

Alkyl Halides

## ALKYL HALIDES

### C1A Physical Properties :

Because of their greater molecular weights, haloalkanes have considerably higher boiling points than alkanes with the same number of carbon atoms.

For a given alkyl group, the boiling point increases with increase of atomic weight of halogen. So fluoride has lowest boiling point and iodide has the highest boiling point.

With branching boiling point decreases.

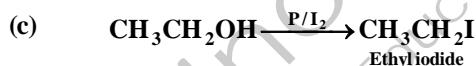
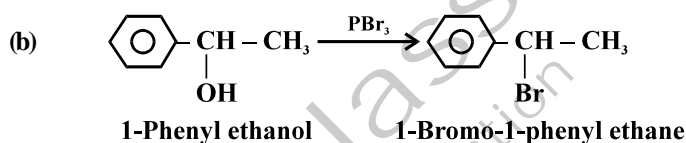
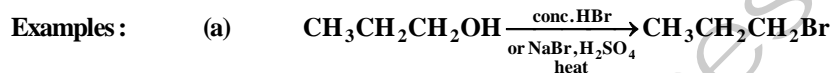
In spite of their modest polarity they are insoluble in water probably because of their inability to form hydrogen bonds.

They are soluble in typical organic solvents of low polarity like benzene, ether, chloroform etc.

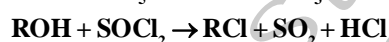
Iodo, bromo and polychloro compounds are more dense than water.

Alkane and Alkyl halide compounds of low polarity are held together by vander waal's forces or weak dipole-dipole attraction.

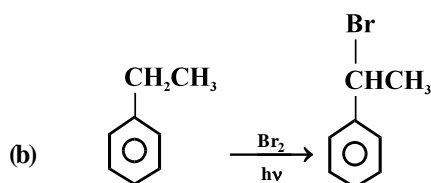
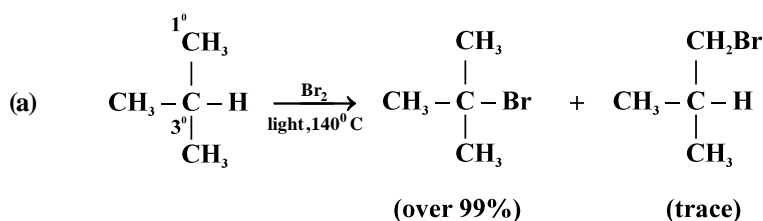
### C1B Method of preparation of Alkyl Halide :



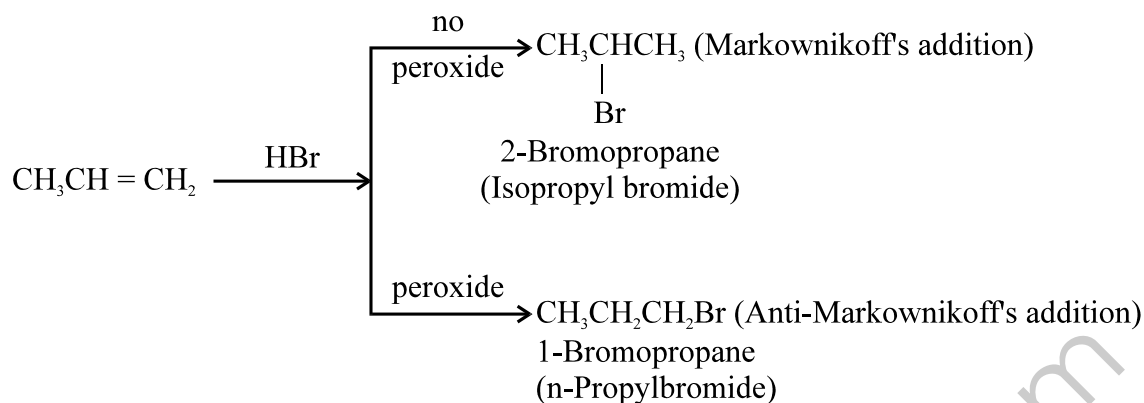
Although certain alcohols tend to undergo rearrangement during replacement of -OH by -X, this tendency can be minimized by use of phosphorous halide.



Examples :

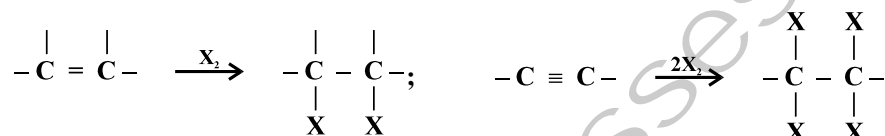


## 3. Addition of Hydrogen halides to alkenes :



Peroxide has no effect on HF, HCl and HI

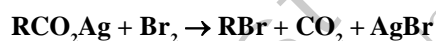
## 4. Addition of halogen to alkenes and alkynes :

5. Halide exchange (Finkelstein reaction)  $\text{R-X} + \text{NaI} \xrightarrow{\text{acetone}} \text{R-I} + \text{NaX}$  (X = Cl, Br)

An alkyl iodide is prepared often from the corresponding bromide or chloride by treatment with a solution of sodium iodide in acetone; the less soluble bromide or sodium chloride precipitate from the solution and can be removed by filtration.

## 6. Hunsdiecker or Borodine-Hunsdiecker reaction :

Silver salts of the carboxylic acids in carbon tetrachloride solution are decomposed by chlorine or bromine to form the alkyl halide e.g.



The yield of halide is primary > secondary > Tertiary.

7. Swarts Reaction :  $\text{CH}_3\text{Br} + \text{AgF} \rightarrow \text{CH}_3\text{F} + \text{AgBr}$ 

(It is the best way to prepare alkyl fluorides by halogen exchange)

Practice Problems :

1. An organic halide with formula  $\text{C}_6\text{H}_{13}\text{Br}$  on heating with alc. KOH gives two isomeric alkenes (A) and (B) with formula  $\text{C}_6\text{H}_{12}$ . On reductive ozonolysis of mixture (A) and (B), the following compounds are obtained :



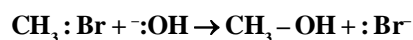
The organic halide is :

- (a) 2-bromohexane (b) 3-bromo-2-methylpentane  
 (c) 2, 2-dimethyl-1-bromohexane (d) none of the above
2. Ethene on treatment with bromine in presence of NaCl solution gives :
- (a) 1,2-dibromoethane  
 (b) 1, 2-dichloroethane  
 (c) a mixture of 1, 2-dibromo and 2-bromo-1-chloro, ethanes  
 (d) no reaction occurs

[Answers : (1) b (2) c]

C2 Chemical properties of Alkyl Halides :

(a) **Nucleophilic Aliphatic Substitution :** When  $\text{CH}_3\text{Br}$  is treated with sodium hydroxide in solvent that dissolves both reagents, there is obtained methanol and sodium bromide. This is a substitution reaction : the  $-\text{OH}$  group is replaced by  $-\text{Br}$  in the original compound. An alkyl halide is converted into alcohol.



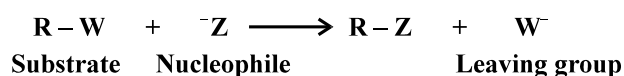
It is clearly heterolytic. This is one example of the class of reactions called nucleophilic substitution reaction.

Nucleophilic substitution is characteristic of alkyl halide.

As halide ion are weak bases. As hydrogen halides show high acidity that is its readiness to release  $\text{H}^+$  ions so halide ions are weak bases and just a halide releases a proton, so it readily releases carbon again to other bases.

Basic, electron rich reagents that tend to attack the nucleus of carbon are called nucleophilic reagents or simply nucleophiles.

When this attack result in substitution it is called nucleophilic substitution reaction.



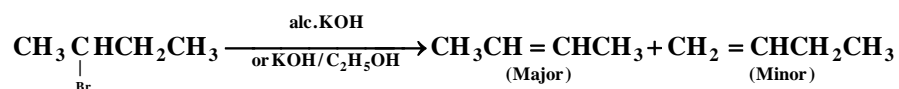
Nucleophile can be neutral with electropair like  $:\text{NH}_3$ ,  $\text{RNH}_2$  or it can be negatively charged.

If  $:\text{Z}$  is neutral then  $\text{R} : \text{Z}$  will be positively charged. If  $:\text{Z}$  is negatively charged then  $\text{R} : \text{Z}$  will be neutral. Nucleophilic substitution is possible by two mechanisms  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$ .

Reactions of Alkyl Halides : ( $\text{S}_{\text{N}}2$ ) (Nucleophilic Substitution)

[ $\text{R}-\text{X}$ ,  $\text{X} \rightarrow -\text{I}, -\text{Cl}, -\text{Br}$ ,  $\text{R} \rightarrow \text{CH}_3-, 1^\circ, 2^\circ$ ]. Examples of Nucleophilic Substitution are as follows :

- (i)  $\text{R} : \text{X} + \text{:Z} \longrightarrow \text{R} : \text{Z} + \text{:X}^-$       (ii)  $\text{R} : \text{X} + \text{:OH}^- \longrightarrow \text{ROH} + \text{:X}^-$
- (iii)  $\text{R} : \text{X} + \text{H}_2\text{O} \longrightarrow \text{ROH}$       (iv)  $\text{R} : \text{X} + \text{:OR}' \longrightarrow \text{ROR}'$  (Williamson's Synthesis)
- (v)  $\text{RX} + \text{:C} \equiv \text{CR}' \longrightarrow \text{R} - \text{C} \equiv \text{CR}$       (vi)  $\text{RX} + \delta^- \text{R}' - \text{M}^{\delta+} \longrightarrow \text{R} - \text{R}'$
- (vii)  $\text{RX} + \text{I}^- \xrightarrow{\text{Acetone}} \text{RI} + \text{X}^-$       (viii)  $\text{RX} + \text{KCN} \longrightarrow \text{RCN} + \text{KX}$   
Alkyl iodide      Alkyl cyanide
- (ix)  $\text{RX} + \text{AgCN} \longrightarrow \text{AgX} + \text{R} - \text{NC}$       (x)  $\text{RX} + \text{R}'\text{COO}^- \longrightarrow \text{R}'\text{COOR} + \text{X}^-$   
Alkyl isocyanide      Ester
- (xi)  $\text{RX} + \text{:NH}_3 \longrightarrow \text{R} - \text{NH}_2 \xrightarrow{\text{RX}} \text{R}_2\text{NH} \xrightarrow{\text{RX}} \text{R}_3\text{N} \xrightarrow{\text{RX}} \text{R}_4\text{N}^+$   
Primary amine
- (xii)  $\text{R} - \text{X} + \text{CH} \begin{array}{l} \text{COCH}_3 \\ \text{CO}_2\text{C}_2\text{H}_5 \end{array} \longrightarrow \text{R} - \text{CH} \begin{array}{l} \text{COCH}_3 \\ \text{CO}_2\text{C}_2\text{H}_5 \end{array}$       (xiii)  $\text{RX} + \text{KSH} \longrightarrow \text{RSH}$   
Acetoacetic ester
- (xiv)  $\text{RX} + \text{KSR} \longrightarrow \text{RSR}$       (xv)  $\text{R} - \text{X} + \text{Ar} - \text{H} + \text{AlCl}_3 \longrightarrow \text{Ar} - \text{R}$  (Alkyl benzene)  
Thio ether (sulphide)      Friedal Craft reaction

(b) Dehydrohalogenation :Elimination

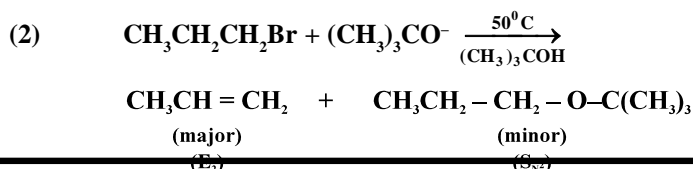
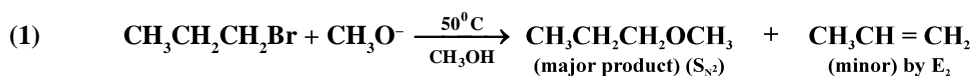
Elimination mechanism is possible in two ways i.e., E<sub>1</sub> and E<sub>2</sub> :

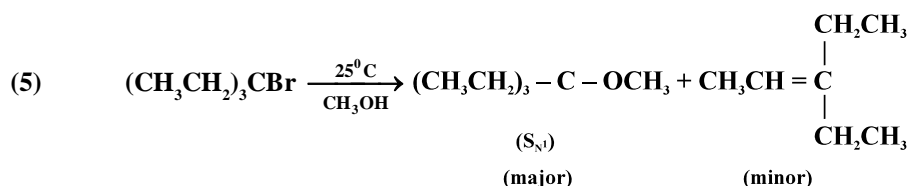
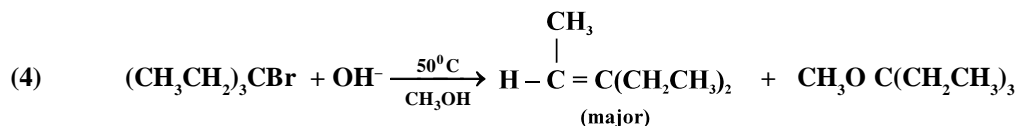
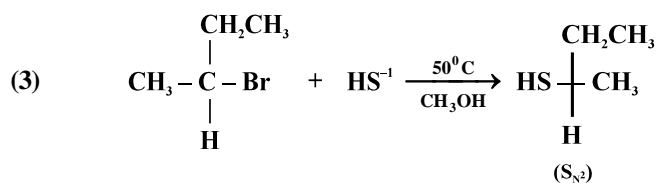
E <sub>1</sub>	E <sub>2</sub>
1. Rate law expression is $r = k[\text{RX}]$	Rate law expression is $r = k[\text{RX}][\text{B}^-]$
2. First order reaction	Second order reaction
3. Intermediate is carbocation	Transition state is formed
4. Order of reactivity of RX $3^\circ > 2^\circ > 1^\circ$	Order of reaction of RX $3^\circ > 2^\circ > 1^\circ$
5. $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$	$\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$

overall summary of S<sub>N</sub><sup>1</sup>, E<sub>1</sub>, S<sub>N</sub><sup>2</sup>, E<sub>2</sub> reactions

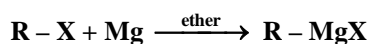
$\text{CH}_3\text{X}$ (Methyl halide)	→	Bimolecular reactions i.e., S <sub>N</sub> <sup>2</sup> only
$\text{RCH}_2\text{X}$ (1 <sup>o</sup> )	→	Gives mainly S <sub>N</sub> <sup>2</sup> reaction
	→	With hindered strong base [e.g., (CH <sub>3</sub> ) <sub>3</sub> CO <sup>-</sup> ] then gives mainly E <sub>2</sub>
$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{CH}-\text{X} \\ (2^\circ) \end{array}$	→	Gives mainly S <sub>N</sub> <sup>2</sup> with weak bases (I <sup>-</sup> , CN <sup>-</sup> , RCO <sub>2</sub> <sup>-</sup> ) and mainly E <sub>2</sub> with strong bases like RO <sup>-</sup> .
$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{CH}-\text{X} \\   \\ \text{R} \\ (3^\circ) \end{array}$	→	Gives mainly S <sub>N</sub> <sup>1</sup> /E <sub>1</sub> or E <sub>2</sub>
	→	No S <sub>N</sub> <sup>2</sup> Reaction
	→	In water solvent gives S <sub>N</sub> <sup>1</sup> /E <sub>1</sub>
	→	Lower temperature S <sub>N</sub> <sup>1</sup> is favoured
	→	When a strong base (e.g. RO <sup>-</sup> ) is used E <sub>2</sub> predominates.

Following are the examples based on S<sub>N</sub><sup>1</sup>, S<sub>N</sub><sup>2</sup>, E<sub>1</sub> and E<sub>2</sub>.

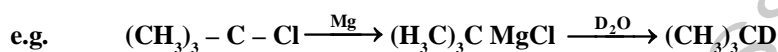




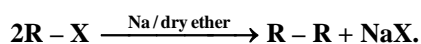
(c) Preparation of Grignard reagent :



(d) Reduction :

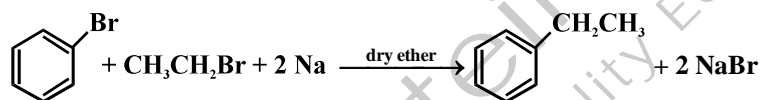


(e) Wurtz Reaction :

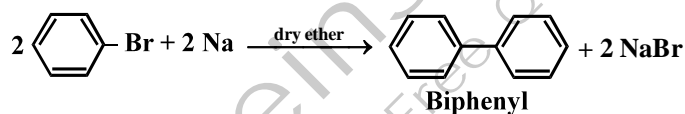


(both molecules of alkyl halides can be used different)

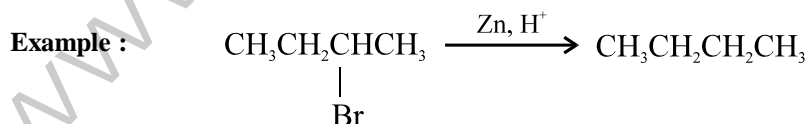
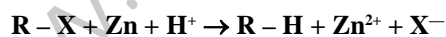
(f) Wurtz Fittig Reaction :



(g) Fittig Reaction :



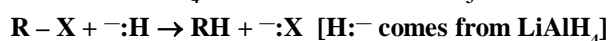
(h) Reduction by metal and acid



sec-Butyl bromide

n-Butane

(i)  $4\text{R} - \text{X} + \text{LiAlH}_4 \rightarrow 4\text{R} - \text{H} + \text{LiX} + \text{AlX}_3$  [X ≠ F]



LiAlH<sub>4</sub> can reduce 1° and 2° alkylhalide

(j)  $\text{R} - \text{X} + n(-\text{C}_4\text{H}_9)_3\text{SnH} \rightarrow \text{RH} + (n - \text{C}_4\text{H}_9)_3\text{SnX}$

Tributyl tin hydride

[It can reduce 1°, 2° and 3° alkyl halide].

(k) Coupling of alkyl halides with organometallic compounds – (Corey-house alkane synthesis)

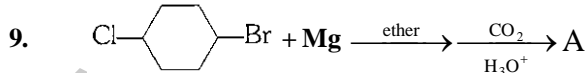
Already discussed in Hydrocarbons.

Practice Problems :

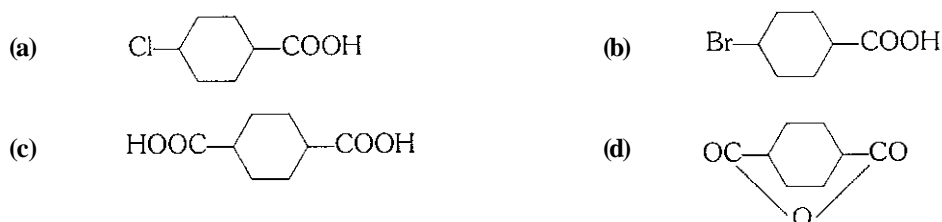
- The non-reactivity of chlorine atom in  $\text{CH}_2 = \text{CH} - \text{Cl}$  is due to
  - inductive effect
  - resonance stabilization
  - electromeric effect
  - electronegativity
- Which of the following is most reactive towards nucleophilic substitution reactions ?
  - $\text{CH}_3\text{CH} = \text{CHCl}$
  - $\text{CH}_2 = \text{CHCl}$
  - $\text{CH}_2 = \text{CHCH}_2\text{Cl}$
  - none of these
- 1-Bromopropane and 2-bromopropane on treatment with sodium in presence of ether gives
  - n-hexane
  - 2,3-dimethylbutane
  - 2-methylpentane
  - a mixture of all these different alkanes
- Compound  $\text{C}_4\text{H}_8\text{Cl}_2$  (A) on hydrolysis gives a compound  $\text{C}_4\text{H}_8\text{O}$  (B) which reacts with hydroxylamine and does not give any test with tollen's reagent. What are (A) and (B).
  - 1,1-dichlorobutane and butanal
  - 2,2-dichlorobutane and butanal
  - 1,1-dichlorobutane and butan-2-one
  - 2,2-dichlorobutane and butan-2-one
- Secondary butyl chloride on boiling with alcoholic potash gives
  - only 1-butene
  - only 2-butene
  - isobutylene
  - a mixture of 1-butene and 2-butene
- Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to
  - the formation of less stable carbonium ion
  - resonance stabilization
  - longer carbon-halogen bond
  - inductive effect
- $\text{C}_8\text{H}_{18}$  (A) is chlorination forms only one type of  $\text{C}_8\text{H}_{17}\text{Cl}$  (B). Hence A can be :



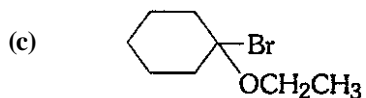
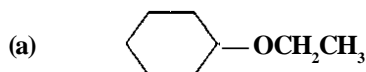
- $(\text{CH}_3)_2\text{CHBr} \xrightarrow[\text{(3) } (\text{CH}_3)_2\text{CHCH}_2\text{Br}]{\text{(1) Li, (2) CuI}} \rightarrow \text{A}$ . This is Corey-House method of synthesis of A which is A ?
  - $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$
  - $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$
  - $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
  - none is correct

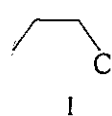
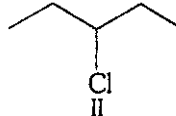
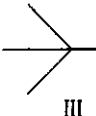


A is :



10. Major product in the following reaction is :  + KOCH<sub>2</sub>CH<sub>3</sub> →



11.  I       II       III. Which are correct statements :

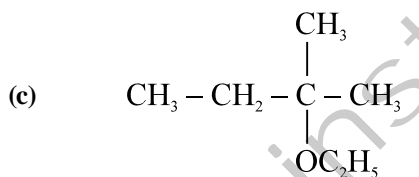
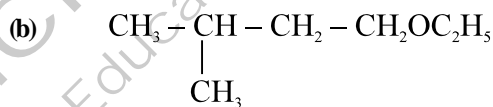
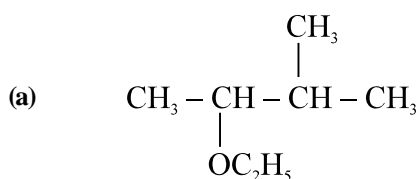
(a) reactivity for S<sub>N</sub>1 reaction is I < III < II

(b) reactivity for S<sub>N</sub>2 reaction is I < II < III

(c) reactivity for S<sub>N</sub>1 reaction is I > II > III

(d) reactivity for S<sub>N</sub>2 reaction is I > II > III

12. Major product of the following S<sub>N</sub>1 reaction is :  $\text{CH}_3 - \underset{\text{Br}}{\text{CH}} - \underset{\text{CH}_3}{\text{C}} - \text{H} - \text{CH}_3 + \text{OC}_2\text{H}_5 \longrightarrow$



(d) none is correct

13.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  I       $\text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_3$  II       $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{Cl}$  III       $\text{CH}_3 - \underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{Cl}$  IV

Increasing tendency for S<sub>N</sub>1 and S<sub>N</sub>2 reaction is :

(A) S<sub>N</sub>1 : I < III < II < IV

(B) S<sub>N</sub>2 : IV < II < III < I

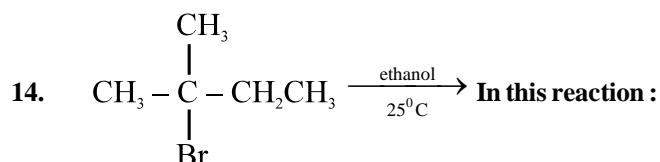
(a) A and B both are correct

(b) only A correct

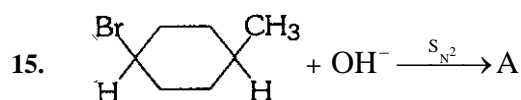
(c) only B correct

(d) both incorrect





- (a) 2-ethoxy-2-methyl butane is the major product in the absence of ethoxide ion  
 (b) mixture of 2-methyl-2-butene and 2-methyl-1-butene is the major product in presence of ethoxide ion  
 (c) both are correct  
 (d) none is correct



A is :

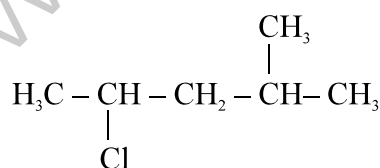
- (a)  (b)   
 (c) both (d) none

16. A halide,  $\text{C}_3\text{H}_{11}\text{X}$ , on treating with alc. KOH gives only pentene-2. What is structure of halide ?

- (a)  $\text{H}_3\text{C} - \text{H}_2\text{C} - \text{H}_2\text{C} - \underset{\text{X}}{\text{HC}} - \text{CH}_3$  (b)  $\text{H}_3\text{C} - \underset{\text{X}}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{CH}_3$   
 (c)  $\text{CH}_3 - \text{CH}_2 - \underset{\text{X}}{\text{CH}} - \text{CH}_2 - \text{CH}_3$  (d) both (a) and (c) are correct

17. An alkyl halide (X) of formula  $\text{C}_6\text{H}_{13}\text{Cl}$  on treatment with potassium tertiary butoxide gives two isomeric alkenes (Y) and (Z) of formula  $\text{C}_6\text{H}_{12}$ . Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict (X).

- (a)  $\text{H}_3\text{C} - \underset{\text{H}_3\text{C}}{\text{HC}} - \underset{\text{H}_3\text{C}}{\text{HC}} - \text{CH}_3$  (b)  $\text{H}_3\text{C} - \text{CH}_2 - \underset{\text{Cl}}{\text{CH}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$   
 (c)  $\text{H}_3\text{C} - \underset{\text{Cl}}{\text{CH}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$



[Answers : (1) b (2) c (3) d (4) d (5) d (6) b (7) d (8) a (9) a (10) b (11) d (12) c (13) a (14) c (15) b (16) d (17) a]