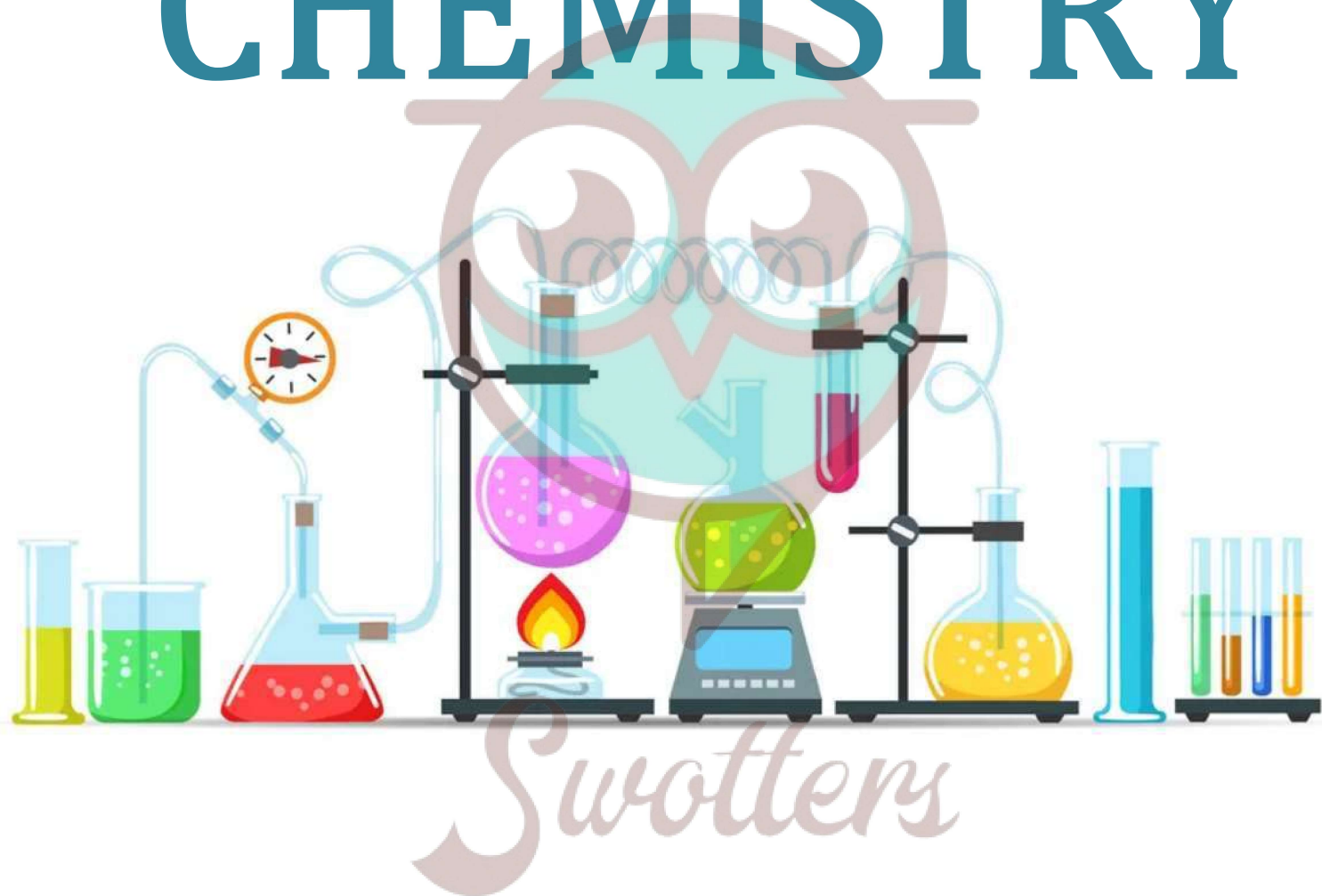


CHEMISTRY

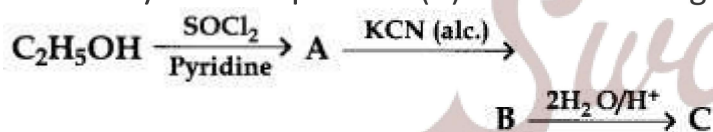


Important Questions

Multiple Choice questions-

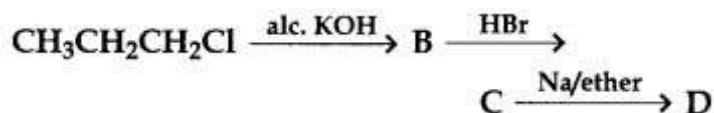
- S_N1 reaction of alkyl halides lead to
 - Retention of configuration
 - Racemisation
 - Inversion of configuration
 - None of these
- p-dichlorobenzene has higher melting point than its o- and m- isomers because
 - p-dichlorobenzene is more polar than o- and m- isomer.
 - p-isomer has a symmetrical crystalline structure.
 - boiling point of p-isomer is more than o- and m-isomer.
 - All of these are correct reasons.
- Chloropicrin is formed by the reaction of
 - steam on carbon tetrachloride.
 - nitric acid on chlorobenzene.
 - chlorine on picric acid.
 - nitric acid on chloroform.
- Fitting reaction can be used to prepare
 - Toluene
 - Acetophenon
 - Diphenyl
 - Chlorobenzene

5. Identify the end product (C) in the following sequence:



- | | |
|---|---|
| <ol style="list-style-type: none"> $\text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$ $\text{C}_2\text{H}_5\text{CONH}_2$ | <ol style="list-style-type: none"> $\text{C}_2\text{H}_5\text{COOH}$ $\text{C}_2\text{H}_5\text{NH}_2 + \text{HCOOH}$ |
|---|---|

6.

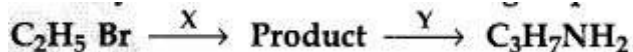


In the above reaction, the product D is

- Propane
- 2, 3-Dimethylbutane

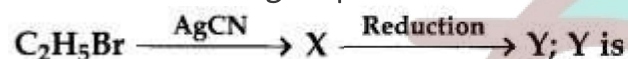
- (c) Hexane
(d) Allyl bromide

7. Identify X and Y in the following sequence



- (a) X = KCN, Y = LiAlH₄
(b) X = KCN, Y = H₃O⁺
(c) X = CH₃Cl, Y = AlCl₃ HCl
(d) X = CH₃NH₂, Y = HNO₂

8. In the following sequence of reactions:

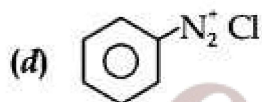
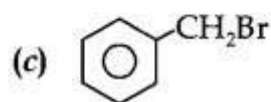
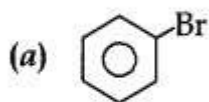


- (a) n-propylamine
(b) isopropylamine
(c) ethylamine
(d) ethylmethanamine

9.

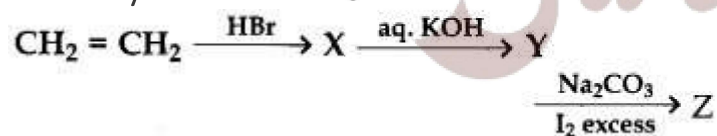


Which of the following cannot be X?



10.

Identify Z in the series

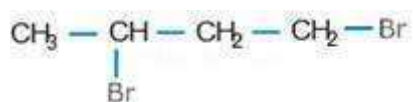


- (a) C₂H₅I
(b) C₂H₅OH
(c) CHI₃
(d) CH₃CHO

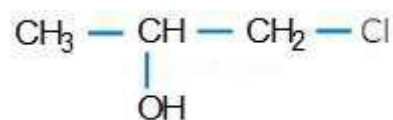
Very Short Questions-

1. Give IUPAC names of following compounds

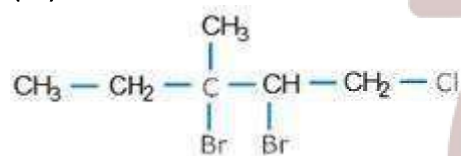
(i).



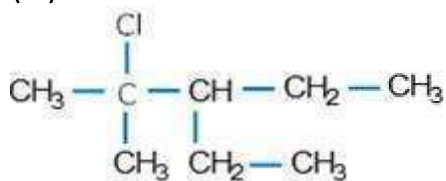
(ii).



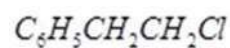
(iii).



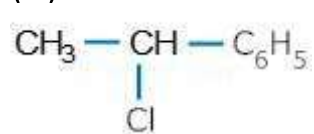
(iv).



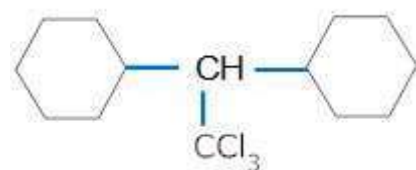
(v).



(vi).

(vii). $\text{C}_5\text{H}_5\text{Cl}_5$

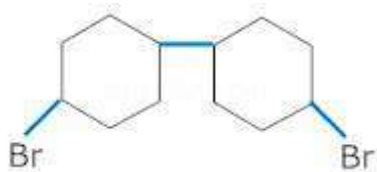
(viii).



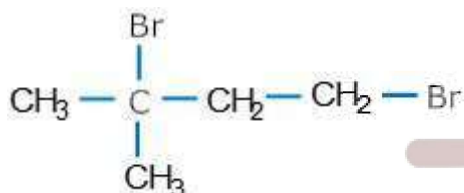
(ix).



Swotters



(x).



Short Questions-

1. Thionyl chloride is preferred for converting alcohol to haloalkane.
2. Phenol cannot be converted to chlorobenzene by reacting with HCl.
3. HNO_3 is added during iodination of benzene.
4. p- dichlorobenzene has higher melting point than meta – dichlorobenzene.
5. The boiling points of isomeric haloalkenes decrease with increase in branching.
6. Hydrolysis of optically active 2- bromobutane forms optically inactive butan – 2 – ol.
7. Chlorobenzene is less reactive towards nucleophilic substitution reaction.
8. Chloroform is stored in dark coloured bottles.
9. The order of boiling points is $RCl < RBr < RI$.
10. Vinyl chloride is less reactive than allyl chloride.

Long Questions-

1. Write structures of the following compounds:

- (i) 2-Chloro-3-methylpentane
- (ii) 1-Chloro-4-ethylcyclohexane
- (iii) 4-tert. Butyl-3-iodoheptane
- (iv) 1,4-Dibromobut-2-ene
- (v) 1-Bromo-4-sec. butyl-2-methylbenzene

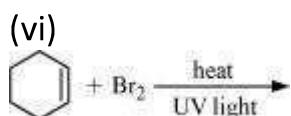
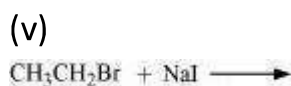
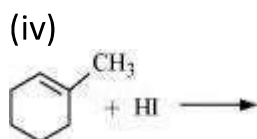
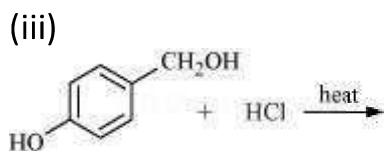
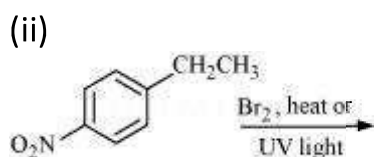
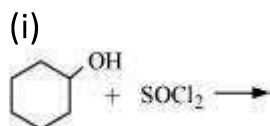
2. Write structures of different dihalogen derivatives of propane.

3. Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical

chlorination yields

- (i) A single monochloride.
- (ii) Three isomeric monochlorides.
- (iii) Four isomeric monochlorides.

4. Draw the structures of major monohalo products in each of the following reactions:

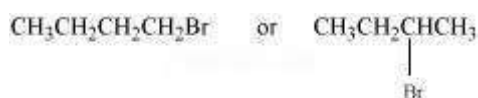


5. Arrange each set of compounds in order of increasing boiling points.

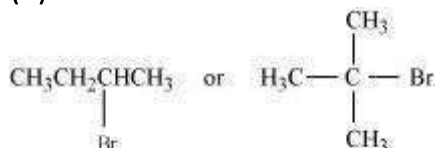
- (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
- (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

6. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

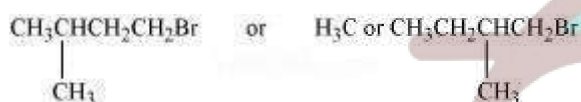
(i)



(ii)

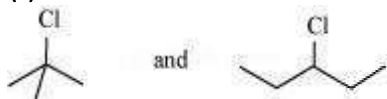


(iii)

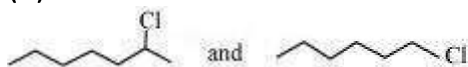


7. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

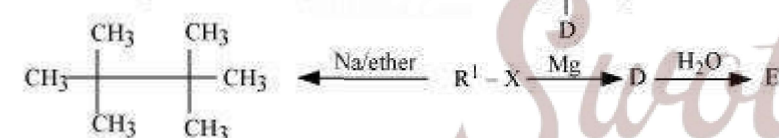
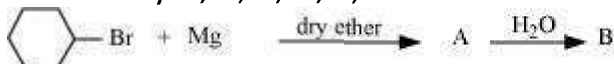
(i)



(ii)



8. Identify A, B, C, D, E, R and R^1 in the following:



Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

Assertion: Isopropyl chloride is less reactive than CH_3Br in $\text{S}_{\text{N}}2$ reactions.

Reason: $\text{S}_{\text{N}}2$ reactions are always accompanied by inversion of configuration.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

Assertion: Lower members of alkyl halides are colourless gases.

Reason: Alkyl iodides in general turn black on exposure to air and light.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Haloarenes are less reactive than haloalkanes. The low reactivity of haloarenes can be attributed to:

- Resonance effect.
- sp^2 hybridisation of C - X bond.
- Polarity of C - X bond
- Instability of phenyl cation (formed by self-ionisation of haloarene).
- Repulsion between the electron rich attacking nucleophiles and electron rich arenes.

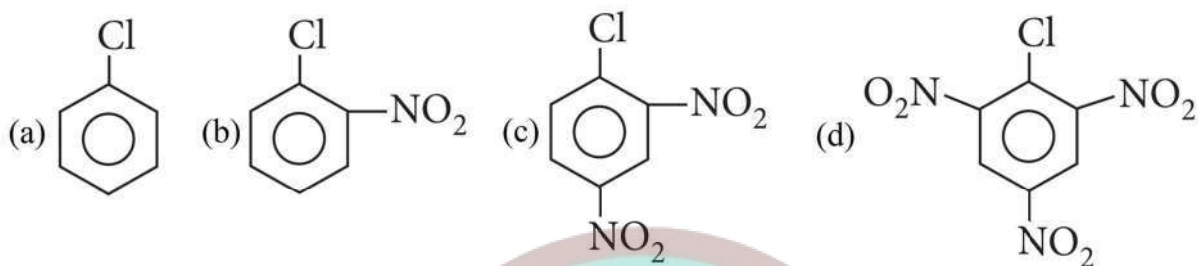
Reactivity of haloarenes can be increased or decreased by the presence of certain groups at certain positions for example, nitro ($-\text{NO}_2$) group at o/ p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

The following questions are multiple choice questions Choose the most appropriate answer:

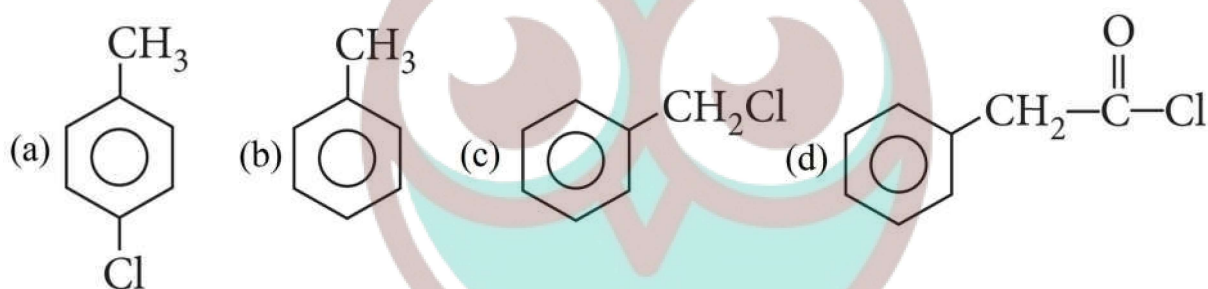
- Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to
 - The formation of less stable carbonium ion.
 - Resonance stabilisation.
 - Larger carbon-halogen bond.

d) Inductive effect.

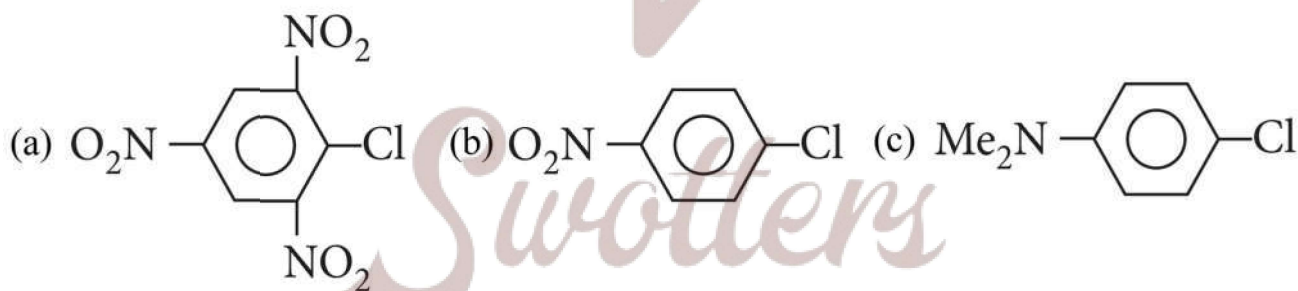
(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?



(iii) Which one of the following will react fastest with aqueous NaOH?



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



d. C_6H_5Cl

(v) The reactivity of the compounds (i) MeBr, (ii) PhCH₂Br, (iii) MeCl, (iv) p-MeOC₆H₄Br decreases as:

- (i) > (ii) > (iii) > (iv)
- (iv) > (ii) > (i) > (iii)
- (iv) > (iii) > (i) > (ii)
- (ii) > (i) > (iii) > (iv)

2. Read the passage given below and answer the following questions:

A chlorocompound (A) on reduction with Zn-Cu and ethanol gives the hydrocarbon (B) with five carbon atoms. When (A) is dissolved in dry ether and treated with sodium metal it gave 2, 2, 5, 5 - tetramethylhexane. The treatment of (A) with alcoholic KCN gives compound (C).

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The compound (A) is:

- a) 1-chloro-2, 2-dimethylpropane.
- b) 1-chloro-2, 2-dimethyl butane.
- c) 1-chloro-2-methyl butane.
- d) 2-chloro-2-methyl butane.

(ii) The reaction of (C) with Na, C₂H₅OH gives:

- a) (CH₃)₃C CH₂CONH₂
- b) (CH₃)₃C NH₂
- c) (CH₃)₃C CH₂CH₂NH₂
- d) (CH₃)₂CHCH₂NH₂

(iii) The reaction of (C) with Na, C₂H₅OH is called:

- a) Gilman reaction.
- b) Mendius reaction.
- c) Grooves process.
- d) Swart's reaction.

(iv) The reaction of (A) with aq. KOH will preferably favour:

- a) S_N1 mechanism.
- b) S_N2 mechanism.
- c) E₁ mechanism.
- d) E₂ mechanism.

(v) Compound (B) is:

- a) N-pentane.
- b) 2, 2-dimethylpropane.
- c) 2-methylbutane.
- d) None of these.

MCQ Answers-

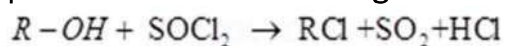
1. Answer: b
2. Answer: b
3. Answer: d
4. Answer: c
5. Answer: c
6. Answer: b
7. Answer: a
8. Answer: d
9. Answer: a
10. Answer: c

Very Short Answers-

- (i) 1, 3- Dibromobutane
- (ii). 1- Chloropropan-2-ol
- (iii). 2, 3 – Dibromo-1-chloro-3-methylpentane
- (iv). 2-Chloro-3-ethyl-2-methyl pentane
- (v). 1-Chloro-2-phenylethane
- (vi). 1-Chloro-1-phenyl ethane
- (vii). 1, 2, 3, 4, 5, 6- hexachlorocyclohexane
- (viii). 2, 2- Dihexyl 1, 1, 1-Trichloro ethane
- (ix). 4, 4-dibromobiphenyl
- (x). 1, 3-Dibromo -3- methyl butane

Short Answers-

Ans 1. Thionyl chloride is preferred for converting alcohol to haloalkane because the by-products formed are all gases which escape into the atmosphere.



Ans 2. In phenol, due to resonance, the carbon-oxygen bond has a partial double bond character and is difficult to break being stronger than a single bond. Therefore, it can-not be converted to chlorobenzene by reacting with HCl.

Ans 3. When benzene is reacted with iodine, the reaction is reversible in nature. It leads to the formation of reactants back. Therefore, an oxidizing agent like HNO_3 oxidizes the HI formed in the reaction and keeps the reaction in forward direction.

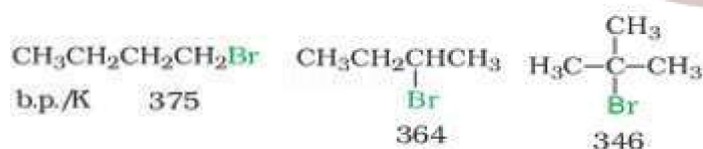
Ans 4.



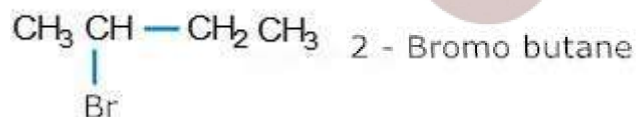
m - dichlorobenzene p - dichlorobenzene

p-dichlorobenzene is having symmetrical structure therefore it can fit better into the crystal lattice which increases its melting point.

Ans 5. The boiling points of isomeric haloalkanes decrease with branching due to decrease in surface areas with branching. As branching increases the structure becomes more spherical and the surface area decreases. e.g. the boiling points of isomers of C_4H_9Br follows the order.



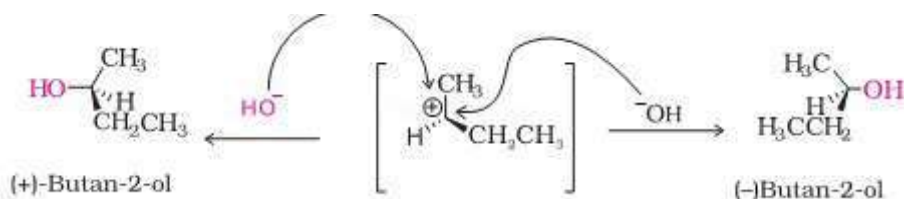
Ans 6.



The compound undergoes hydrolysis by S_N1 mechanism via the formation of carbocation which is planar.

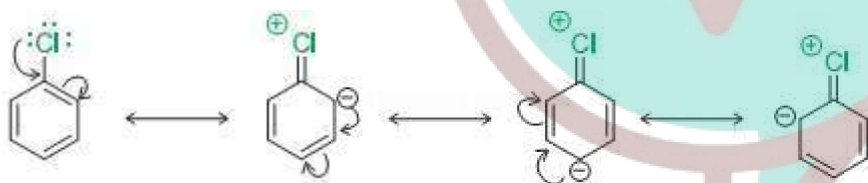


The attack of nucleophile can result in product which is a mixture of compounds both with same configuration and inverted configuration.



Therefore it results in the formation of racemic mixture which is optically inactive.

Ans 7. Chlorobenzene is less reactive towards nucleophilic substitution due to –
i. resonance, C-Cl bond acquires a double bond character and becomes stronger than a single bond.

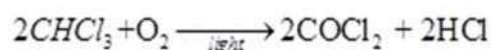


ii. sp^2 hybridisation in C of C-X bond, the carbon becomes more electronegative and holds the electron pair of C-X bond more tightly decreasing the bond length.

iii. Instability of phenyl cation.

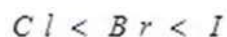
iv. Repulsion for incoming nucleophile from electron rich ring.

Ans 8. Chloroform gets oxidised slowly by air in the presence of light to an extremely poisonous gas phosgene. Therefore, to avoid any exposure to air and sunlight, it is kept in dark coloured bottles.



Ans 9. The boiling points of alkyl halides depends on dipole and van-der-waal's interaction. These attractions get stronger as the molecules get bigger in size and have more electrons.

As the size of halogens increases in the order –



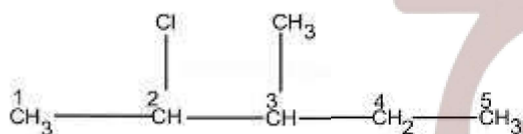
The boiling points also follow the order



Ans 10. Due to resonance C-Cl bond gets double bond character and becomes stronger than a single bond, making vinyl chloride less reactive than allyl chloride.

Long Answers-

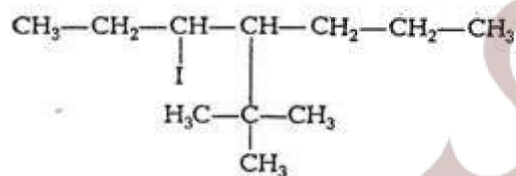
Ans 1. (i) 2-Chloro-3-methyl pentane



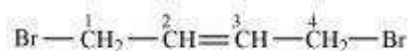
(ii) 1-Chloro-4-ethylcyclohexane



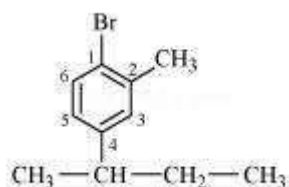
(iii) 4-tert-Butyl-3-iodoheptane



(iv) 1, 4-Dibromobut-2-ene

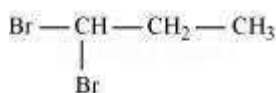


(v) 1-Bromo-4-sec-butyl-2-methylbenzene

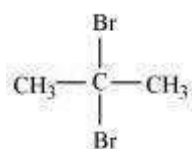


Ans 2. There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

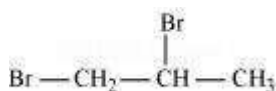
(i) 1, 1-Dibromopropane



(ii) 2, 2-Dibromopropane



(iii) 1, 2-Dibromopropane

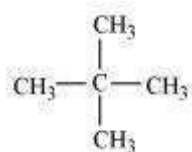


(iv) 1, 3-Dibromopropane



Swotters

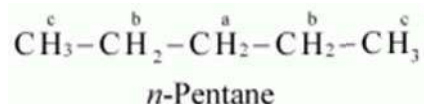
Ans 3. (i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12} . This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



Neopentane

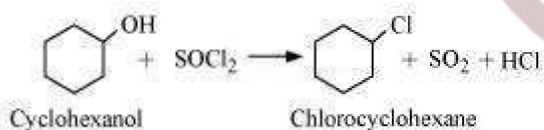
(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.

Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.

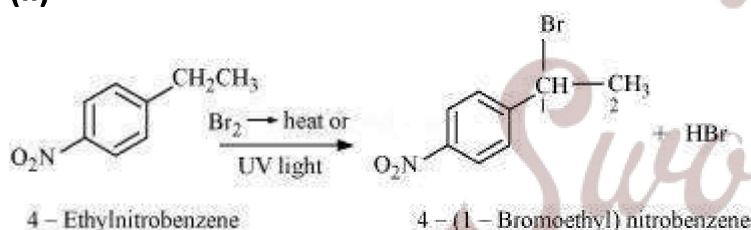


(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H atoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.

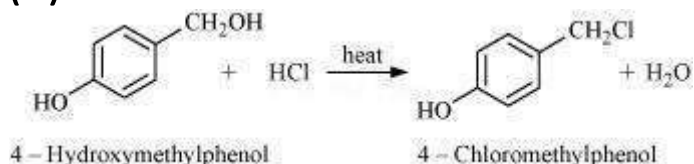
Ans 4. (i)



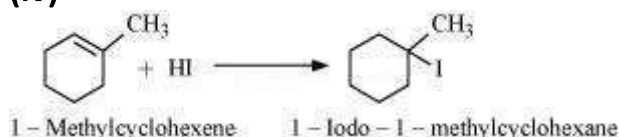
(ii)



(iii)



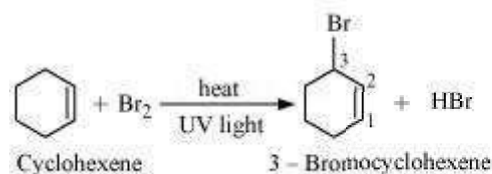
(iv)



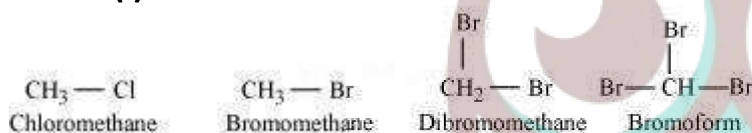
(v)



(vi)



Ans 5. (i)



For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

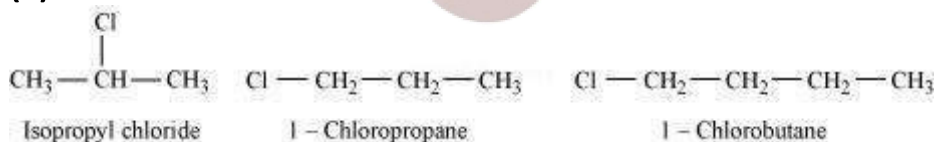
Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform.

Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)



For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

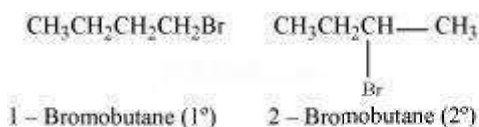
Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

Hence, the given set of compounds can be arranged in the increasing order of their boiling

points as:

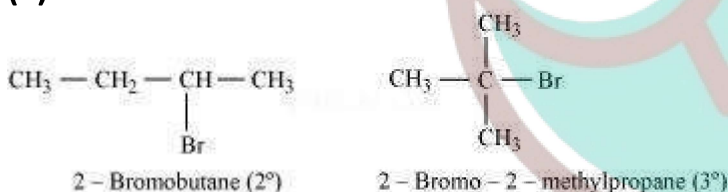
Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

Ans 6. (i)



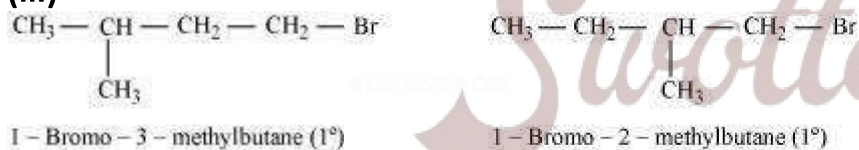
2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(ii)



2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

(iii)

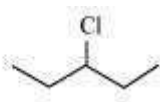


Both the alkyl halides are primary. However, the substituent $-\text{CH}_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

Ans 7. (i)



2-Chloro-2-methylpropane (3°)
(I)



3-chloropentane (2°)
(II)

S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2° . Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)



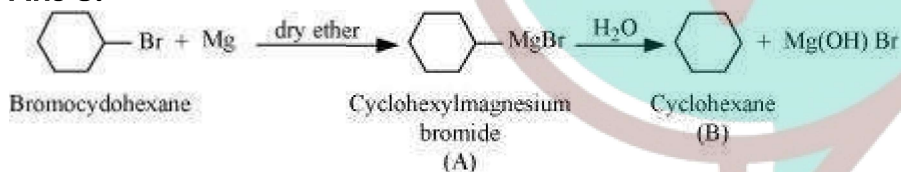
2-chloroheptane (2°)
(I)



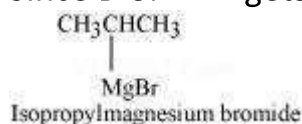
1-chlorohexane (1°)
(II)

The alkyl halide (I) is 2° while (II) is 1° . 2° carbocation is more stable than 1° carbocation. Therefore (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

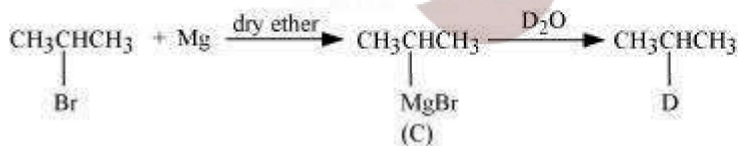
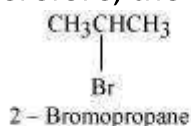
Ans 8.



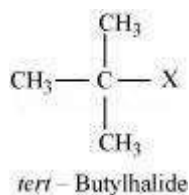
Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is



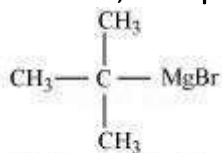
Therefore, the compound R - Br is



When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, R^1-X , is

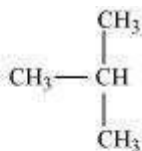


Therefore, compound D is

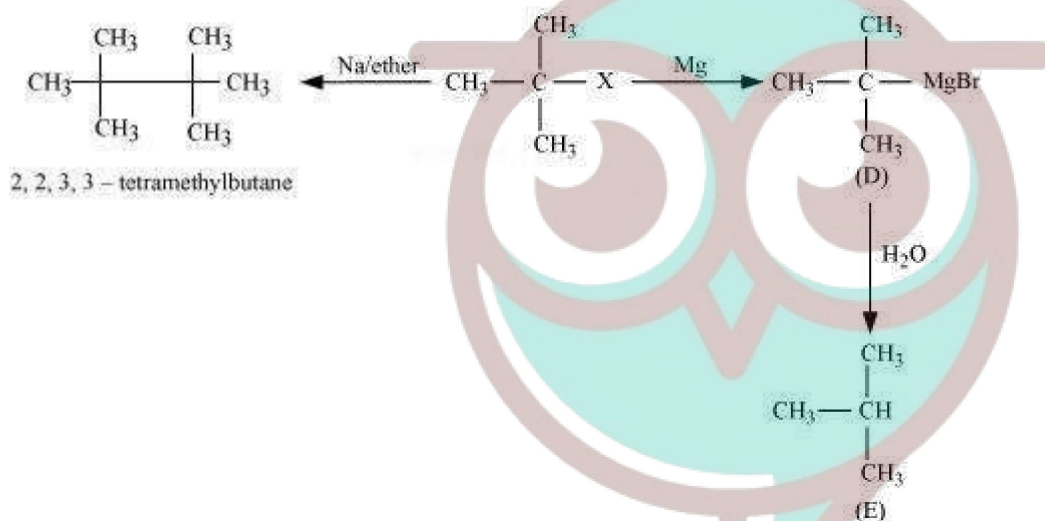


tert - Bulytmagnesiumbromide

And, compound E is



2 - Methylpropane



Assertion and Reason Answers-

1. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Explanation:

As the size of the alkyl groups increases, the $\text{S}_{\text{N}}2$ reactivity decreases, further C - Cl bond is stronger and more difficult to cleave than C - Br bond. So CH_3Br is more reactive than $(\text{CH}_3)_2\text{CHCl}$.

2. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

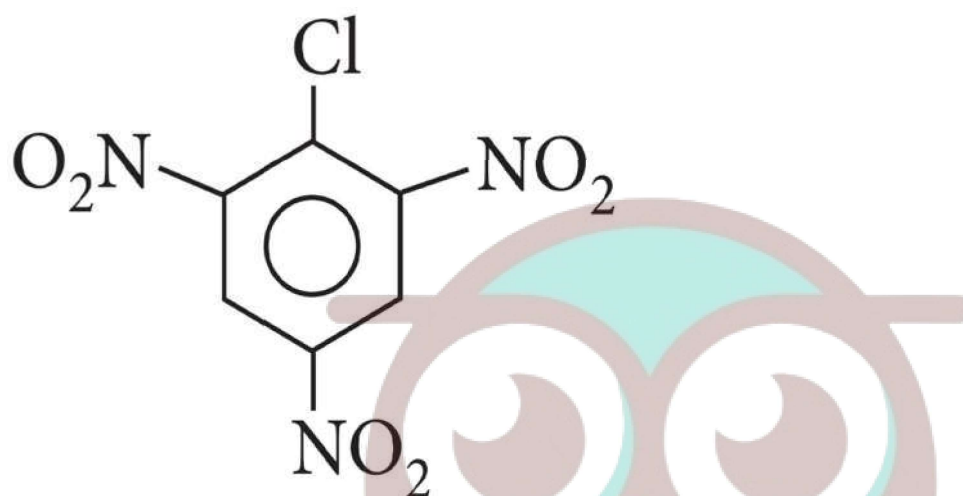
Alkyl iodides in general turn brown due to liberation of I^2 on decomposition by the action of air and light.

Case Study Answers-

1. Answer :

(i) (b) Resonance stabilisation.

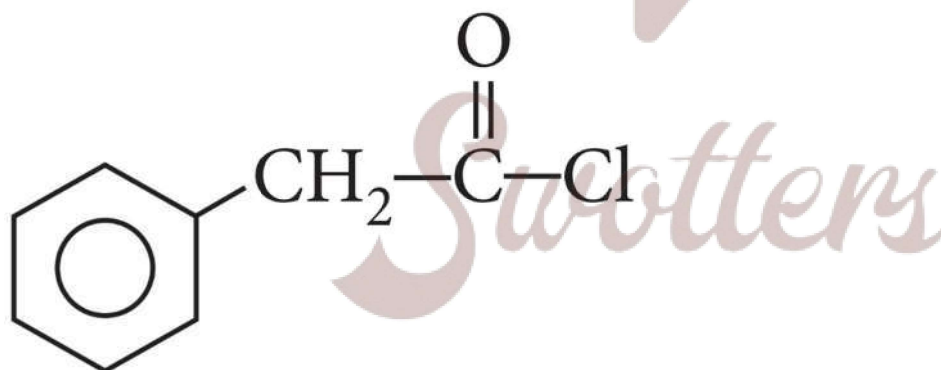
(ii) (d)



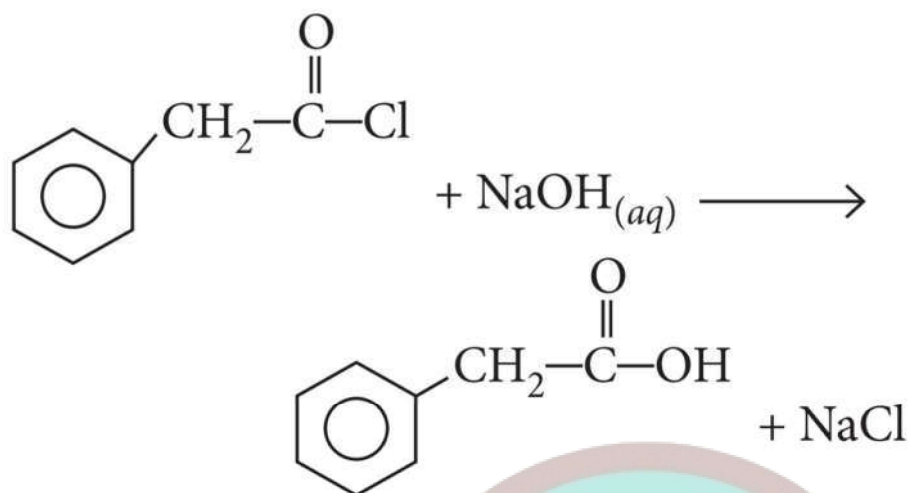
Explanation:

When in aryl halides the electron withdrawing groups are attached at ortho and para positions to the chlorine atom then the removal of chlorine atom as Cl⁻ ion becomes easy, therefore, 2,4,6-trinitro chlorobenzene is the most reactive among given aryl halides.

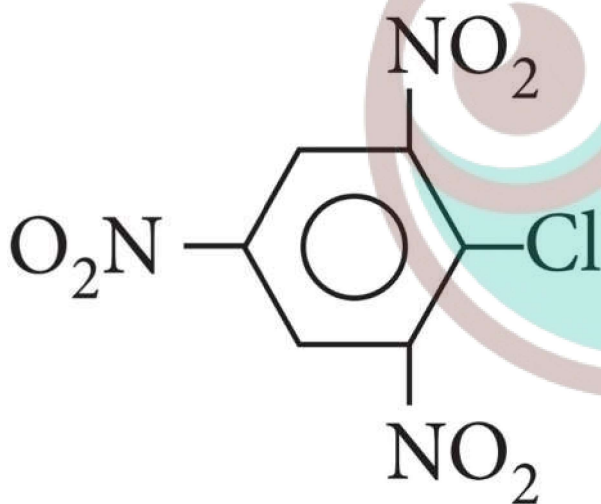
(iii) (d)



Explanation:



(iv) (a)

**Explanation:**

Cl in 2,4,6-trinitrochlorobenzene is activated by three NO_2 groups at o, and p-positions and hence undergoes hydrolysis most readily.

(v) (d) (ii) > (i) > (iii) > (iv)

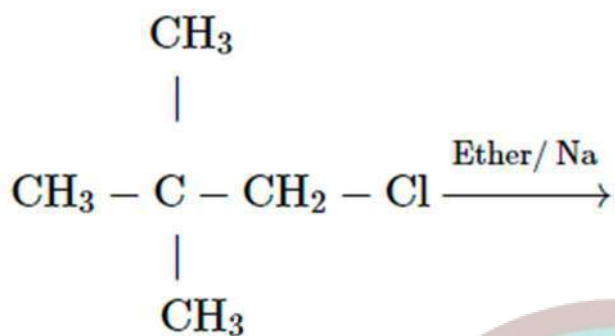
Explanation:

The order of reactivity follows the sequence: benzyl halides > alkyl halides > aryl halides. Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is PhCH_2Br (ii) > MeBr (i) > MeCl (iii) > p - $\text{MeOC}_6\text{H}_4\text{Br}$ (iv).

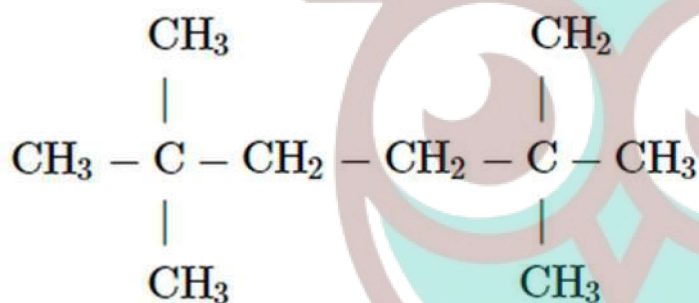
2. Answer :

i. (a) 1-chloro-2, 2-dimethylpropane.

Explanation:



I-Chloro-2, 2-di methylpropane

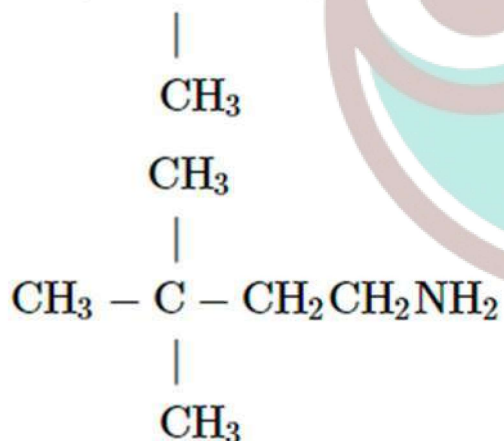
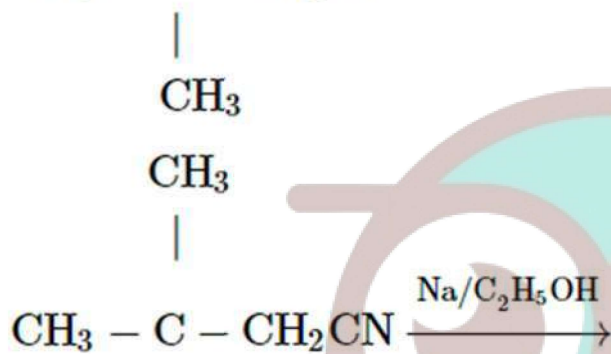
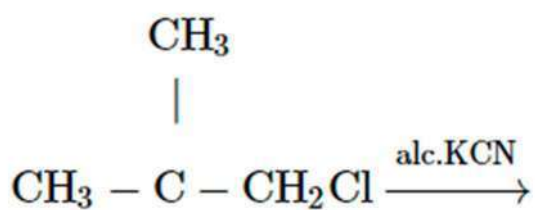


2, 2, 5, 5-Tetramethylhexane

Swotters

ii. (c) $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{NH}_2$

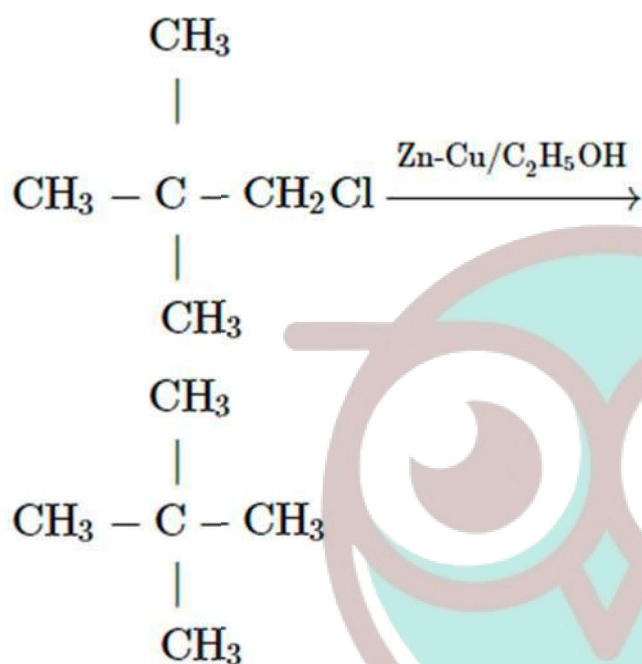
Explanation:



Swotters

- iii. (b) Mendius reaction.
iv. (a) S_N1 mechanism.
v. (b) 2, 2-dimethylpropane.

Explanation:



Swotters