

Solution

CET25C6 HALOALKANES AND HALOARENES

Class 12 - Chemistry

1. **(d)** a mixture of two different alkyl halides has to be used.
Explanation: Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as the Wurtz reaction and is used for the preparation of higher alkanes containing even a number of carbon atoms. Many side products are formed when two different alkyl halides are used. So this method is not preferred to prepare alkanes having an odd number of C atoms.
2. **(d)** 1, 4 – dibromobutane
Explanation: Of all the given options, it is possible with 1,4-dibromobutane to form cyclobutane as shown by intramolecular wurtz reaction.

$$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \\ | \qquad \qquad \qquad | \\ \text{Br} \qquad \qquad \qquad \text{Br} \end{array} + 2 \text{Na} \xrightarrow{\text{ether}} \boxed{} + 2 \text{NaBr}$$

1,4 dibromobutane Cyclobutane
3. **(b)** $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
Explanation: As we move down the group 17, the size of atom increases as $\text{F} < \text{Cl} < \text{Br} < \text{I}$. Thus the bond strength of hydrogen halides reduces as $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$. So, it is easiest to break the H-I bond. Hence, the decreasing order of reactivity for the conversion of ROH to RX is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.
4. **(a)** All of these
Explanation: When a haloalkane with β -hydrogen atom is heated with an alcoholic solution of potassium hydroxide, there is an elimination of hydrogen atom from β -carbon and a halogen atom from the α -carbon atom. As a result, an alkene is formed as a product. Since the β -hydrogen atom is involved in elimination, it is often called β -elimination.
5. **(b)** passing dry hydrogen chloride gas through a solution of alcohol.
Explanation: The preparation of alkyl chloride is carried out by passing dry hydrogen chloride gas through a solution of alcohol.

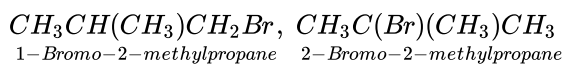
$$\text{ROH} + \text{HCl} \rightarrow \text{RCl} + \text{H}_2\text{O}$$

The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, ZnCl_2 . With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature.
6. **(d)** $\text{R-X} + \text{NaI} \xrightarrow{\text{Dry acetone}} \text{R-I} + \text{NaX}$
Explanation: $\text{R-X} + \text{NaI} \xrightarrow{\text{Dry acetone}} \text{R-I} + \text{NaX}$
7. **(c)** Chloroquine
Explanation: Chloroquine is a synthetic halogen compound. It is used for the treatment of malaria.
8. **(c)** 1 – Bromobutane, 2 – Bromobutane, 1 – bromo- 2 – methylpropane, and 2 – bromo-2 – methylpropane
Explanation: Isomers are compounds having the same molecular formula but different structures. In the given straight-chain 4-C compounds, Br is placed at different positions but the molecular formula is same.

$$\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$$

2-Bromobutane 1-Bromobutane

In the given branched 4-C compounds, there is a branching of $-\text{CH}_3$ at carbon 2 but Br is placed at positions 1 and 2 respectively.



So, all of these are isomers since they have the same molecular formula but different structures.

9.

(b) 1-Bromo-2,2-dimethylpropane.

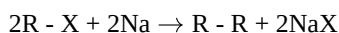
Explanation: neo-Pentyl bromide is $(CH_3)_3CCH_2Br$. C attached to Br is given position 1, so 2 $-CH_3$ groups are placed on 2nd C of the propane (parent chain).

Therefore, the IUPAC name of neo-Pentyl bromide **1-Bromo-2,2-dimethylpropane**.

10.

(d) Wurtz reaction

Explanation: The **Wurtz reaction**, named after Charles-Adolphe **Wurtz**, is a coupling reaction in organic chemistry, organometallic chemistry and recently inorganic main group polymers, whereby two alkyl halides are reacted with sodium metal in dry ethereal solution to form a higher alkane:



11.

(d) 2-chloro, 2-methyl propane

Explanation: Longest chain will be of three carbon to which Cl and CH_3 will be attached at 2 positions.

12.

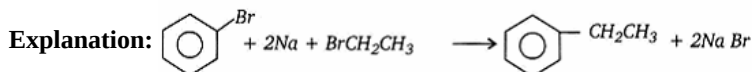
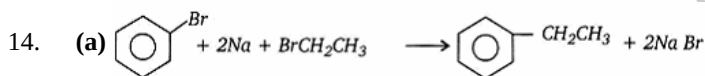
(a) Ethanol

Explanation: Ethanol

13.

(b) (C) > (B) > (A)

Explanation: Haloalkanes are prepared from alcohol and halogen acids where the hydroxyl group of the alcohol is replaced by the halogen. Options (A) (B) and (C) are primary, secondary, tertiary alcohols respectively. Tertiary alcohols are more reactive than secondary and primary alcohol, the secondary halide is more reactive than primary halide and they form haloalkanes from haloacids at room temperature without catalysts. The order of reactivity of alcohols is $3^\circ > 2^\circ > 1^\circ$.



A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction. In above reaction ethyl bromide and bromobenzene react with sodium in dry ether to give ethyl benzene.

15.

(a) sp^3 -hybridized carbon atom, next to an aromatic ring bonded to a halogen.

Explanation: Benzylic halides are the compounds in which the halogen atom is bonded to an sp^3 -hybridized carbon atom next to an aromatic ring. For example $C_6H_5CH_2Cl$.

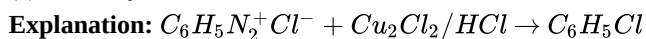
16.

(d) Electrophilic substitution reaction

Explanation: This is example of electrophilic aromatic substitution (EAS) reaction. Single Cl ion replaces hydrogen atom and here $FeCl_3$ acts as halogen carriers.

17.

(c) Sandmeyer's reaction



Mixing the solution of the freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by $-Cl$ or $-Br$. This is called Sandmeyer's reaction.

18.

(b) $CH_3CH_2CH_2CH_2Cl$

Explanation: The forces of attraction between the molecules of a compound get stronger as they get bigger in size and have more electrons. Also, for a straight-chain compound, the points of interaction between the molecules are more than for a branched compound having the same molecular formula. Thus $CH_3CH_2CH_2CH_2Cl$ has the highest melting point since it is the longest chain compound among the given options.

19. **(b)** Ethyl bromide + alcoholic KCN
Explanation: $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \rightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{KBr}$
20. **(d)** $\text{Cl}_2/\text{UV light}$
Explanation: Production of alkyl chlorides from alkanes can be carried out by chlorination under the presence of UV light. Chlorine molecule (Cl_2) under the influence of UV light forms free radicals, which react with alkanes to form a mixture of isomeric monohaloalkane and polyhaloalkanes.
21. **(b)** a halogen atom bonded to an sp^2 -hybridized carbon atom of a carbon-carbon double bond.
Explanation: Vinylic halides are the compounds in which the halogen atom is bonded to an sp^2 -hybridized carbon atom of a carbon-carbon double bond ($\text{C} = \text{C}$). For example $\text{CH}_2=\text{CHBr}$.
22. **(a)** Fluorine
Explanation: Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery. So fluorine is the element used in these blood substitutes.
23. **(b)** (a), (b), (c)
Explanation: Asymmetric/chiral carbon atom is that in which all of its four valencies with four different groups or atoms (can not be superimpose). In molecules (i), (ii), and (ii), all have asymmetric carbon as each carbon has satisfied all four valencies with four different groups of atoms.
24. **(b)** Swartz reaction
Explanation: The synthesis of alkyl fluorides is best accomplished by Swarts reaction which can be given as follows: $\text{R-X} \rightarrow \text{R-F} + \text{AgX}$.
25. **(a)** 3, 4, 4 - trimethylpent - 2 - ene
Explanation: The longest chain contains a double bond and five carbon i.e pent-2-ene and 2 methyl is attached to the 4th carbon and one is attached to 3rd carbon. Therefore IUPAC name is 3, 4, 4 - trimethylpent - 2 - ene.
26. **(a)** $\text{CH}_2 = \underset{\text{Br}}{\text{C}} - \text{CH}_3$
Explanation: $\text{CH}_2 = \underset{\text{Br}}{\text{C}} - \text{CH}_3$ belongs to vinyl halides
27. **(d)** $\text{S}_{\text{N}}1$ reaction
Explanation: Racemisation occurs in $\text{S}_{\text{N}}1$ reaction not in $\text{S}_{\text{N}}2$ reaction because in case of $\text{S}_{\text{N}}1$ a group (base/nucleophile) attack from (in front and back side) both sides.
28. **(a)** $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$
Explanation: $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)^+$ carbocation formed is more stable.
29. **(b)** a substitution reaction
Explanation: $\text{R-X} + \text{NaOH} \rightarrow \text{R-OH} + \text{NaX}$
30. **(b)** Chloramphenicol
Explanation: Chlorine containing antibiotics, chloramphenicol, produced by soil microorganisms is very effective for the treatment of typhoid fever. Chloramphenicol is an antityphoid drug.
31. **(d)** 3

Explanation: CH_3NH_2 can act as a nucleophile to cause substitution reaction. $(\text{CH}_3)_4\text{N}^+$ this is formed when 3 moles of CH_3NH_2 reacts with methyl halide.

32. (a) Cl^+

Explanation: Cl^+ attacks the benzene to form chloro benzene

33.

(b) $\text{CH}_2 = \text{CH} - \text{Cl}$

Explanation: $\text{CH}_2 = \text{CH} - \text{Cl}$

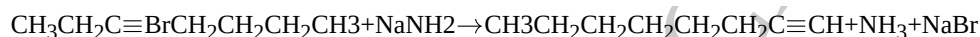
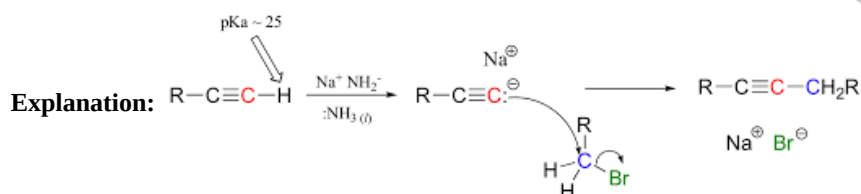
34. (a) Methanamine (CH_3NH_2)

Explanation: $\text{CH}_3\text{Cl} + \text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{HCl}$

Ammonia molecule is a nucleophile in nature as it has unpaired electrons. This nucleophile attacks the chloromethane CH_3Cl molecule and forms methylamine or methenamine by a nucleophilic substitution reaction mechanism. The carbon atom is partially positive in the molecule, due to the electronegativity of the halide attached which is partially negative. The electron-rich nucleophile attacks the positive ion, causing the halide ion to be separated from the molecule.

35.

(d) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$

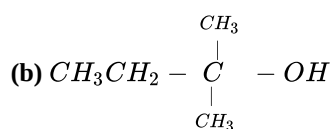


NaNH_2 is a very strong base it will abstract H from alkyne (But-1-yne in this case) and then nucleophilic substitution reaction will occur as shown where the resulting compound will be Oct-1-yne as here the reactants contain a total of 8 C.

36. (a) $\text{S}_{\text{N}}1$ reaction

Explanation: Retention of configuration is observed in $\text{S}_{\text{N}}1$ reaction

37.



Explanation: Alkyl halides can be obtained by treating alcohol with haloacids. The reactivity of tertiary alcohols with the haloacids is the highest and primary alcohols are the lowest. Formation of alkyl chloride using primary and secondary alcohols requires the usage of a catalyst ZnCl_2 , where dry hydrogen chloride gas is passed through a solution of alcohol or by heating a mixture of alcohol and concentrated aqueous halogen acid. Reaction with tertiary alcohols does not require a catalyst and can be carried out by using tertiary alcohols. the reaction is conducted by simply shaking with concentrated HCl at room temperature.

38.

(b) 1-Bromo-2-methylbutane

Explanation: First, we need to identify the longest carbon chain. Once we do that, the actual structure should read $\text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{Br}$. -Br, the functional halide group is attached to the first carbon atom (1- Bromo), so we start the numbering from that position. The methyl group branch is bond to the second carbon atom in the chain(2-methyl). The number of carbons in the unbranched parent chain is four, thus giving the name butane. The IUPAC is named 1-Bromo-2-methylbutane.

39. (a) $\text{C}_2\text{H}_5\text{-I}$

Explanation: For the same alkyl group the boiling points of haloalkanes are in the order of $\text{RF} < \text{RCl} < \text{RBr} < \text{RI}$ as with the increase in size of halogen atom the magnitude of van der Waals forces of attraction increases, resulting in higher boiling points.

40. (a) $(\text{CH}_3)_3\text{C—I}$

Explanation: $\text{S}_{\text{N}}1$ reactions are generally carried out mainly in polar protic solvents (like H_2O) and they follow first-order kinetics. This means that the rate of reaction depends only on one reactant. This reaction favours tertiary alkyl halides because of the high stability of the formed carbocation. The carbocation forms when the molecule is polarized in water to form a carbocation and halide ion attacked by the nucleophile. The reactivity of the halides are $\text{R—I} > \text{R—Br} > \text{R—Cl} > \text{R—F}$. Hence, $(\text{CH}_3)_3\text{C—I}$ will undergo the reaction most readily.

41.

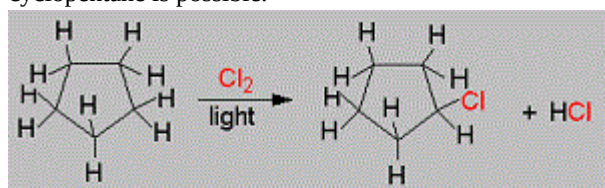
(c) a dehydrohalogenation reaction

Explanation: When alkyl halides are heated in the presence of alcoholic potash (alcoholic potash is when potassium hydroxide is dissolved in alcohol), the product we get is an alkene. In this one molecule of halogen is eliminated to give alkene. This type of reaction is also known as dehydrohalogenation reaction.

42.

(d) Cyclopentane

Explanation: Cyclopentane is nearly inert chemically, they react with halogens in the presence of light through the substitution of one hydrogen atoms. Since the cyclic structure confers a high degree of symmetry on the molecule, only one monochloro cyclopentane is possible.



43.

(d) shorter and stronger

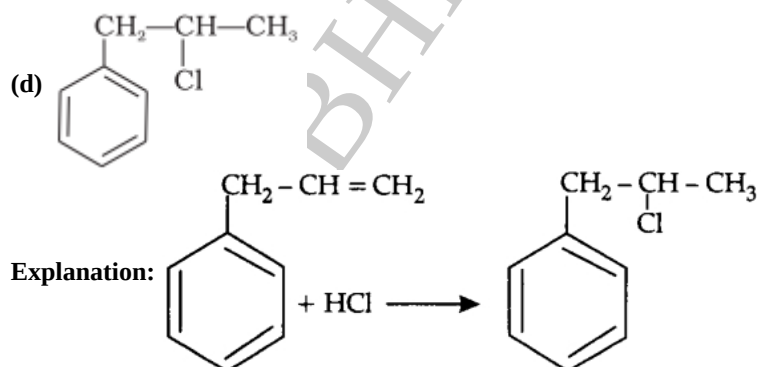
Explanation: In chlorobenzene, the hybridization of carbon attached to Cl is sp^2 , and in methyl chloride hybridization of C attached to Cl is sp^3 . In sp^2 hybridization, s-character is 33% and in sp^3 s-character is 25%. The sp^2 hybridized carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridized carbon in haloalkane with less s-character resulting in a short bond length of C—Cl bond. Since it is difficult to break a shorter bond than a longer bond, means it is stronger. Also in chlorobenzene, the electron pairs on Cl atom are in conjugation with π -electrons of the ring, so C—Cl bond acquires a partial double bond character due to resonance which makes the bond stronger.

44.

(b) $\text{CH}_3\text{C}^*\text{HClCH}_2\text{Br}$

Explanation: $\text{CH}_3\text{C}^*\text{HClCH}_2\text{Br}$

45.

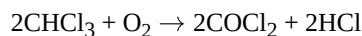


The products obtained can be explained by Markonikov's rule. According to the rule, the hydrogen from HCl will get added to the carbon directly bonded to the most hydrogen atoms (addition reaction), and the —Cl will get bonded to the carbon directly bonded to the least hydrogens.

46. (a) gets slowly oxidized by air in the presence of light and form a poisonous gas.

Explanation: In the presence of light chloroform slowly oxidizes in air to form phosgene (carbonyl chloride COCl_2), which is

a poisonous gas. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.



47.

(c) Thyroxine

Explanation: Our body produces iodine-containing hormone, thyroxine, the deficiency of which causes a disease called a goiter.

48.

(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Explanation: When alkanes larger than ethane are halogenated, isomeric products are formed.

49.

(d) $\text{S}_{\text{N}}2$ reaction

Explanation: Inversion of configuration occurs in $\text{S}_{\text{N}}2$ reaction

50.

(d) Cyclopentane

Explanation: Alkanes undergo free radical halogenation in the presence of sunlight to give a mixture of isomeric mono- and polyhaloalkanes. So cyclopentane must be the compound with formula C_5H_{10} which must have reacted with Chlorine in presence of sunlight (but not in dark) to form $\text{C}_5\text{H}_9\text{Cl}$.

51.

(c) gem-dihalide

Explanation: Gem-dihalides are dihaloalkanes that have two halogen atoms of the same type attached to the same carbon atom in a molecule. The common naming system of gem-dihalides (geminal halide) is alkylidene dihalides. Ethylidene dichloride thus is a gem-dihalide. The chemical formula of ethylidene dichloride is $\text{C}_2\text{H}_4\text{Cl}_2$.

52. (a) $\mu = 0$

Explanation: CCl_4 is a symmetrical molecule. Hence, the dipole moment is zero.

53. (a) SOCl_2 in presence of pyridine

Explanation: The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides, or thionyl chloride. Thionyl chloride (SOCl_2) is preferred because the other two products SO_2 and HCl are escapable gases. Hence, the reaction gives pure alkyl halides.



54. (a) All of these

Explanation: Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarized; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.

55. (a) Na

Explanation: The Wurtz reaction, named after Charles-Adolphe Wurtz, is a coupling reaction in organic chemistry, organometallic chemistry and recently inorganic main group polymers, whereby two alkyl halides are reacted with sodium metal in dry ether solution to form a higher alkane: $2\text{R-X} + 2\text{Na} \rightarrow \text{R-R} + 2\text{NaX}$.

56.

(c) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane

Explanation: Due to the polar nature of alkyl halides and the increase in molecular weight compared to their parent alkanes, the boiling points of alkyl halides are higher than that of their parent alkanes. The boiling points of alkyl halides depend on the molecular mass and the size of the halogen atom (decrease from I to F). With the increase in size, mass, and the number of electrons in halogen atoms, the magnitude of Van Der Waals forces increase and the boiling point also increases. The boiling point of alkyl halides reduces in the order $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$.

Therefore, the order of increasing order of boiling points should be Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane.

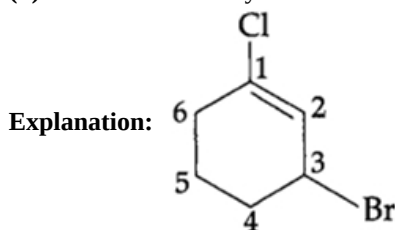
57.

(d) Neopentane

Explanation: Neopentane has all same type of hydrogen and has molecular weight 72u.

58.

(b) 3-bromo-1-chlorocyclohexene



IUPAC name: 3-bromo 1-chlorocyclohexene

59.

(b) Wurtz - Fittig reaction

Explanation: Wurtz - Fittig reaction

60. (a) $R-X + NaI \rightarrow RI + NaX$

Explanation: Halogen exchange reactions are those reactions in which one halide replaces another. This reaction is known as the Finkelstein reaction. In

- Halogen (-X) is replaced by iodine (presence of dry acetone).
- Addition of hydrogen halide on the alkene.
- Halogen replaces the alcoholic group.
- Halogen replaces the hydrogen of the benzoic ring.

61.

(d) (a)

Explanation: A mixture containing two enantiomers in equal proportions but with zero optical activity because the opposite optical rotations of the two enantiomers cancel out each other rotation is called a racemic mixture.

Options (a) is a chiral carbon atom and it will undergo an S_N1 substitution mechanism to give a racemic mixture.

Option (b) is not an asymmetric carbon.

Option (c) contains a secondary carbon asymmetric atom, which has less reactivity towards an S_N1 substitution mechanism.

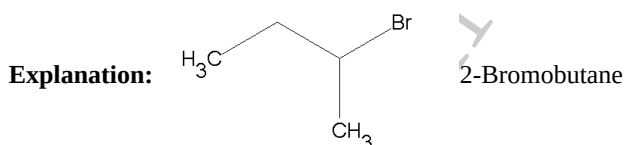
62.

(c) 2-Methylbutan-2-ol

Explanation: 2-Methylbutan-2-ol

63.

(c) 2-Bromobutane



It is a chiral molecule since it does not contain plane symmetry and centre of symmetry.

64.

(d) b, c

Explanation: Chiral molecules (the object which is non-superimposable on their mirror image) contain one carbon atom surrounded by four non-identical species. All straight-chain molecules cannot be chiral because of the presence of two or more identical groups like hydrogens. Even the carbons with double or triple bonds to a group cannot be considered as a chiral carbon. An asymmetric carbon needs to be surrounded by four species different from each other through covalent bonds. Hence, the atoms b and c are asymmetric.

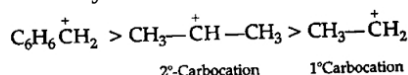
65.

(d) Benzyl chloride

Explanation: The S_N1 is carried out in two steps:

Step (i) : Formation of carbocation (based on its stability).

Step (ii) : Attack of nucleophile.

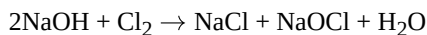
Stability order of carbocation :

Thus due to formation of stable carbocation benzyl chloride undergo $\text{S}_{\text{N}}1$ mechanism.

66.

(c) NaCl and NaClO

Explanation: Chlorine reacts with cold and dilute NaOH to produce a mixture of sodium chloride (NaCl) and sodium hypochloride (NaOCl).

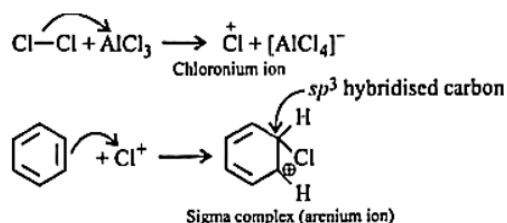


67.

(c) Cl^+

Explanation:

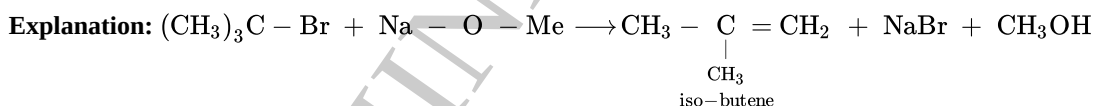
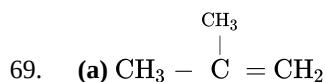
Aluminum chloride (AlCl_3) is a Lewis acid catalyst and works in the same way as FeCl_3 does. Benzene (C_6H_6) is converted into chlorobenzene by chlorination of benzene in the presence of AlCl_3 . The reaction occurs by an electrophilic substitution reaction. Cl_2 forms a coordination complex with AlCl_3 , forming $\text{Cl}^+\text{AlCl}_4^-$ complex, which gives a slight positive charge to Cl, and AlCl_4^- is negatively charged. This Cl^+ then reacts with the aromatic double bond of the benzene ring to form an additional product, followed by deprotonation to form chlorobenzene and AlCl_3 and HCl as the side products.



68.

(d) o-Dichlorobenzene

Explanation: o-Dichlorobenzene



Tert-halide with strong base favours elimination reaction not the substitution reaction.

70. (a) methylamine

Explanation: methylamine