

## Hydrocarbons

### Key Points

#### Alkanes

1. Alkyl halides on reduction with  $Zn/HCl$ ,  $Zn/CH_3COOH$  or red  $P/HI$  or of subjected to Wurtz reaction or Frankland reaction give alkanes.
2. Compounds containing only two elements carbons & hydrogen are known as hydrocarbons.
3. Alkanes are open chain (acyclic) hydrocarbons comprising the homologous series with the general formula where 'n' are an integer.
4. The potential energy of staggered form is minimum and that of eclipsed form is maximum for ethane.
5. In the halogenation of alkanes the reactivity with respect to halogens follows the order  $F_2 > Cl_2 > Br_2 > I_2$ . Reactivity of with respect to C—H follows the order tertiary hydrogen > secondary hydrogen > primary hydrogen.
6. Thus Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atoms but the method is useful for the preparation of symmetrical alkanes
7. The boiling point of alkanes increases with increase in molecular weight due to increase in van der Waals forces with increase in molecular weight i.e. Boiling point: pentane > hexane > heptanes
8. The boiling point of isomeric alkanes show the order: pentane > isopentane > neopentane.
9. A mixture of alkanes and chlorine remains unaffected in the dark but a vigorous reaction occurs when it is exposed to light or at a higher temperature.

10. The ease of substitution at various carbon atoms is of the order tertiary > secondary > primary which is the same as the stability of various alkyl radicals.

### Alkenes

1. Dehydration of alcohols leads to the formation of alkenes. Dehydrating agents are  $\text{H}_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$ . The ease of dehydration follows the order  $3^\circ > 2^\circ > 1^\circ$ .
2. Dehydrohalogenation of alkyl halides gives alkenes. The ease of dehydrohalogenation is  $3^\circ > 2^\circ > 1^\circ$ .
3. Alkenes are unsaturated hydrocarbons having carbon-carbon double bonds. The general molecular formula for alkene is.
4. Alkenes and cycloalkanes are isomeric compounds because both have same general molecular formula.
5. Alkenes with more highly substituted double bonds are more stable than isomers with less substituted double bond.
6. The formation of less substituted alkene as major product is called Hofmann elimination.
7. Trans-but-2-ene is more stable than cis-but-2-ene.
8. The greater the numbers of alkyl groups attached to the doubly bonded carbon atoms the more stable the alkene.
9. Hydrogenation of alkynes by Lindlar's catalyst or nickel boride produces nearly 100% cis-alkene. The catalyst provides a heterogeneous surface on which alkyne molecules get absorbed.
10. Alkenes react with HX to form alkyl halides. The order of reactivity of HX is  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ .

11. A cis isomer has high boiling and melting point than trans because of more polar nature.
12. Hydroxylation of alkenes by cold aqueous alkaline  $\text{KMnO}_4$  solution (Baeyer's reagent is a syn-addition.)
13. Addition of  $\text{HBr}$  to unsymmetrical alkenes in presence of organic peroxide is an anti Markownikov's addition
14. Oxymercuration-demercuration is a markownikov's addition of water to a double bond.
15. Periodic acid ( $\text{HIO}_4$ ) or leadtetra acetate  $[(\text{CH}_3\text{COO})_4 \text{Pb}]$  oxidizes alkenes into glycols and finally gives aldehydes or ketones depending upon the nature of alkene.
16. NBS (N-Bromosuccinimide) is used for the bromination of alkenes at the allylic position.
17. A more widely used method for locating the double bond of an alkene involves the use of ozone ( $\text{O}_3$ ).

### Alkynes

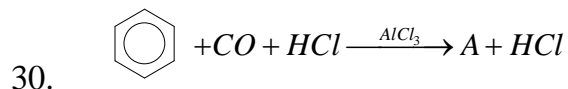
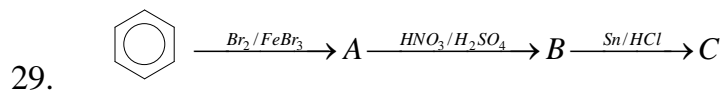
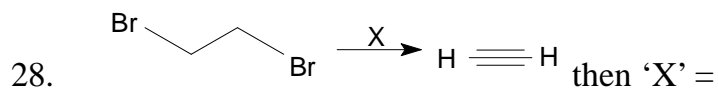
1. Unsaturated hydrocarbons having a carbon-carbon triple bond are called alkynes. They correspond to general formula.
2. The acidic character of Ethyne, Ethene and Ethane follows the order  $\text{H} - \text{C} \equiv \text{C} - \text{H} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$ .
3. The order of boiling point in hydrocarbons has been explained in terms of polarity. Alkynes possess more polarity and thus have higher boiling point.
4. The basic character of their conjugate base follow the order  $\text{CH} \equiv \text{C}^- > \text{CH}_2 = \text{CH}^- > \text{CH}_3 - \text{CH}_2^-$
5. The hydrogen bonded to the carbon of terminal alkyne is considerably more acidic than those bonded to carbons of alkenes and alkanes.

- Acetylene and terminal alkynes react with ammoniacal cuprous chloride solution to give a red precipitate of corresponding alkynides.
- In ethyl anion the lone pair electrons are in  $sp^3$  hybrid orbitals, in vinyl anion the lone pair is in the  $sp^2$  hybrid orbital and in acetylide ion the lone pair is in  $sp$  hybrid orbital.
- Alkynes can be reduced directly to alkanes by the addition of in the presence of as a catalyst.
- Alkynes cannot be hydrated more easily than alkenes because of their low reactivity towards electrophilic addition reactions.
- Acetylene undergoes polymerisation yielding different types of polymeric compounds under different conditions.

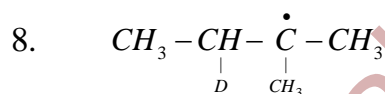
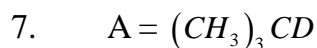
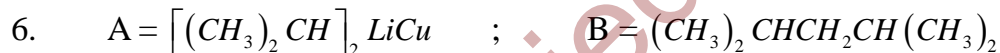
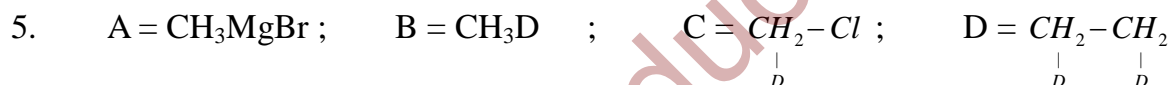
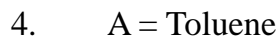
**Sub Topic Name: Some Important Conversions**

- $CH_3CH_2Br \xrightarrow{Mg/ether} (A) \xrightarrow{C_2H_5OH} (B) + Mg(OC_2H_5)Br$
- $CH_3Br \xrightarrow{Na/ether} (A) \xrightarrow{Br_2/h\nu} (B) \xrightarrow{Na/ether} C$
- $CH_3COOH \xrightarrow{NaOH} (A) \xrightarrow{NaOH+CaO} (B) \xrightarrow{Br_2/h\nu} C$
- $CH_3(CH_2)_5CH_3 \xrightarrow[600^\circ C/15 atm]{Cr_2O_3/Al_2O_3} (A)$
- $CH_3Br \xrightarrow{Mg/ether} (A) \xrightarrow{D_2O} (B) \xrightarrow[one\ mole]{Cl_2, \Delta} (C) \xrightarrow{Na/ether} (D)$
- $(CH_3)_2CHBr \xrightarrow[(ii) CuI]{(i) Li} (A) \xrightarrow{(CH_3)_2CHCH_2Br} (B)$
- $(CH_3)_3C-MgCl \xrightarrow{D_2O} A$
- $CH_3-\underset{\substack{| \\ D}}{CH}-\underset{\substack{| \\ CH_3}}{CH}-CH_3 + \overset{\cdot}{Br} \rightarrow X + HBr$  (Major product)
- $\begin{array}{l} H_3C \\ | \\ H_3C-CH-OH \end{array} \xrightarrow{P+Br_2} \xrightarrow{Na} X$ , 'X' is
- $CH_3-C \equiv C-H + CH_3MgX \rightarrow$  Main product (X)

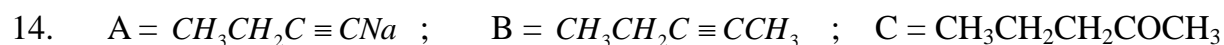
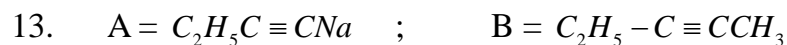
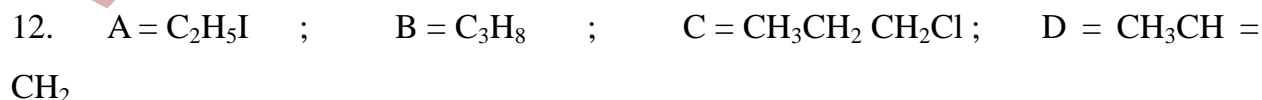
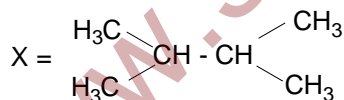
11.  $C_6H_6 \xrightarrow{Br_2/h\nu} A \xrightarrow{Alc.KOH} B$
12.  $H_2C = CH_2 \xrightarrow{HI} A \xrightarrow{Li(CH_3)_2Cu} B \xrightarrow{Cl_2/h\nu} C \xrightarrow{Alc.KOH} D$
13.  $CH_3CH_2C \equiv CH \xrightarrow{NaNH_2} A \xrightarrow{CH_3I} B$
14.  $CH_3CH_2C \equiv CH \xrightarrow[Li.NH_3]{NaNH_2} A \xrightarrow{CH_3I} B \xrightarrow[HgSO_4, H_2O]{H_2SO_4(dil)} C$
15.  $CH_3 - CH_2 - CH = CH_2 \xrightarrow[(ii) Zn/H_2O]{(i) O_3/CH_2Cl_2} A + B$
16.  $CH_3CH_2CH_2CH_2I \xrightarrow{Alc.KOH} A \xrightarrow{HBr/R-O-O-R} B$  (Major Product)
17. 
$$\begin{array}{c} C_3H_7 \\ | \\ C = C \\ / \quad \backslash \\ CH_3 \quad H \\ \quad \quad | \\ \quad \quad CH_3 \end{array} \xrightarrow[(ii) Zn/H_2O]{(i) O_3/CH_2Cl_2} A + B$$
18.  $CH_3CH_2CH_2OH \xrightarrow[\Delta]{Conc.H_2SO_4} A \xrightarrow{HOCl} B$
19. 
$$\begin{array}{c} Ph \\ | \\ C = C \\ / \quad \backslash \\ H \quad H \\ \quad \quad | \\ \quad \quad CH_3 \end{array} \xrightarrow{HBr} A$$
 (Major product)
20.  $C_2H_5OH \xrightarrow[170^\circ C]{Conc.H_2SO_4} A \xrightarrow{Br_2} B \xrightarrow{Alc.KOH} C \xrightarrow[Hg^{+2}]{CH_3COOH} D$
21. 
$$\text{Cyclohexene} \xrightarrow{NBS} A \xrightarrow{Alc.KOH} B$$
22.  $HC \equiv CH \xrightarrow{2HCl} A \xrightarrow{Alc.KOH} B$
23.  $CH_3CH = CH_2 \xrightarrow[Feroxide]{HBr} A \xrightarrow{Na/ether} B$
24. 
$$CH_3CH_2CH_2C \equiv C-CH_3 \begin{cases} \xrightarrow{H_2/N_2} A \\ \xrightarrow{H_2/Lindlars\ catalyst} B \\ \xrightarrow{Na/Liq.NH_3} C \end{cases}$$
25.  $CH_3CH_2C \equiv CH \xrightarrow[(ii) CH_3CH_2Br]{(i) NaNH_2} (X) \xrightarrow[Pd/BaSO_4]{H_2} (Y) \xrightarrow{Alkaline.KMnO_4} (Z)$
26.  $CaO \xrightarrow{\Delta} A \xrightarrow{H_2O} B \xrightarrow{HgSO_4/H_2SO_4} C$
27.  $3CH_3CH = CH_2 \xrightarrow{BH_3} (X) \xrightarrow{H_2O_2/OH^-} \text{Product (A)} + H_3BO_3$



### Answers



9.



15. A = HCHO ; B = CH<sub>3</sub>CH<sub>2</sub>CHO
16. A = CH<sub>3</sub>CH<sub>2</sub>CH = CH<sub>2</sub> ; B = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br
17. A = CH<sub>3</sub>CHO ; B = CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
18. A = CH<sub>3</sub> - CH = CH<sub>2</sub>; B = CH<sub>3</sub>CH (OH) CH<sub>2</sub>Cl
19. A = PhCH(Br) CH<sub>2</sub>CH<sub>3</sub>
20. A = C<sub>2</sub>H<sub>4</sub> ; B =  $\begin{matrix} \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{Br} \quad \text{Br} \end{matrix}$  ; C = C<sub>2</sub>H<sub>2</sub> ; D = H<sub>2</sub>C = CH (CH<sub>3</sub>COO)

