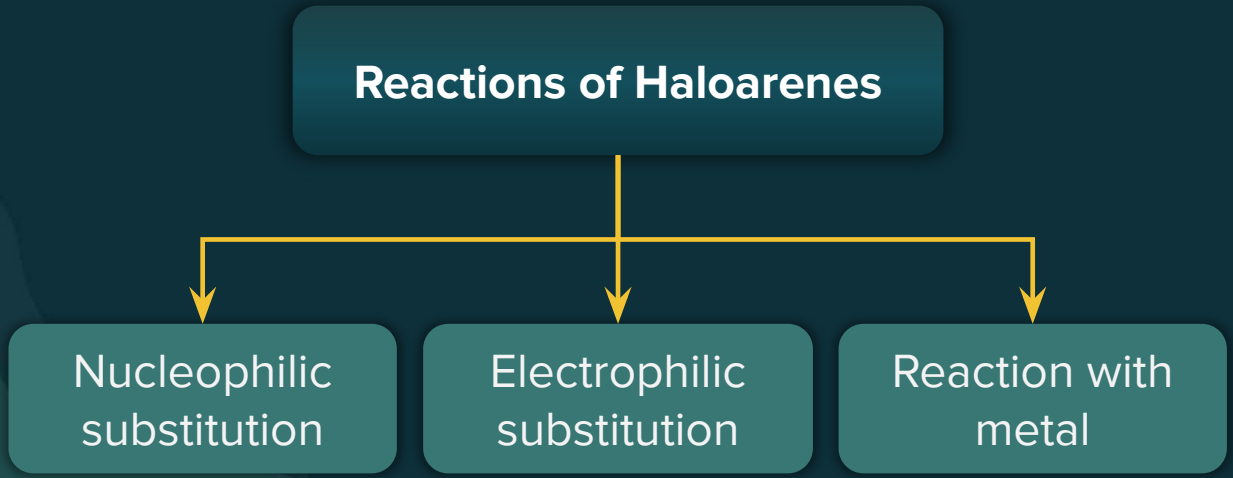
Identify D and E in the following reaction sequence:



Solution



Reactions of Haloarenes

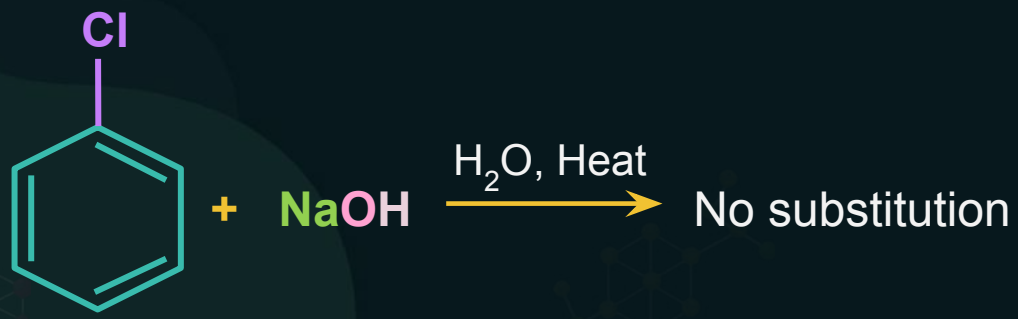


Nucleophilic Aromatic Substitution

Simple aryl halides are relatively **unreactive** towards nucleophilic substitution under conditions that would give **rapid nucleophilic substitution** with alkyl halides.

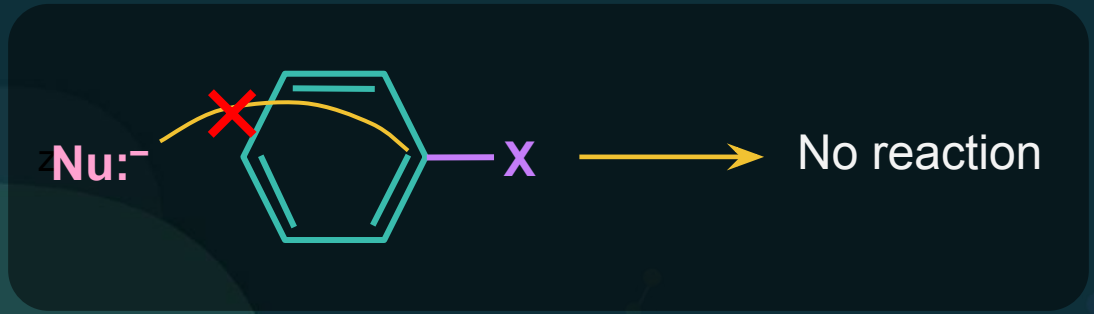
Nucleophilic Aromatic Substitution

Chlorobenzene can be boiled with **sodium hydroxide** for days without producing a **detectable amount of phenol** (or sodium phenoxide).



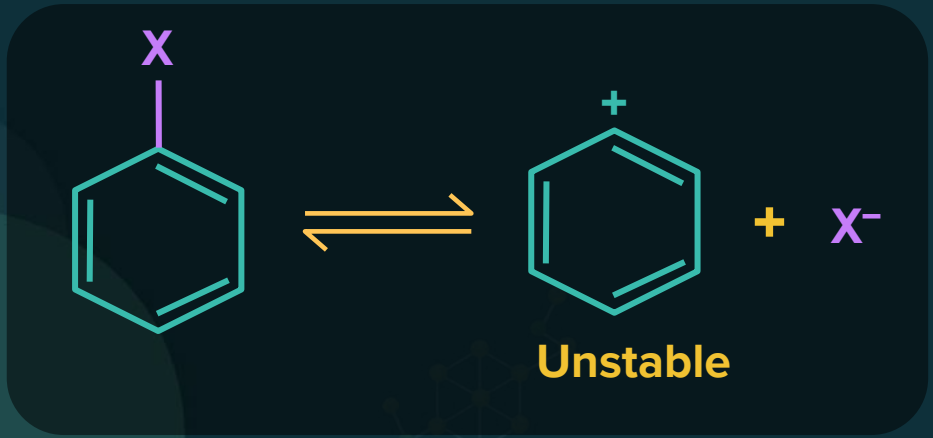
Nucleophilic Aromatic Substitution

1. The benzene ring of an aryl halide prevents the **back-side attack** in an S_N2 reaction.



Nucleophilic Aromatic Substitution

2 Phenyl cations are very unstable, hence, S_N1 reactions **do not occur**.

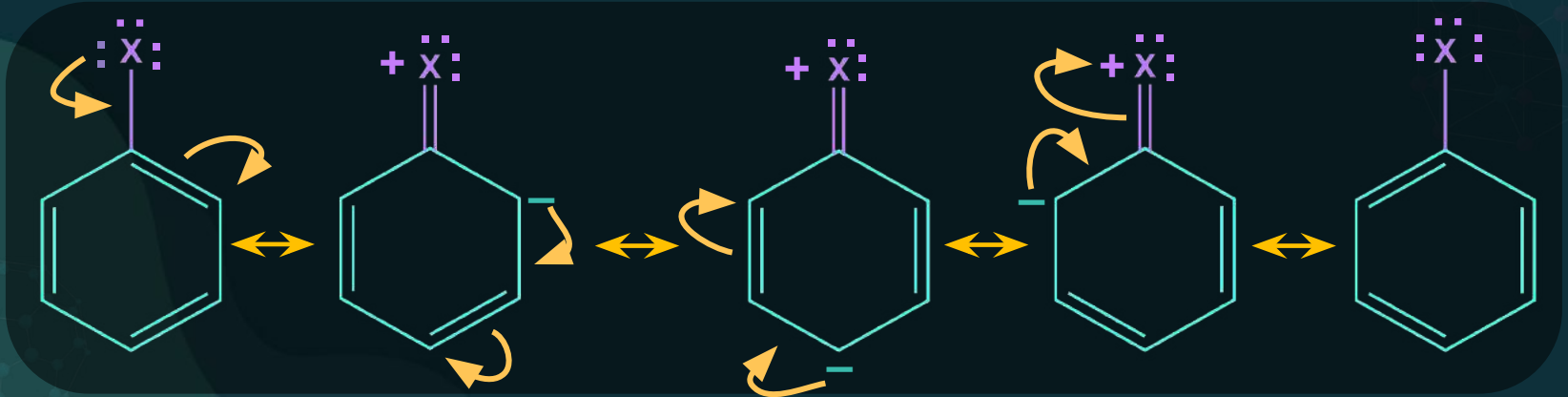


Nucleophilic Aromatic Substitution

3 The C–X bond of aryl halides are **shorter and stronger** than those of alkyl, allylic, and benzylic halides

Bond breaking by either an S_N1 or S_N2 mechanism **requires more energy**

Nucleophilic Aromatic Substitution



Resonating structures of Halobenzene

Nucleophilic Aromatic Substitution

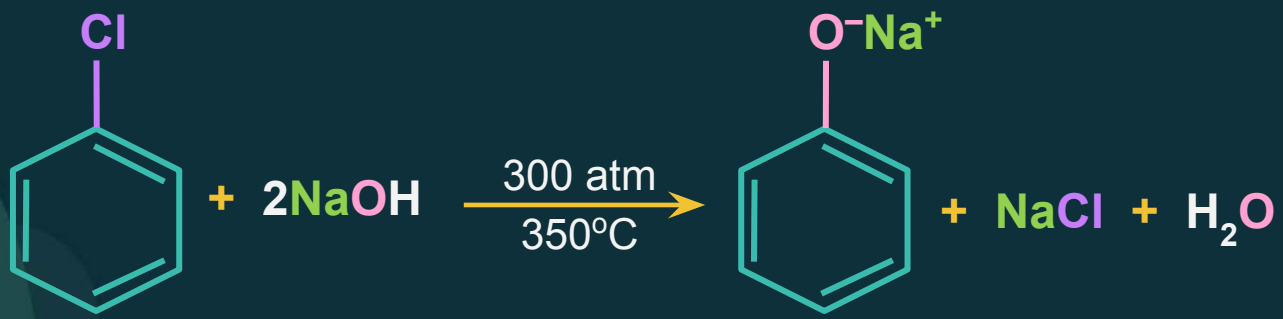
Aryl halides can be remarkably reactive towards nucleophiles if

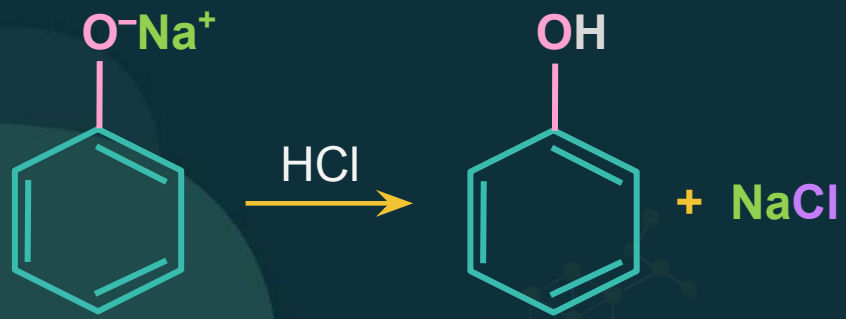
- They react under the **proper conditions**
- They bear **certain substituents**

Dow's Process

Chlorobenzene is heated at **350 °C** (under high pressure) with aqueous sodium hydroxide. The reaction produces **sodium phenoxide**, which on acidification yields phenol

Dow's Process





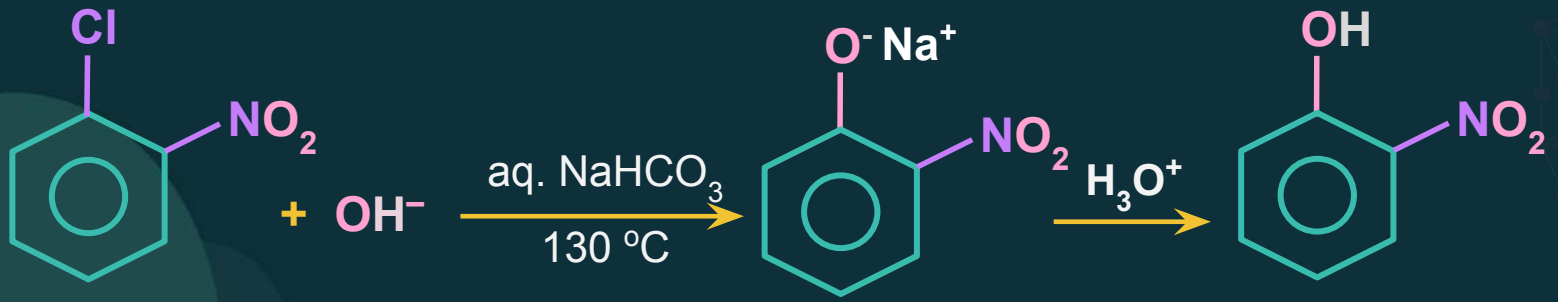
Phenol

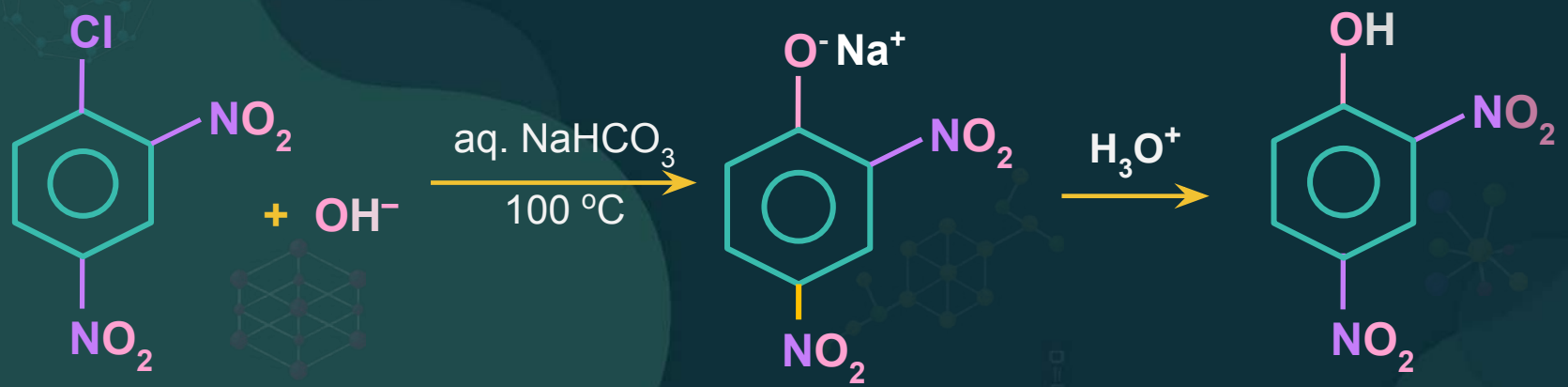
Nucleophilic Aromatic Substitution

Nucleophilic substitution reactions of aryl halides do **occur readily** when an electronic factor makes the aryl carbon bonded to the halogen **susceptible to a nucleophilic attack**

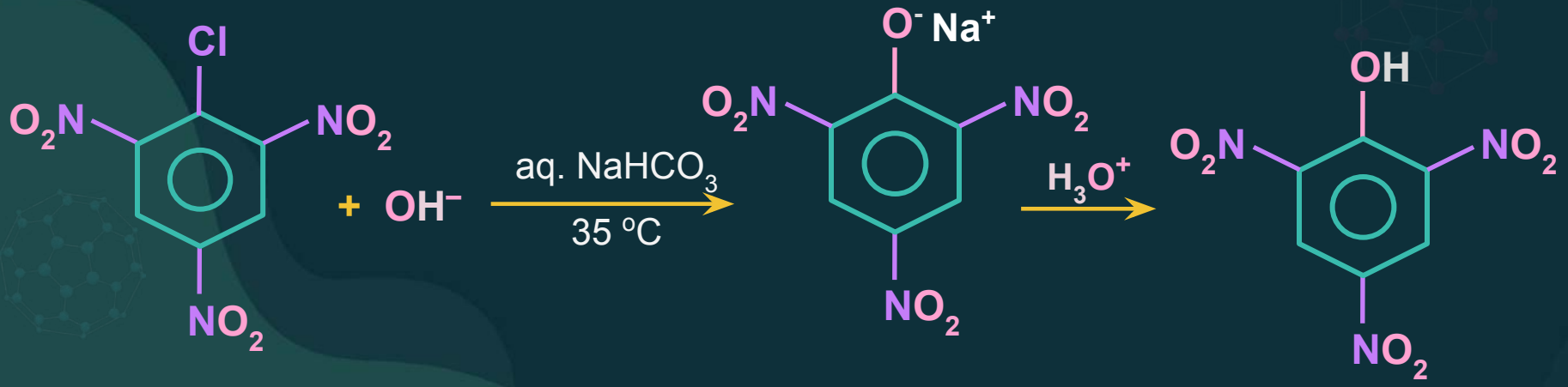
A nucleophilic aromatic substitution reaction can occur when **strong electron-withdrawing** groups are **ortho or para** to the halogen atom

Nucleophilic Aromatic Substitution





Nucleophilic Aromatic Substitution



S_NAr Mechanism

o-Nitrochlorobenzene requires the **highest temperature** (p-Nitrochlorobenzene reacts at 130 °C as well)

2,4,6-Trinitrochlorobenzene requires the **lowest temperature**

A meta-nitro group **does not** produce a similar activating effect as that of ortho and para.

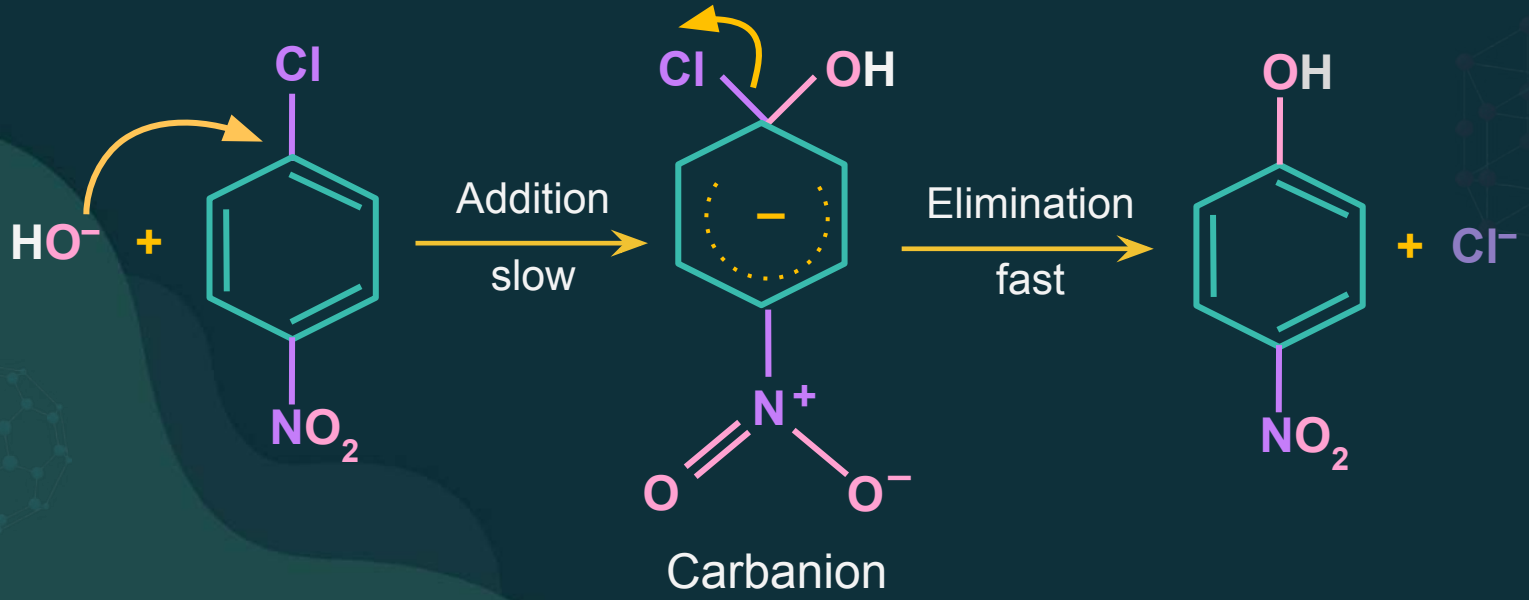
For example, m-Nitrochlorobenzene gives **no corresponding reaction**

Nucleophilic Aromatic Substitution

The mechanism that operates in these reactions is known as addition -elimination mechanism

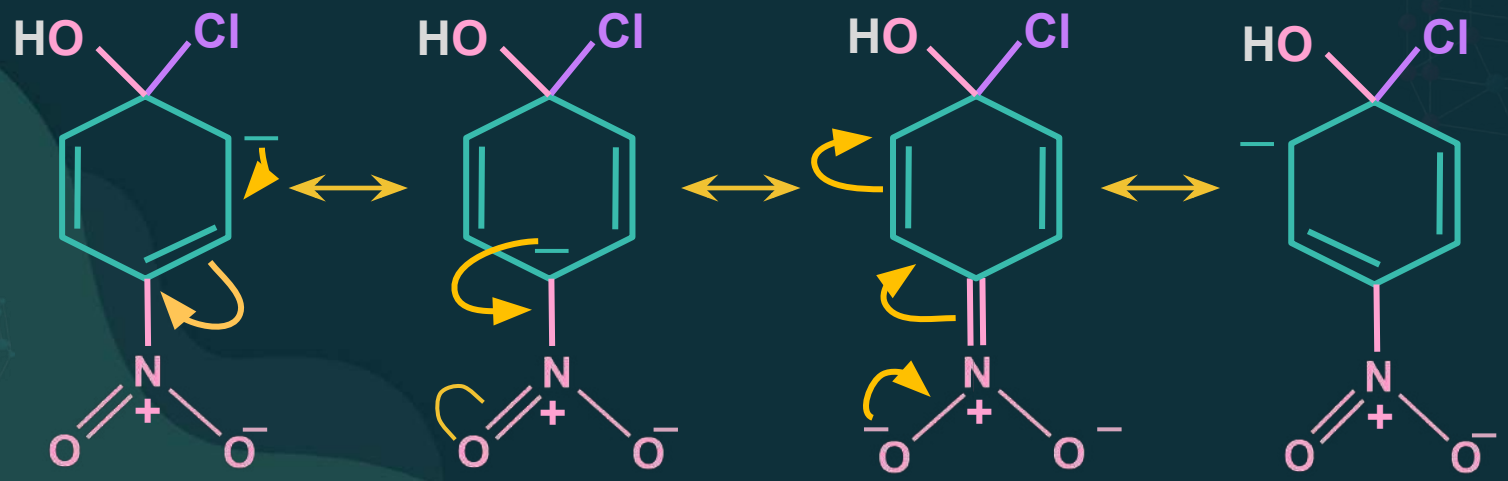
And the process is known as nucleophilic aromatic substitution (S_NAr)

S_NAr Mechanism



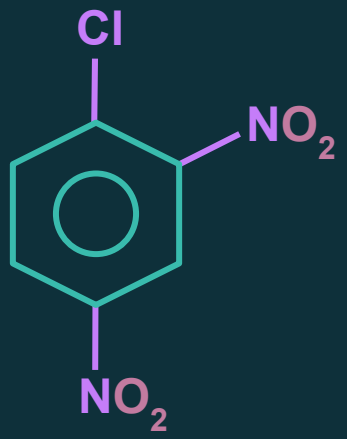
The carbanion is stabilized by **electron- withdrawing groups** in the positions ortho and para to the halogen atom.

S_NAr Mechanism

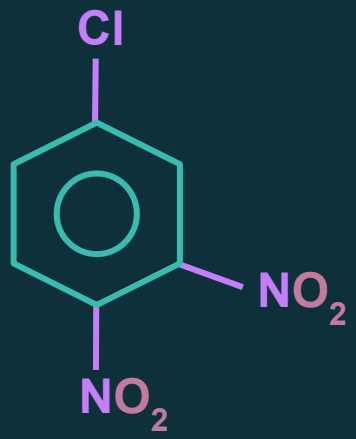


Resonating structures

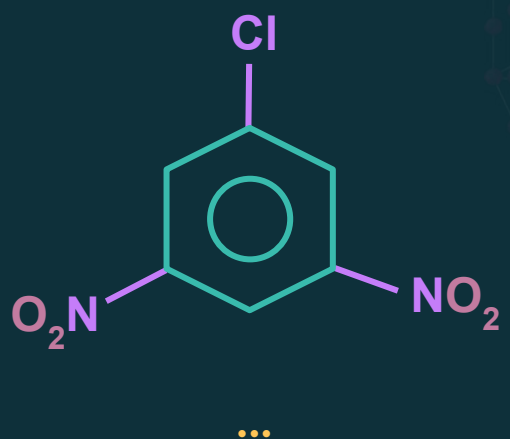
Arrange the following compounds in their order of reactivity with NaOH.



i



ii



iii

Solution

(i) 2,4-dinitrochlorobenzene : It has two electron withdrawing groups at ortho and para position and so they withdraw the electron pair towards them self and make the ring more susceptible for nucleophilic substitution.

Solution

(ii) 3,4-dinitrochlorobenzene : It has two electron withdrawing groups at meta and para position and so the para position group withdraws the electron density towards itself and make the ring susceptible for nucleophilic substitution, also we know a meta-nitro group does not produce a similar activating effect towards nucleophilic substitution as that of ortho and para.

(iii) 3,5-dinitro chlorobenzene : It has two electron withdrawing groups at meta and para position and a meta-nitro group does not produce a similar activating effect as that of ortho and para.

Hence, the reactivity order is i > ii > iii

Assertion: The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.
Reason: The intermediate carbanion is stabilised due to the presence of nitro group.

a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

b) If both Assertion and Reason are correct but the Reason is not a correct explanation of the Assertion.

c) If the Assertion is correct but Reason is incorrect.

d) If both the Assertion and Reason are incorrect.

Solution

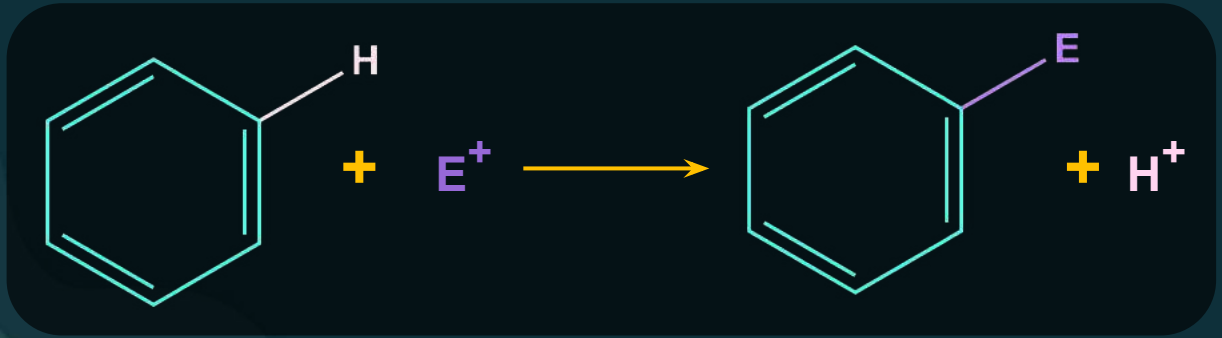
A nucleophilic aromatic substitution reaction can occur when strong electron-withdrawing groups are ortho or para to the halogen atom and $-NO_2$ is electron withdrawing in nature so **assertion is correct.**

The generally accepted mechanism of nucleophilic aromatic substitution of aryl halides has two steps ; In the first step involves the nucleophile OH^- reacting with the carbon bearing the halogen substituent to form an intermediate carbanion and the carbanion is stabilized by electron-withdrawing groups in the positions ortho and para to the halogen atom so **reason is also the correct explanation of Assertion.**

Hence, option (a) is the correct answer.

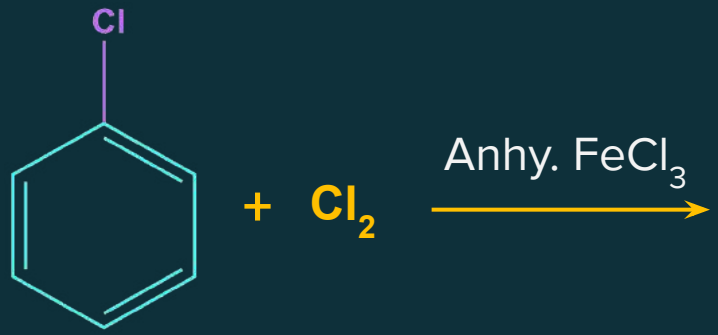
Electrophilic Substitution in Haloarenes

General reaction

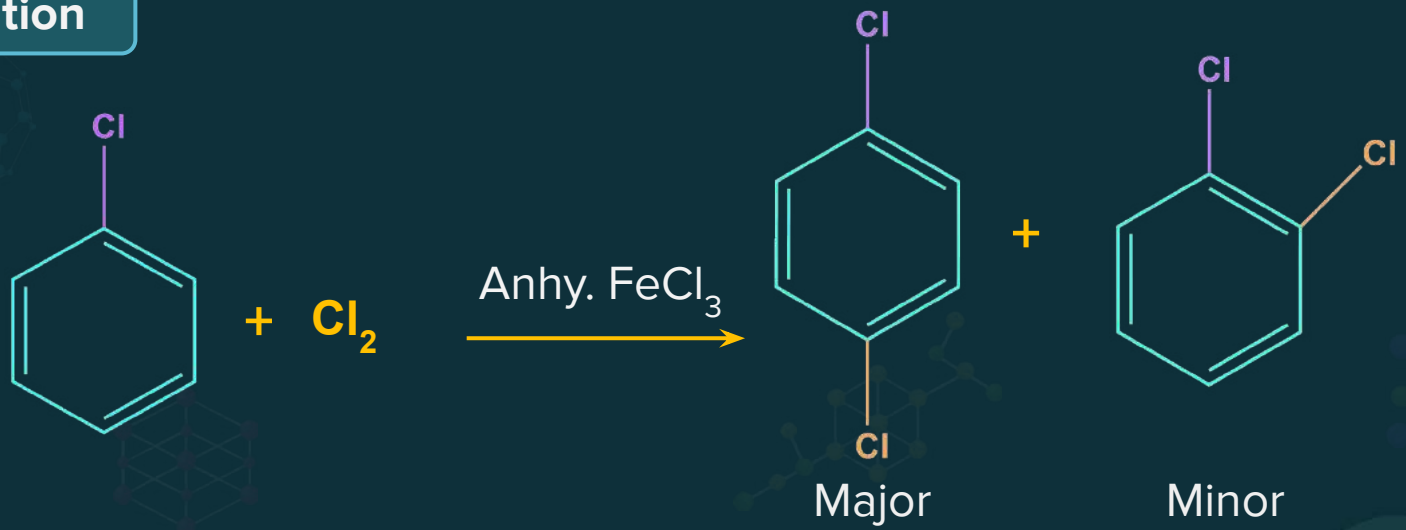


Halo groups are **ortho-para** directors,
and are **deactivating** groups as well!!

Identify the major and minor products in the given reaction.



Solution



Identify the major and minor products in the given reaction.

HNO_3

$Conc.\ H_2SO_4$

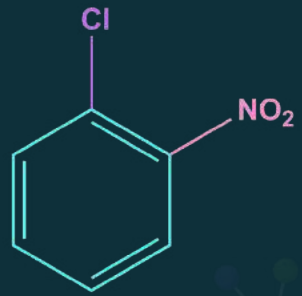
Solution

HNO_3

$Conc.\ H_2SO_4$

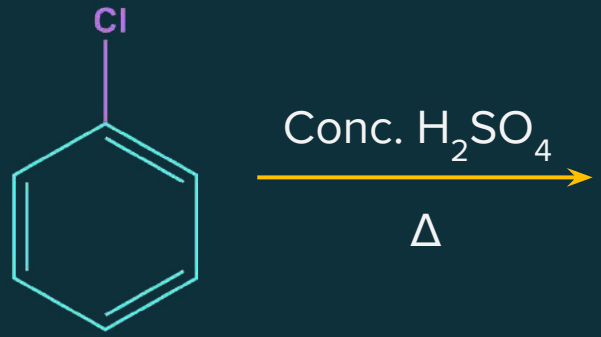
Major

+

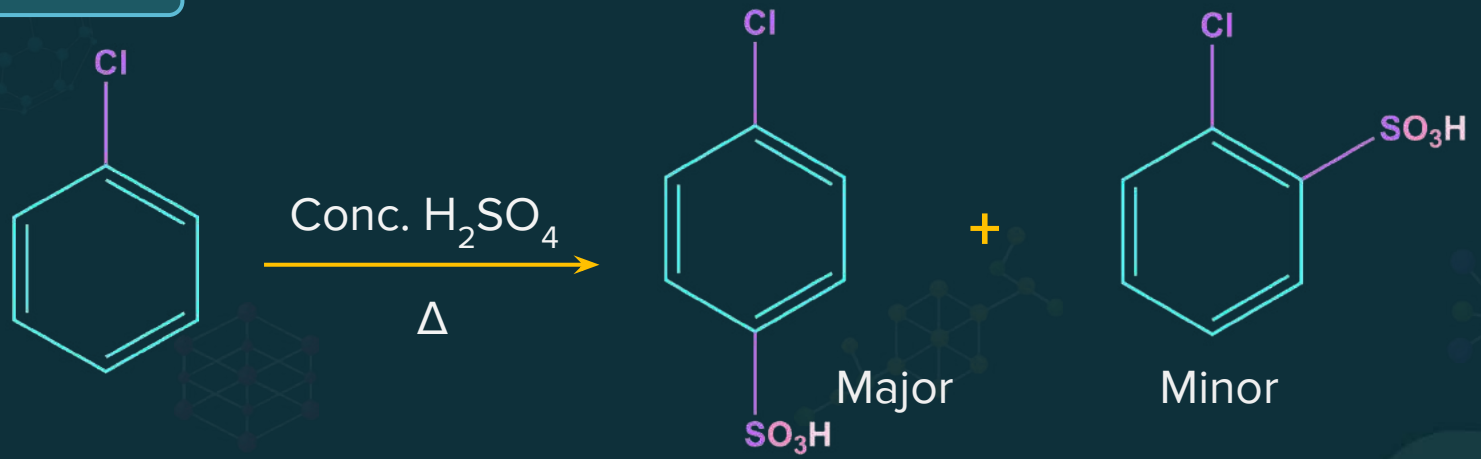


Minor

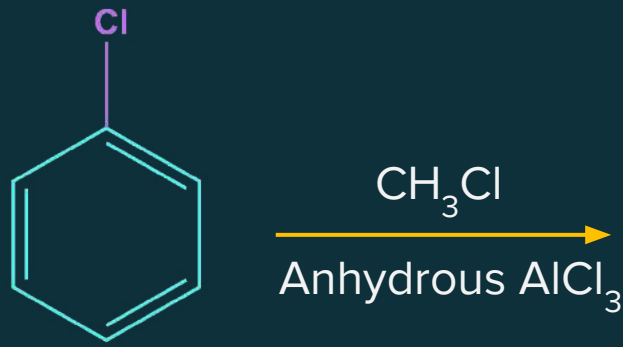
Identify the major and minor products in the given reaction.



Solution



Identify the major and minor products in the given reaction.



CH_3Cl

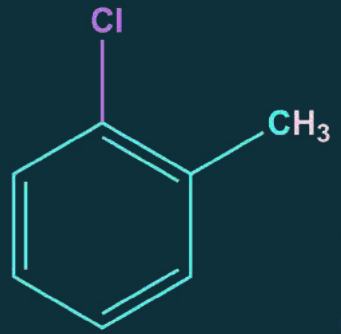
Anhydrous $AlCl_3$

Solution

CH_3Cl

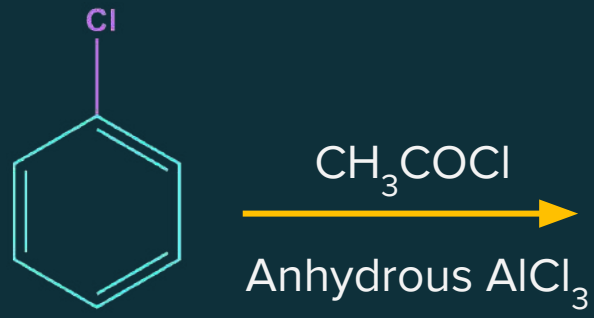
Anhydrous $AlCl_3$

+

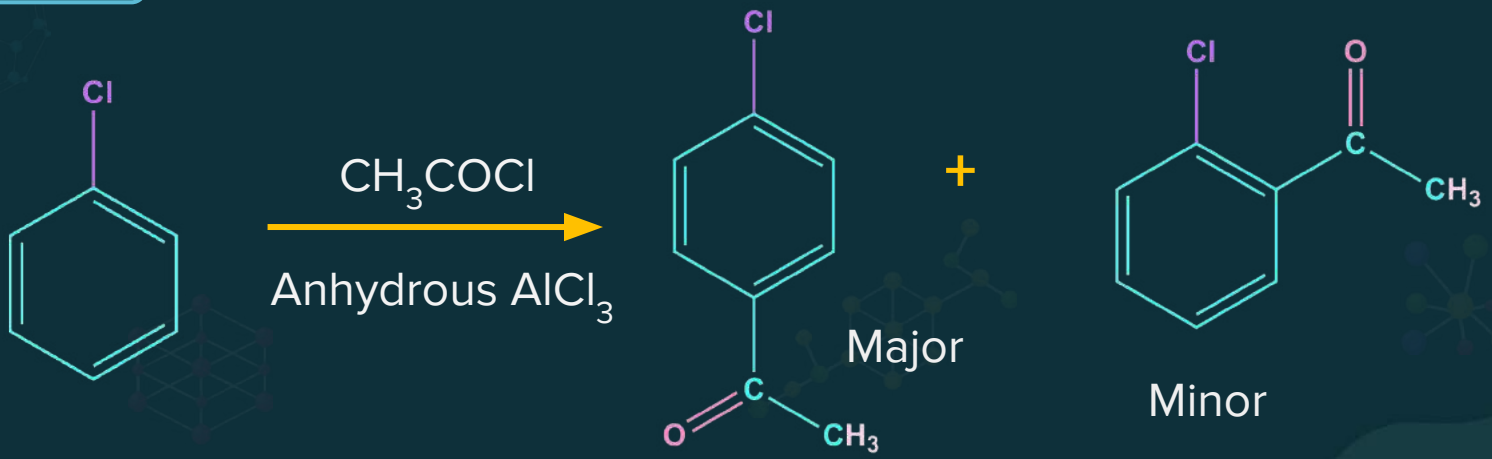


Minor

Identify the major and minor products in the given reaction.



Solution



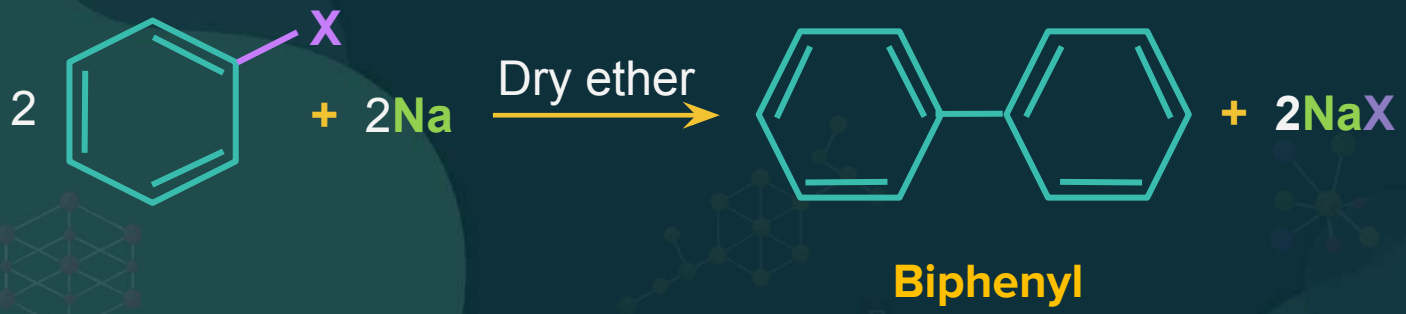
Wurtz-Fittig Reaction

The mixture of an **alkyl and an aryl halide** is treated with **sodium** to give an **alkylated aromatic** compound

General reaction

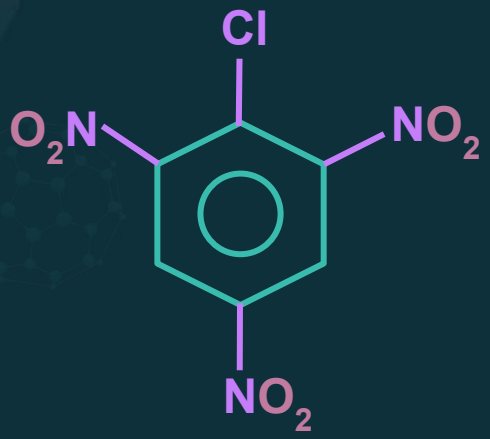
Fittig Reaction

Aryl halides also give analogous compounds when treated with **sodium in dry ether**, in which two aryl groups are joined together.



Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

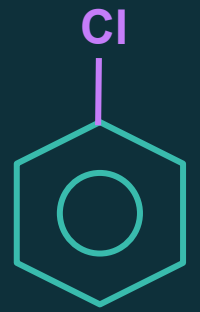
a)



b)

c)

d)

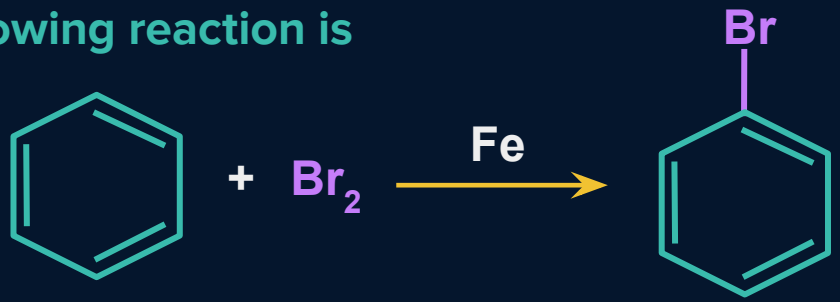


Solution

$-NO_2$ (nitro) is an electron-withdrawing group. Generally, more the number of electron-withdrawing groups present, faster is the aromatic nucleophilic substitution reaction. The hydroxide ion (OH^-) readily attacks 2,4,6-trinitrochlorobenzene (d) to form picric acid (yellow-coloured compound) hydroxy derivative.

Thus, option (d) is the correct answer.

The following reaction is



a) Electrophilic addition

b) Nucleophilic addition

c) Free radical substitution

d) Electrophilic substitution

Solution

$$2Fe + 3Br_2 \rightarrow 2FeBr_3$$

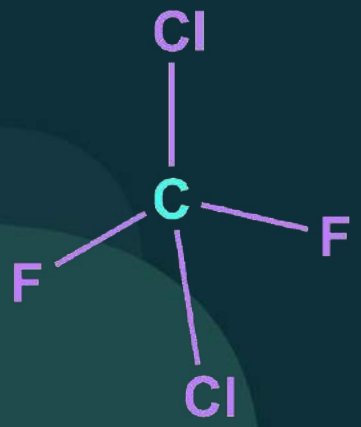
It acts as a Lewis acid and this is an example of electrophilic substitution reaction.

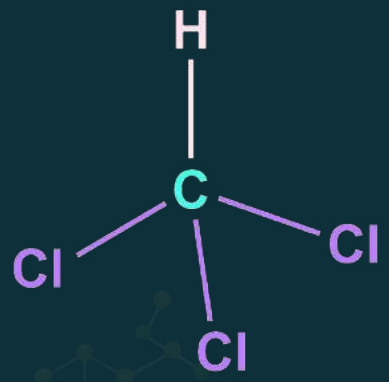
Hence, option (d) is the correct answer.

Polyhalogen Compounds

Carbon compounds containing **more than** one halogen atom

Examples



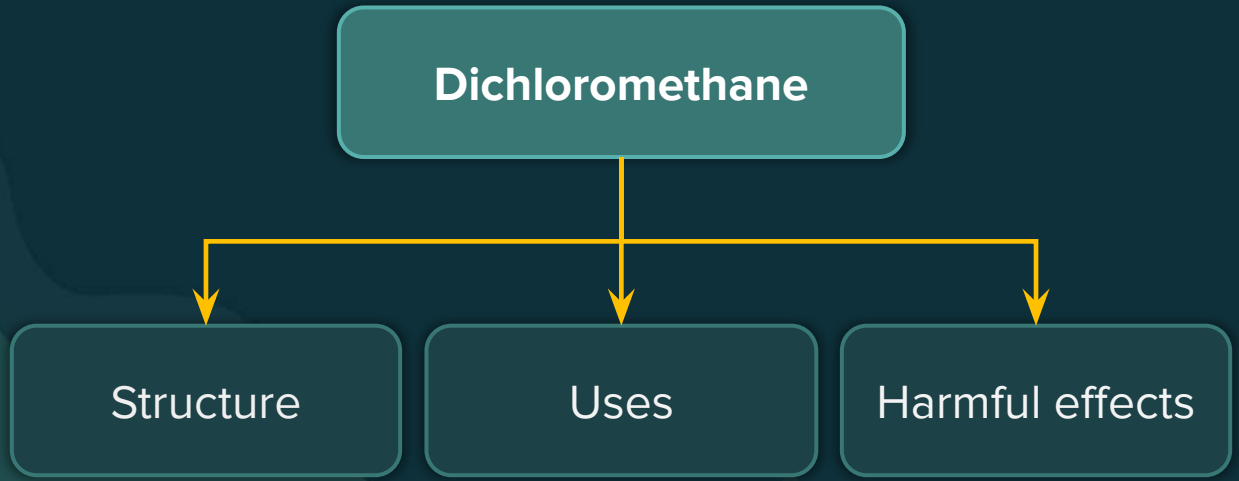


Polyhalogen Compounds

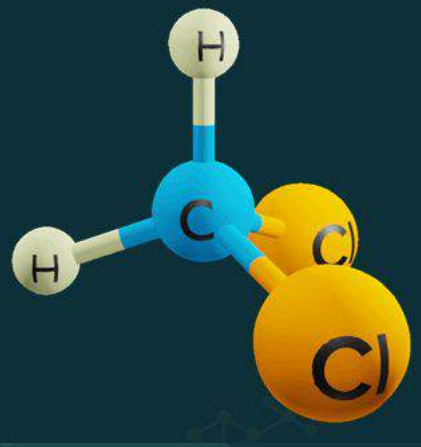
- Dichloromethane
- Trichloromethane
- Triiodomethane
- Tetrachloromethane
- Freons
- DDT

Polyhalogen Compounds

Dichloromethane



Polyhalogen Compounds



Structure of Dichloromethane

Dichloromethane

- Paint remover
- Propellent in aerosol
- Metal cleansing
- As a solvent

Dichloromethane

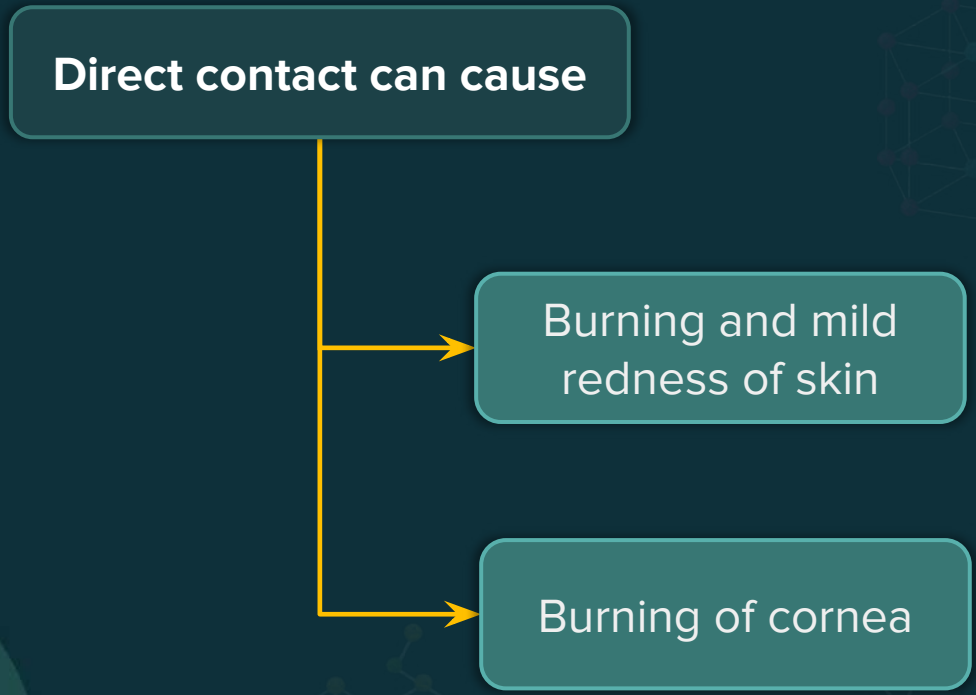
Harmful Effects

- Slight hearing and vision impairment
- Harms the human central nervous system
- Tingling and numbness in the fingers and toes
- Nausea

Direct contact can cause

- Burning and mild redness of skin
- Burning of cornea

Harmful Effects of Dichloromethane



Which of the following is a polyhalogen compound?

a) Chloroform

b) Iodoform

c) DDT

d) All of these

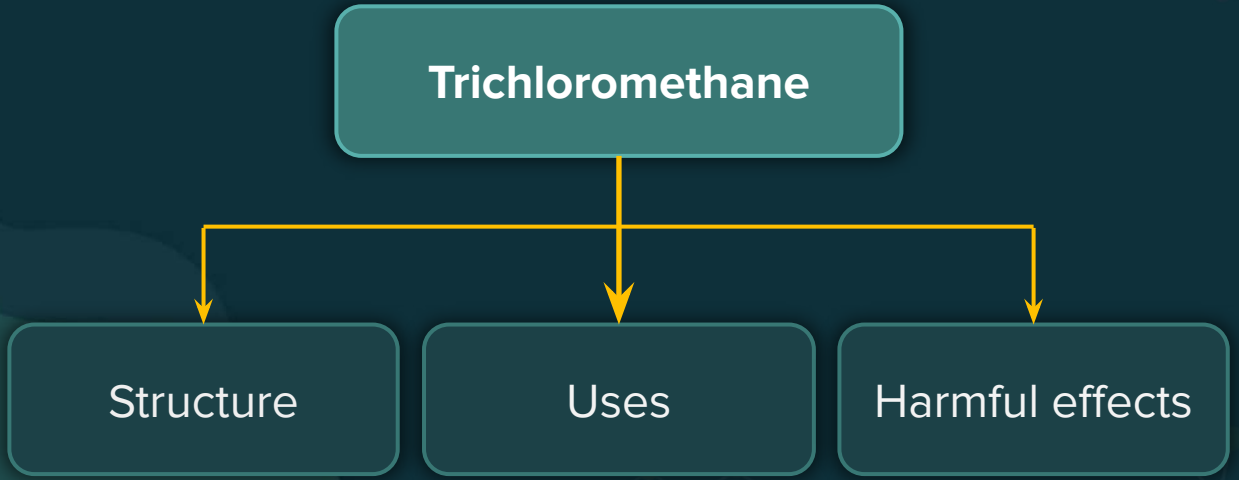
Solution

All of these are polyhalogen compound.

Hence, option (d) is the correct answer.

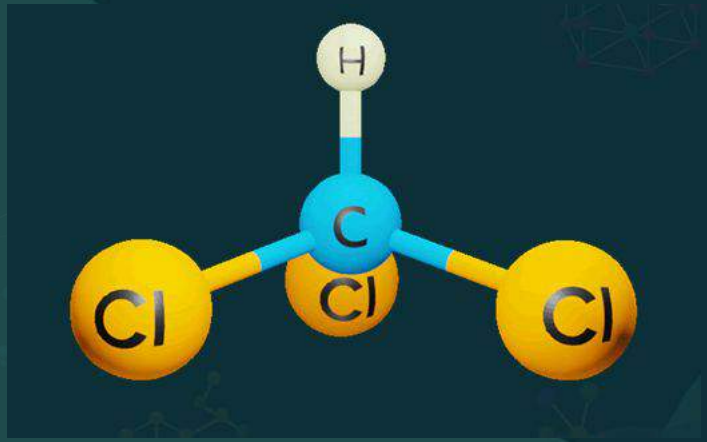
Polyhalogen Compounds

Trichloromethane



Polyhalogen Compounds

Structure



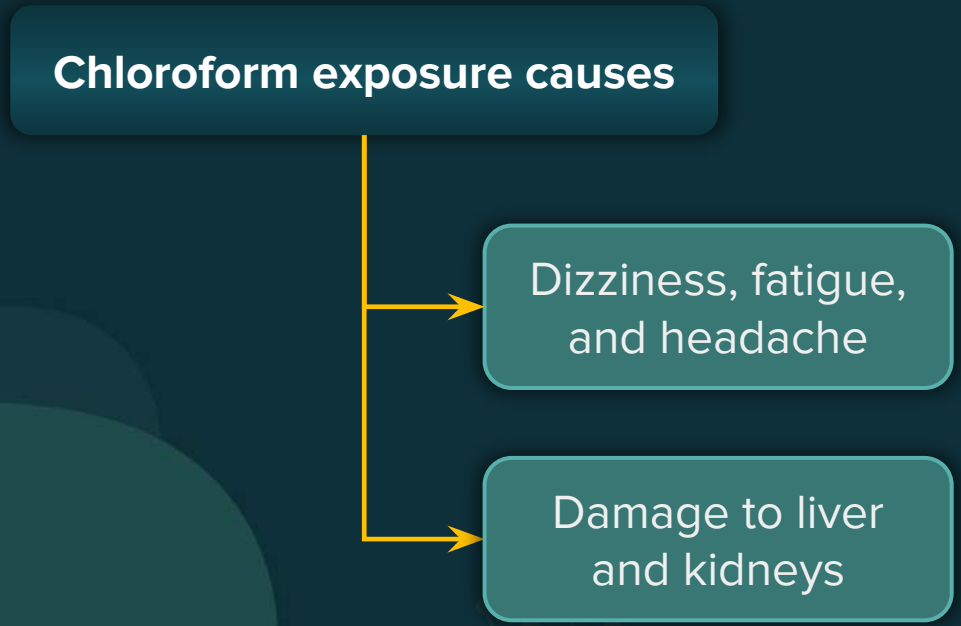
Structure of Trichloromethane

Uses

- Solvent for fats, alkaloids and iodine
- Production of freon refrigerants (R-22)
- Anesthetic in surgery

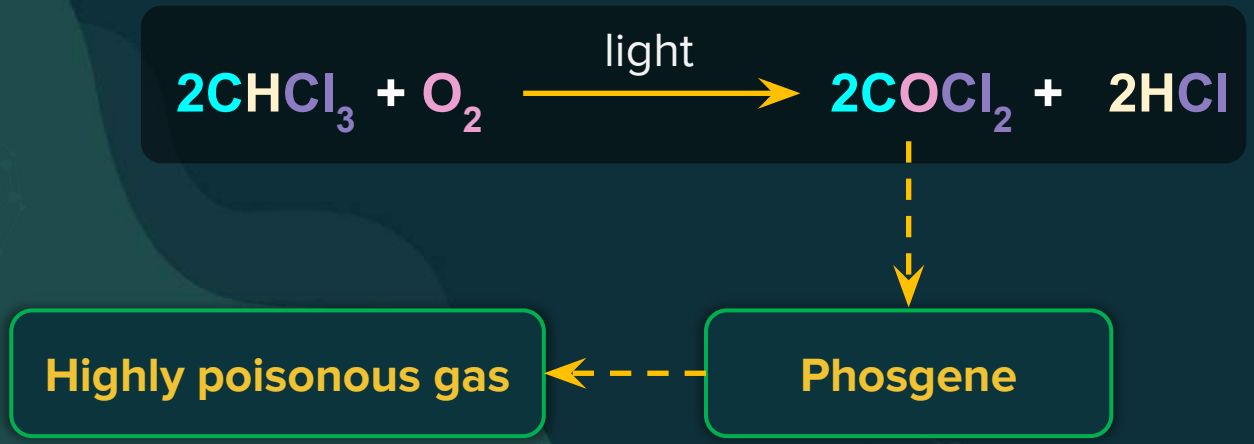
Polyhalogen Compounds

Harmful Effects of Trichloromethane

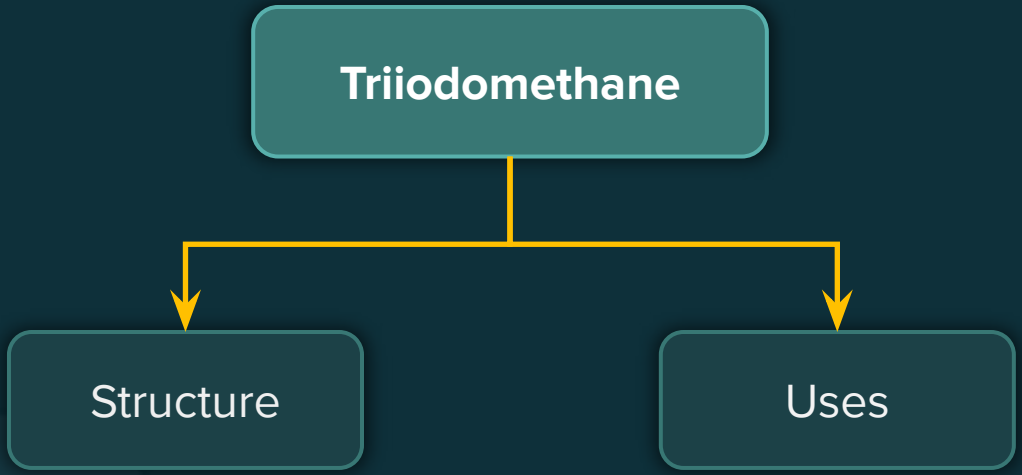


Polyhalogen Compounds

Harmful Effects of Trichloromethane

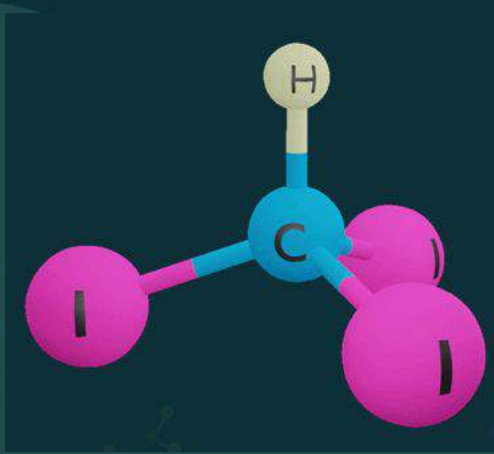


Polyhalogen Compounds



Polyhalogen Compounds

Structure

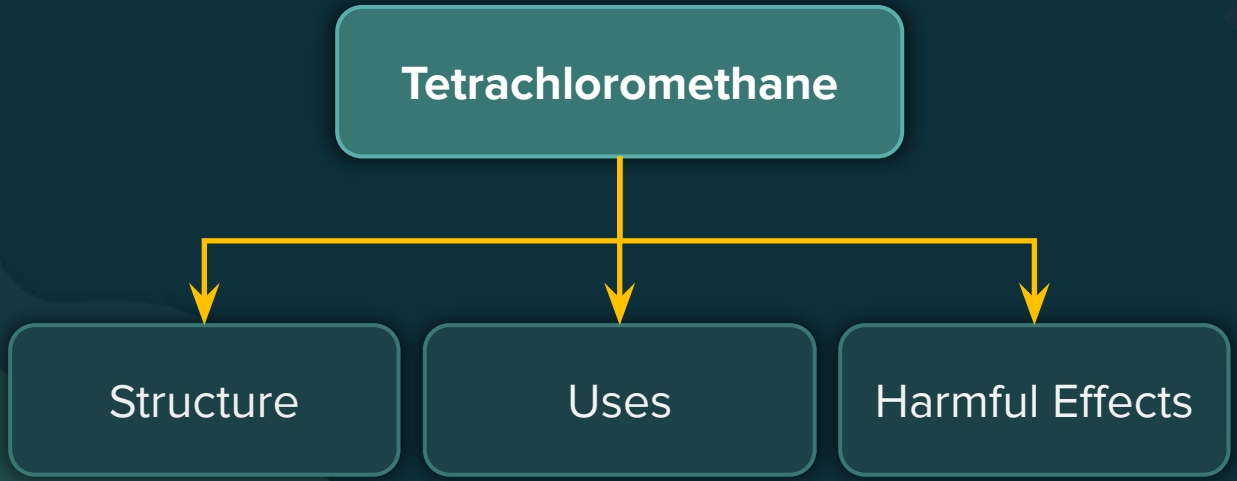


Structure of Triiodomethane

Has **antiseptic** properties due to the liberation of free iodine.

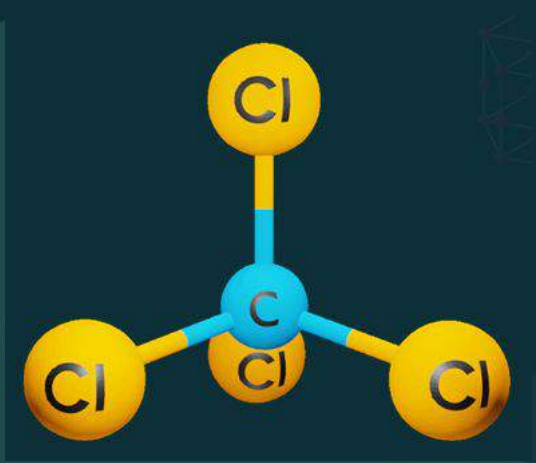
Polyhalogen Compounds

Tetrachloromethane



Polyhalogen Compounds

Structure



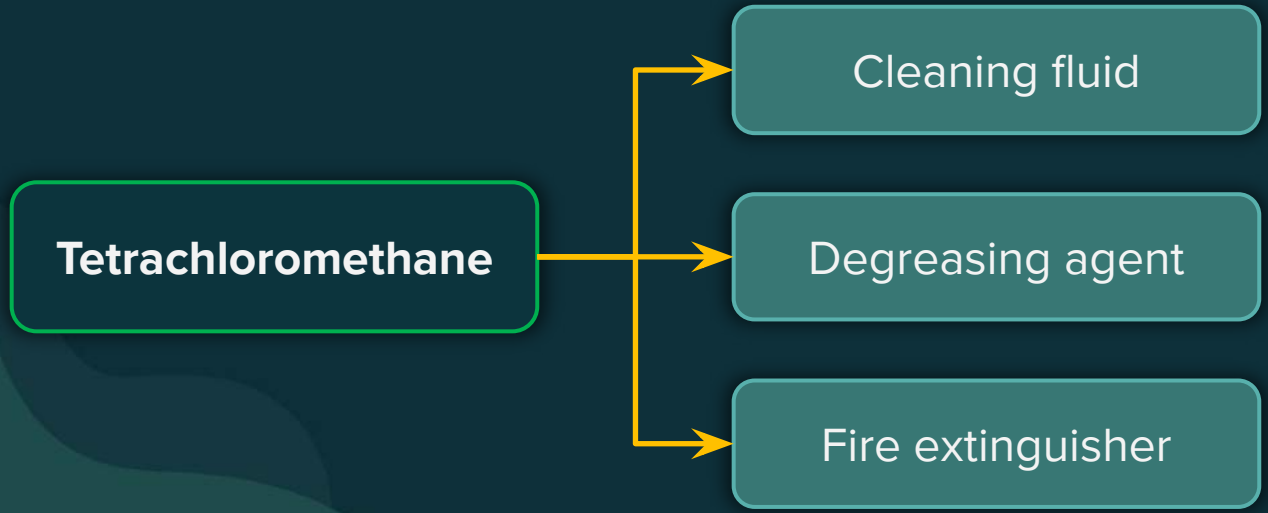
Structure of Tetrachloromethane

Uses

- Manufacture of refrigerants and propellants for aerosol cans
- Feedstock in the synthesis of chlorofluorocarbons
- Pharmaceuticals manufacturing

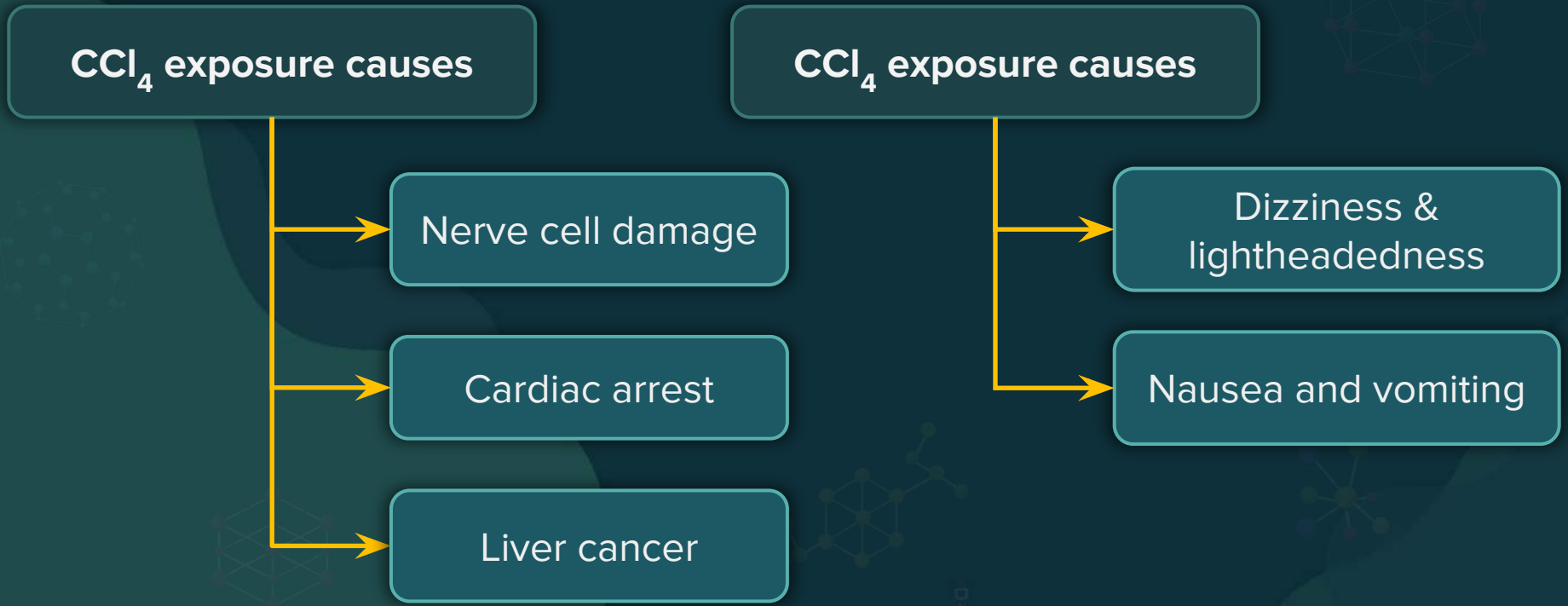
Polyhalogen Compounds

Uses



Polyhalogen Compounds

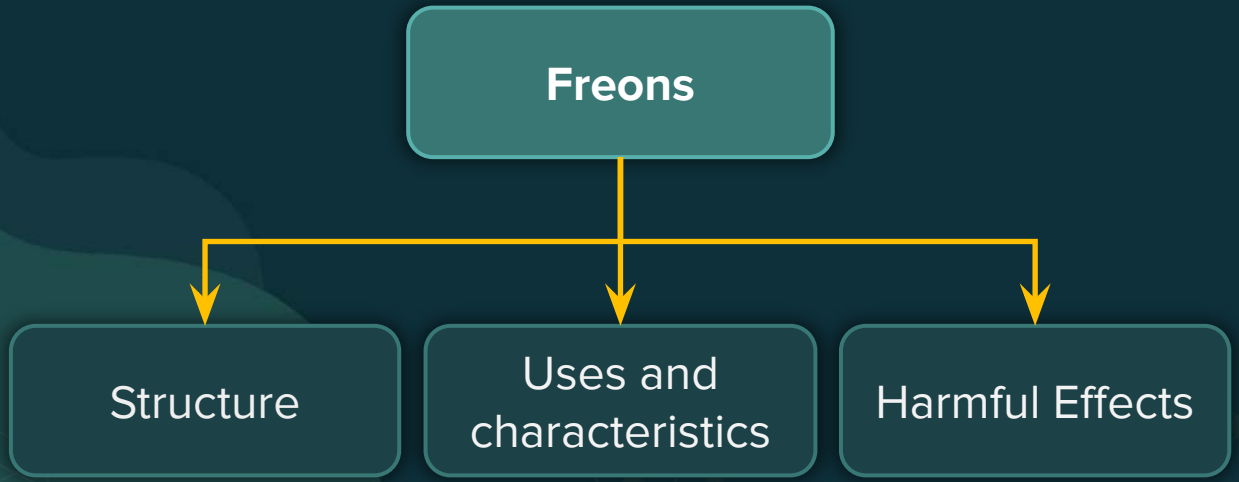
Harmful Effects of Tetrachloromethane



Polyhalogen Compounds

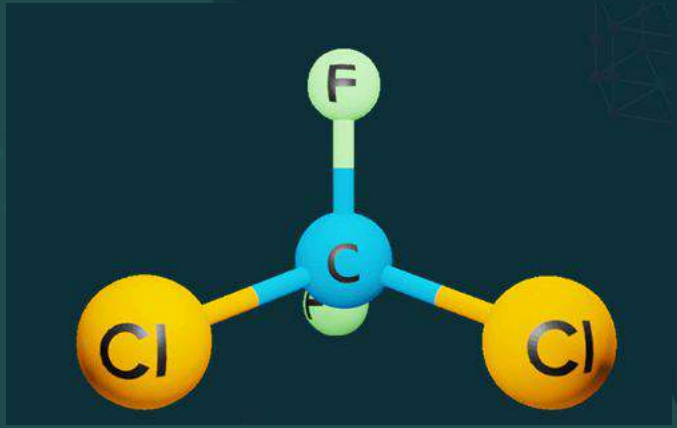
Freons

Chlorofluorocarbon compounds of methane and ethane are collectively known as **freons**.



Polyhalogen Compounds

Structure



Structure of Feron

Uses of Freon-12

- Aerosol Propellants
- Refrigerators
- Air-conditioners

Polyhalogen Compounds

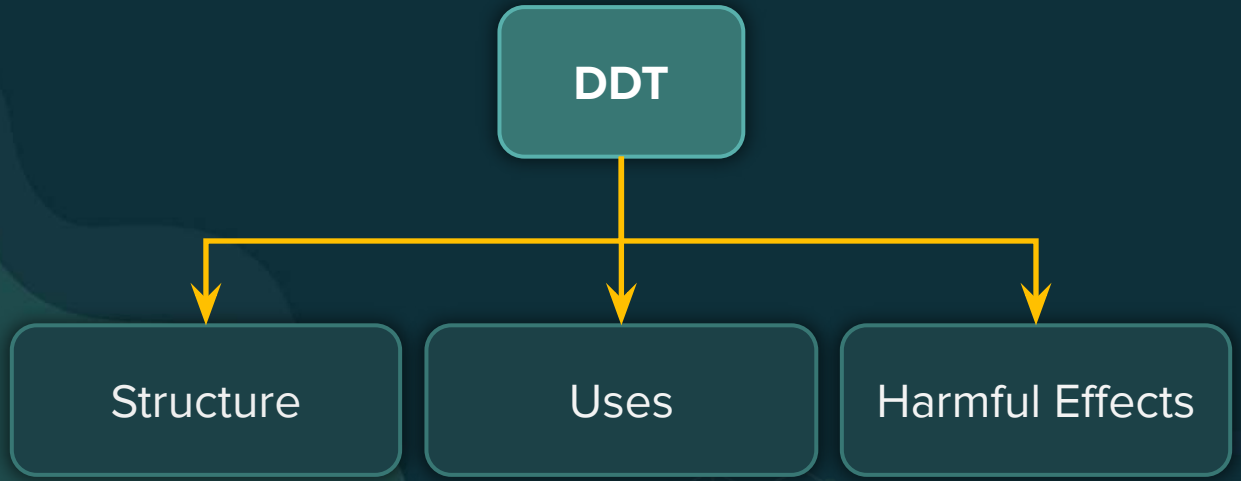
Freons are

- Stable
- Non-reactive
- Non-toxic
- Liquefiable gases

In **stratosphere**, freon is able to initiate radical chain reactions that can upset the natural **ozone balance.**

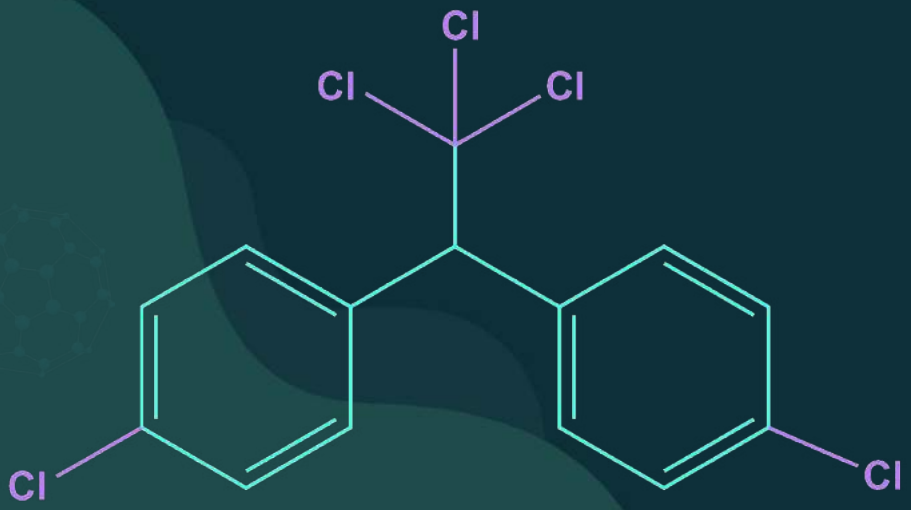
Polyhalogen Compounds

DDT



Polyhalogen Compounds

Structure



Structure of DDT

Harmful effect

DDT is not metabolised very rapidly by **animals**

↓

Deposited and stored in the **fatty tissues**.

Which of the following is a chiral molecule?

a) Dichloromethane

b) Chloroform

c) Iodoform

d) None of these

Solution

Chiral : A carbon atom is asymmetric or chiral if it has four different chemical groups attached. A compound is said to be chiral if it exists in two stereoisomeric forms which are **non-superimposable mirror images** of each other.

What is the degree of unsaturation in Dichlorodiphenyltrichloroethane (DDT)?

a) 7

c) 8

b) 6

d) 9

Solution

DDT has two benzene rings in its structure. Degree of unsaturation of one benzene is 4 because of three double bonds and one ring. So, Total degree of unsaturation = 4 + 4 = 8.

Thus, (c) is the correct answer.

Since, as all the given molecules do not have different atoms attached to carbon atom, no compound is said to be chiral.

Hence, option (d) is correct answer.