

HYDROCARBONS

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S.No.	CONTENTS	Page
1.	Alkanes	145
2.	Introduction	145
3.	General methods of Preparation	145
4.	Physical and chemical properties	149
5.	Petroleum	151
6.	Alkenes	153
7.	Introduction	153
8.	General methods of Preparation	153
9.	Physical and chemical properties	155
10.	Alkynes	161
11.	Introduction	161
12.	General methods of Preparation	161
13.	Physical and chemical properties	162
14.	Aromatic Hydrocarbons	170
15.	Introduction	170
16.	General methods of Preparation	170
17.	Physical and chemical properties	172
18.	Exercise -I (Conceptual Questions)	174
19.	Exercise-II (Previous Years Questions)	177
20.	Exercise-III (Analytical Questions)	179
21.	Exercise-IV (Assertion & Reason)	180

NEET SYLLABUS

Alkanes - Physical properties, chemical reactions, combustion and pyrolysis. Alkenes - Structure of double bond, physical properties, methods of preparation, chemical reactions, ozonolysis, oxidation. Alkynes - Structure of triple bond, physical properties, methods of preparation, chemical reactions, acidic character of alkynes, benzene, resonance, aromaticity, carcinogenicity and toxicity.

OBJECTIVES

After studying this unit, we will be able to :

- learn about various methods of preparation of hydrocarbons;
- distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;
- appreciate the role of hydrocarbons as sources of energy and for other industrial applications;
- comprehend the structure of benzene, explain aromaticity;
- predict the directive influence of substituents in monosubstituted benzene ring;
- learn about carcinogenicity and toxicity.

"Once your mind stretches to a new level it never goes back to its original dimension"

A.P.J. Abdul Kalam

HYDROCARBONS

5.0 ALKANES

5.1.1 Introduction of Alkanes

- (a) Branched and unbranched aliphatic saturated open chain hydrocarbons are called member of alkanes.
- (b) CH_4 is also known as Marsh gas (fire damp).
- (c) Calore gas : Mixture of n-butane and isobutane.
- (d) LPG (Liquefied petroleum gas) : liquid propane, isobutane.
- (e) Natural gas : 80% methane + 10% ethane + 10% propane + small amounts of H_2 , N_2 , CO_2 etc.
- (f) Water gas : $CO + H_2$ (1:1)
- (g) Synthesis gas : CO + $3H_2$ (1:3)

5.1.2 General Methods of Preparation

 From alkenes and alkynes (Sabatier and Senderens reaction) or (By hydrogenation of alkenes and alkynes): Alkenes and alkynes on catalytic hydrogenation give alkanes.

$$\begin{array}{ccc} R & - CH = CH - R + H_2 & \underline{\quad Catalyst} & R - CH_2 - CH_2 - R \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

Catalyst :

- (a) Pd/Pt at ordinary temperature and pressure
- (b) Ni, 200–300° C (sabatier)
- (c) Raney Nickel at room temp.
- (d) Methane can not be prepared by this method
- (2) From alkyl Halides (By reduction) :

$$R - X \xrightarrow[(Nascent Hydrogen)]{2H} R - H + HX$$

Catalyst :

(i) Zn + HCl (ii) $Zn + CH_3 COOH$ (iii) Zn—Cu couple in C_2H_5OH (iv) Red P + HI (v) Al – Hg + ethanol

GOLDEN KEY POINTS

- Alkyl halides can also be reduced to alkane by H_2/Pd or $LiAlH_4$ or H_2/Ni .
- Halogen atom of alkyl halide is replaced by hydrogen atom to obtain an alkane.

(3) From alkyl halide (By Wurtz reaction): A solution of alkyl halide in ether on heating with sodium gives alkane.

$$R \longrightarrow X + 2Na + X \longrightarrow R \xrightarrow{Dry} R \longrightarrow R + 2NaX$$

(a) Two moles of alkyl halide are treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

- (b) Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.
- (c) Two different alkyl halides, on wurtz reaction give all possible alkanes.
- (d) The separation of mixture into individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

(4) From Frankland Reagent:

$$R \rightarrow X + 2Zn + RX \rightarrow R_2Zn + ZnX_2$$

Frankland reagent

$$R_{2}Zn + R \longrightarrow R \longrightarrow R + RZnX$$

(5) From Carboxylic Acid (By decarboxylation) : Sodium salt of saturated monocarboxylic acid on dry distillation with sodalime give alkane.

RCOONa + NaOH
$$\xrightarrow{\Lambda}_{Cao}$$
 R—H + Na₂CO₃

Note :- Sodalime \Rightarrow NaOH + CaO

GOLDEN KEY POINTS

- The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.
- The alkane formed by decarboxylation contains one carbon atom less than the original acid.
- Decarboxylation of sodium formate gives H₂

$$\begin{array}{c} (\text{HCOONa} + \text{NaOH} (\text{CaO}) & \stackrel{\Delta}{\longrightarrow} & \text{H}_2 + \text{Na}_2\text{CO}_3 \\ (\text{CH}_3\text{COONa} + \text{NaOH} + \text{CaO} \stackrel{\Delta}{\longrightarrow} & \text{CH}_4 + \text{Na}_2\text{CO}_3 \end{array} \right)$$

• If in a compound two carboxylic groups are present and they are attached to same carbon atom then decarboxylation of one of the carboxylic groups takes place simply on heating.

$$CH_2 \begin{pmatrix} COOH \\ COOH \end{pmatrix} \longrightarrow CH_3COOH + CO_2$$

- $CH_3 CH_2 CH_3$ can be prepared by Butanoic acid and 2-Methyl propanoic acid.
- β -Keto acids are decarboxylated readily simply on heating (soda lime is not required)

$$\begin{array}{ccc} R \longrightarrow C \longrightarrow CH_2COOH & \xrightarrow{\Delta} R \longrightarrow C \longrightarrow CH_3 \\ & & \parallel \\ O & & O \end{array}$$

146

(6) From carboxylic acid (By Kolbe's electrolysis process) : Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

 $2C_2H_5 - COONa \xrightarrow{electro.}{2H_2O} C_2H_5 - C_2H_5 + 2CO_2 + 2NaOH + H_2$

GOLDEN KEY POINTS

 Electrolysis of an acid salt gives symmetrical alkane, However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.

 $R'COOK + R''COOK \xrightarrow{Electrolysis} (R'-R'' + R'-R' + R''-R'') + 2CO_2 + H_2 + 2NaOH$

- At anode alkane and CO_2 gas is formed while at cathode NaOH and H_2 gas is formed.
- The concentration of NaOH in solution is increased with time so pH of solution is also increased.

(7) From alkanol, alkanals, Alkanone and alkanoic acid (By reduction) :

The reduction of either of the above compound in presence of red P and HI gives corresponding alkane.

$$R - OH + 2HI \qquad \xrightarrow{\text{Red }P} \qquad R - H + H_2O + I_2$$

 $R-CHO + 4HI \xrightarrow{\text{Red P}} RCH_3 + H_2O + 2I_2$

 $R-CO-R+4HI \xrightarrow{Red P} R-CH_2-R+H_2O + 2I_2$

RCOOH + 6HI
$$\xrightarrow{\text{Red P}}$$
 R—CH₃ + H₂O + 3I₂

In the above reaction I_2 is formed which may react with alkane to form alkyl halide. So red P is added in the reaction to remove I_2 formed in the reaction.

 $R-CH_3 + I_2 \qquad \Longleftrightarrow \qquad R-CH_2-I + HI$ $2P + 3I_2 \qquad \longrightarrow \qquad 2PI_3$

(8) From alkanones (By Clemmensen's method) : Carbonyl compound may also be reduced with Zinc amalgam and concentrated HCl (Zn–Hg/HCl), this reaction is called Clemmensen reduction.

$$R - CO - R' + 4H \xrightarrow[con.HCl]{Zn-Hg} R - CH_2 - R' + H_2O$$

(9) From alkanals and alkanones (By Wolf Kishner reaction) :

$$> C = O \xrightarrow{(1) \text{ NH}_2\text{NH}_2} > CH_2$$

(10) From G.R. :

(a) Formation of alkanes with same number of C atoms : Grignard reagent reacts with the compounds having active hydrogen to form alkane.

 $\begin{array}{cccc} R - Mg - X + H - O + H & \longrightarrow & R - H + Mg (OH) X \\ & + R - O + H & \longrightarrow & R - H + Mg (OR) X \\ & + R - NH - H & \longrightarrow & R - H + Mg (NHR) X \end{array}$

This reaction is used to determine the number of active H-atoms in the compound this is known as Zerewitnoff's method.

(b) G.R. react with alkyl halide to give higher alkanes :

 $RMgX + R' - X \longrightarrow R - R' + MgX_{2}$

(11) Corey-House Synthesis : This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R—R'

$$R \xrightarrow{(i)Li} R - R' + RCu + LiX$$

Note: In Corey-house reaction symmetrical and unsymmetrical alkane both can be formed.

(12) From metal carbide (By hydrolysis) :

Only CH₄ can be obtained by the hydrolysis of Be or Al carbides

 $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

 $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

BEGINNER'S BOX-1

- 1. If two moles of Isopropyl chloride reacts with Na in presence of dry ether. Which alkane is obtained.
 - (1) Hexane (2) 2, 3-Dimethyl butane
 - (3) Isopentane (4) Neopentane
- **2.** If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.
 - (1) n-Butane (2) 2-Methyl butane
 - (3) 2, 3-Dimethyl butane (4) All of them
- 3. Which of the following compound can not be obtained from single alkyl halide by wurtz reaction.

(3) 2

(4) 5

- (1) ethane (2) butane (3) isobutane (4) hexane
- 4. How many acids can be taken to obtain isobutane by decarboxylation ?
 - (1) 4 (2) 3

5.	Give reactivity order for	r decarboxylation ?			
	(I) CH ₃ —CH ₂ —COOH	(II) CH ₂ =CHCO	OH	(III) CH≡C -	-COOH
	(1) $I > II > III$	(2) III > II > I	(3) III > I >	· II	(4) None is correct
6.	Which of the following	does not give alkane with	n R—Mg—X.		
	(1) Ph—OH	(2) C ₆ H ₆	(3) CH ₃ COC	ЭH	(4) HCl
7.	Which of the following	reaction can not be used	to obtained	propane in	good yield.
	(1) Wurtz reaction		(2) Corey-h	ouse reactior	1
	(3) Decarboxylation of a	acid salt	(4) All of th	nem	

5.1.3 Physical & Chemical Properties of alkane

Physical properties

- (i) Solubility : Alkanes being non polar and thus insoluble in water but soluble in nonpolar solvents
- **Ex.** C_6H_6 , CCl_4 , ether etc.
- (ii) **Boiling point** ∞ molecular weight (for n-alkanes)
 - \therefore Vander Waals force of attraction \propto molecular weight \propto surface area of molecule.

i.e. boiling point Pentane < hexane < heptane

Also boiling point

 $\propto \frac{1}{\text{number of side chain}}$

because the shape approaches to spherical which results in decrease in van der Waal's forces (as surface area decreases)

Thus boiling point n-Pentane > Isopentane > neopentane

(iii) Melting Point : M.P. of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher M.P. than their adjacents alkanes of odd number of carbon atoms. The abnormal trend in M.P. is due to the fact that alkanes with odd carbon atoms have their end carbon atom on the same cide of the melecule and in even carbon atom alkane the end Carbon.

carbon atom on the same side of the molecule and in even carbon atom alkane the end Carbon atom on opposite side. Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.



Odd number of carbon

Even number of carbon

Chemical Properties

(1) Oxidation :

(a) **Complete oxidation or combustion :** Alkanes burn readily with non-luminous flame in presence of air or oxygen to give CO_2 and water with evolution of heat. Therefore, alkanes are used as fuels.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O+Q; (\Delta H = -ve)$$

<

(b) Incomplete oxidation : In limited supply of air, alkane gives carbon black and CO.

 $\begin{array}{cccc} 2CH_4 + 3O_2 & \longrightarrow & 2CO + 4H_2O \\ CH_4 + O_2 & \longrightarrow & C + 2H_2O \end{array}$

C-black (used in printing ink)

(c) Catalytic oxidation :

(i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

$$2CH_4 + O_2 \xrightarrow[High P and T]{Red hot Cu or Fe tube} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$$

(ii) Alkanes on oxidation in presence of maganese acetate give fatty acids.

$$CH_3(CH_2)_n CH_3 \xrightarrow{(CH_3COO)_2 Mn} CH_3(CH_2)_n COOH$$

(iii) Tertiary alkanes are oxidized to give tertiary alcohols by KMnO₄.

$$CH_{3} \xrightarrow[]{[O]}{} CH_{3} \xrightarrow[]$$

- (2) Substitution Reactions : Substitution reaction in alkanes shows free radical mechanism.
- (3) Isomerization: Unbranched chain alkanes on heating with AlCl₃ + HCl / 200°C are converted in to branched chain alkanes

$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{AlCl_3 + HCl} CH_3 - CH_3 - CH_3 - CH_3$$

n-butane

Isobutane

Branched chain alkanes converted to more branched alkane.

$$\begin{array}{c} CH_{3} \\ H_{3} \\ CH_{3} \\ -CH \\ -CH_{2} \\ -CH_{2} \\ -CH_{2} \\ -CH_{3} \\ -CH_{3}$$

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

(4) Pyrolysis or Cracking or thermal decomposition : When alkanes are heated to 500-700°C they are decomposed in to lower hydrocarbon. This decomposition is called pyrolysis.

Ex.
$$CH_4 \xrightarrow{1000^{\circ}C} C + H_2$$

$$CH_{3} - CH_{3} \xrightarrow{500^{\circ}C} CH_{2} = CH_{2} + H_{2}$$

$$CH_{3}CH_{2}CH_{3} \longrightarrow CH_{2} = CH_{2} + CH_{4}$$

$$CH_{3}-CH = CH_{2} + H_{2}$$

n-Butane $_$ Cracking \rightarrow 1-Butene + 2-Butene + Ethane + Ethane + Propene + CH₄ + H₂

(5) Aromatization:

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Unbranched higher alkanes (from 6 to 10 carbon atoms) when heated in presence of oxides of Cr, Mo, V on Al_2O_3 support at 500° C aromatic hydrocarbons are formed.



n-heptane

Toluene

5.1.4 PETROLEUM

Flash Point : Flash point of an oil is that minimum temperature at which the oil gives so much vapour that it starts burning in the presence of air when it comes in contact with a spark. Flash point depends on local temperature of countries.

Flash point of kerosene in India \Rightarrow 44°C, in France \Rightarrow 35°C, in England \Rightarrow 23°C

Knocking : Preignition of the fuel-air mixture in the cylinder ahead of the flame causes knocking. knocking reduces efficiency of the engine and also damages the cylinder and piston of the engine.

Octane Number (Quality of Gasoline) : Octane no. is a scale which is used to determine the quality of a fuel in an internal engine. Two pure hydrocarbons are selected as standard.

- (i) n heptane straight chain hydrocarbon knocks very badly have octane no. zero
- (ii) Iso-octane branched hydrocarbon, good antiknocking properties, have octane no. 100.

Octane no. of a fuel : The percentage of iso-octane by volume in a mixture of iso-octane and n-heptane which has the same antiknocking properties as the fuel under examination.

For example – Let knocking of a fuel is same as a mixture of 70% iso-octane and 30% n-heptane, then its octane no. is 70.

Order of quality of Gasoline or petrol : (i) Length of chain \uparrow , the octane no. \downarrow

(ii) branches \uparrow octane no. \uparrow

Straight chain alkane < branched chain alkane < olefins < cycloalkane < aromatic compound

Octane number can be increased by : (i) Cracking (ii) Isomerization (iii) Aromatization

Antiknocking agents - (Gasoline additives) : Quality of a fuel is increased by :

- (i) By using fuel of higher octane no.
- (ii) By addition of certain compounds to the gasoline which reduce knocking. These are called antiknocking agents.
- **Ex.** Tetraethyl lead (TEL) Pb $(C_2H_5)_4$

Tetra methyl lead – $Pb(CH_3)_4$

Pre-Medical : Chemistry

In cylinder of engine $Pb(C_2H_5)_4$ decomposes in ethyl radicals which combine with the radicals produced due to irregular combustion and this prevents knocking.

$$Pb(C_2H_5)_4 \xrightarrow{heat} Pb + 4CH_3\dot{C}H_2$$

but combustion of TEL with petrol gives Litharge (PbO) which deposited in cylinder walls and piston has jammed. So Ethylene dibromide is added with petrol.

 $Br - CH_2 - CH_2 - Br \longrightarrow CH_2 = CH_2 + Br_2$ $Pb + Br_2 \longrightarrow PbBr_2^{\uparrow}$ (Volatile)

BEGINNER'S BOX-2

1. Which of the following reactions of alkanes involve free radical intermediates

	(1) Halogenation	(2) Pyrolysis
	(3) Nitration	(4) All of the above
2.	$(CH_3)_3CMgCl$ on reaction with D_2O produces	
	(1) (CH ₃) ₃ CD	(2) (CH ₃) ₃ OD
	(3) (CD ₃) ₃ CD	(4) (CD ₃) ₃ OD
3.	The compound with the highest boiling point is-	
	(1) n-hexane	(2) n-pentane
	(3) 2,2-dimethyl propane	(4) propane
4.	Photochemical chlorination of alkane is initiated by	a process of
	(1) pyrolysis	(2) substitution
	(3) Homolysis	(4) Peroxidation
5.	Isomerization in alkane may be brought about by us	ing :
	(1) Al ₂ O ₃	
	(2) $\operatorname{Fe_2O_3}$	
	(3) AlCl ₃ and HCl	
	(4) Concentrated H_2SO_4	
6.	Bromination of an alkane as compared to chlorinati	on proceeds
	(1) At a slower rate	
	(2) At a faster rate	
	(3) With equal rates	
	(4) With equal or different rate depends upon the ter	mperature
1 60		
エヘン		-

5.2 ALKENES (OLEFINS)

5.2.1 Introduction of Alkenes

Alkene are also called olefins (oil forming) since the first member ethylene (C_2H_4) was found to form an only liquid on reaction with chlorine.

 $CH_2 = CH_2 + Cl_2 \longrightarrow Cl - CH_2 - CH_2 - Cl_2$

5.2.2 General Methods of Preparation

Ethanol

(1) From Alcohols : Alkenes can be prepared from monohydric alcohols or alkanols by the loss of H_2O and the reaction is known as **dehydration reaction**.



Alcohol

The dehydration can be carried with Al_2O_3 or with mineral acid upon heating.

(a) Dehydration with Al_2O_3 : Ethene is prepared by heating ethanol with Al_2O_3 at 620 K.

$$CH_3 \longrightarrow CH_2 \longrightarrow OH \longrightarrow Al_2O_3 \longrightarrow CH_2 \longrightarrow CH_2 + H_2O$$

Ethanol Ethene

(b) Dehydration with mineral acid : Alcohols upon heating with conc. H_2SO_4 form alkenes and the reaction is called acidic dehydration.

 $CH_{3} \longrightarrow CH_{2} \longrightarrow OH \xrightarrow{conc. H_{2}SO_{4}} OH_{2} \longrightarrow CH_{2} \longrightarrow CH_{$

Ethene

$$CH_{3} \xrightarrow{\text{CH}} CH_{3} \xrightarrow{\text{CONC. } H_{2}SO_{4}} CH_{3} \xrightarrow{\text{CH}} CH_{2} = CH_{2} + H_{2}O$$

$$Propan-2-ol Propene$$

$$CH_{3} \xrightarrow{\overset{}{\underset{}}_{l}} CH_{3} \xrightarrow{\overset{}{\underset{}}_{363K}} CH_{3} \xrightarrow{\overset{}{\underset{}}_{363K}} CH_{3} \xrightarrow{\overset{}{\underset{}}_{l}} CH_{3} \xrightarrow{\overset{}{\underset{}}_{l}} CH_{2} + H_{2}O$$

2-Methylpropan-2-ol 2-Methylpropene From the above reactions, it is clear that the order of acidic dehydration in different

alcohols is Tertiary > Secondary > Primary

(2) From Alkyl halide (By dehydrohalogenation): Removal of HX from a substrate by alcoholic KOH or NaNH₂

$$RCH_2CH_2X \xrightarrow{KOH(Alc.)\Delta} RCH = CH_2$$

Ex.
$$CH_3 - CH_2 - CH_3 - CH_3 \xrightarrow{KOH(Alc.)\Delta} CH_3CH = CH_3CH_3 + CH_3CH_2CH = CH_2$$

 X (Saytzeff product) (Hoffmann's product)

ALLEN

The ease of dehydrohalogenation show the order

For alkyl group	tertiary > secondary			>	primary
For hologon in holida	Indida >	Bro	mida > Chlorid		flourida

It is single step and synchronous process. Removal of proton, the formation of multiple bond between $C\alpha$ and $C\beta$ and the release of the leaving group X take place simultaneously. (E₂ mechanism)

Ex.
$$HO^{+}CH_{3}-C-C-H \longrightarrow CH_{3}-C=C-H-H_{2}O+Br^{\circ}$$

 $HO^{+}CH_{3}-C-H \longrightarrow HO^{+}CH_{3}-C=C-H-H_{2}O+Br^{\circ}$

Rate of reaction \propto [CH₃CH₂CH₂Br] [OH]

Ex.
$$CH_3CH_2CH_2CH_2Br \xrightarrow{KOH(Alc)} CH_3CH_2CH = CH_2$$

1–Butene

Ex.
$$CH_{3}CH_{2}CHCH_{3} \xrightarrow{KOH (Alc)} CH_{3}CH = CHCH_{3}$$

 Br 2 -Butene (major)

(3) From Alkyl dihalide (By dehalogenation of Vicinal or Gem dihalide) : Removal of X₂ from a substrate by Zn dust or Zn—Cu in alcoholic Solution..

(a) From Vicinal dihalide : same number carbon alkene is obtained.

(b) From gem dihalide : Higher alkene obtained

 $CH_{3}CH X_{2} + 2Zn + X_{2} CHCH_{3} \longrightarrow CH_{3} - CH = CH - CH_{3} + ZnX_{2}$

(4) By the controlled hydrogenation of alkynes :

Alkynes can be converted into alkenes as a result of **controlled reduction** in two ways:

(a) **By the use of Lindlar's catalyst :** Lindlar's catalyst is a mixture of palladium catalyst deposited over barium sulphate or calcium carbonate. The catalytic mixture is slightly poisoned by quinoline or sulphur and allows the reduction or hydrogenation of alkyne with hydrogen only upto the alkene stage. The major product is cis-Alkene.

Ex.
$$CH_3 - C \equiv C - CH_3 + H_2$$
 $\xrightarrow{\text{Lindlar's catalyst}}_{Pd/CaCO_3}$ $\xrightarrow{CH_3}_{H} > C = C <_{H}^{CH_3}$
But-2-yne cis-but-2-ene

In place of Lindlar's catalyst Nickel-boride (Ni-B also called P-2 catalyst) can also be used.

(b) By the action of sodium in liquid ammonia : This is known as Birch reduction and the major product is a **trans alkene** i.e., the two hydrogen atoms get attached on the opposite side of the double bond. For example,

 $CH_{3} - C \equiv C - CH_{3} \xrightarrow{\text{Na/Liquid NH}_{3}} \binom{CH_{3}}{H} > C = C < \binom{H}{CH_{3}}$

But-2-yne

trans-but-2-ene

(5) By Pyrolysis of ester :

allen

$$CH_{3} \xrightarrow{-C} \underbrace{-CH_{2}}_{0} \xrightarrow{CH-R} \xrightarrow{400-500^{\circ}C} CH_{3}COOH + CH_{2} = CHR$$

Hoffmann's Rule : Less substituted or less stable alkene is major product.

In the reaction to form an alkene a β -hydrogen from alkyl ester is attracted by oxygen atom of keto group.

- (6) By Pyrolysis of tetra alkyl ammonium hydroxide :
- (7) By Kolbe's method: Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.

 $\begin{array}{ccc} CH_{2}COONa & \underbrace{\ electrolysis} \\ | \\ CH_{2}COONa & & \\ Aqueous & \\ Aft Anode \end{array} \rightarrow \begin{array}{ccc} CH_{2} + 2CO_{2} & + 2NaOH + H_{2} \\ | \\ CH_{2} & \\ At Cathode \end{array}$

CH₃—CHCOONa _	electrolysis CH3-CH+2CC	0₂+ 2NaOH + H₂
CH ₃ —CHCOONa	/	At Cathode
Aqueous	At Anode	

5.2.3 PHYSICAL & CHEMICAL PROPERTIES OF ALKENES

Physical Properties

- (1) All are colourless and have no characteristic odour. Ethene has pleasant smell.
- (2) Lower members (C_2 to C_4) gaseous medium (C_5 to C_{17}) liquid and higher members are solid.
- (3) The B.P., M.P. and specific gravity show a regular increase with increase in molecular weight
- (4) The increase in branching in carbon chain decreases the B.P. among isomeric alkenes.
- (5) The B.P. and M.P. of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable π bond.
- (6) Insoluble in water because they can not form H-bond with water molecule, they dissolve freely in organic solvent like benzene, $CHCl_3$, CCl_4 etc.

Chemical Properties : Alkenes are more reactive than alkane this is because -

- (a) The π electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.
- (b) π bond is weaker than σ bond and more easily broken.

The reactivity order for alkenes -

 $CH_2 = CH_2 > R - CH = CH_2 > R_2C = CH_2 \approx RCH = CHR \qquad > R_2C = CHR > R_2C = CR_2$ (Trans < Cis)

The reactivity order of alkenes has been delt in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation ($\Delta H = -ve$), more is the reactivity, the reactivity of alkene is however also related to

(i) Steric hinderance (ii) Hyperconjugation

Alkenes give the following type of reactions :

- (A) Addition reaction. (B) Oxidation reaction. (C) Substitution reaction.
- (D) Polymerization Reaction. (E) Isomerisation
- (A) Addition Reaction :

[A₁] Free Radical Addition

(1) Addition of H_2 :

 $R-CH=CH_2+H_2 \xrightarrow{Ni,PtorPd} R-CH_2-CH_3+ \text{ Heat of Hydrogenation.}$

(a) Reaction is exothermic, Heat released in reaction is called heat of hydrogenation.

(1)	Stability of alkene or	1	a	1
(b)	oldonity of differre	heat of hydrogenation		reactivity of alkene with H_2

(c) The process is used to obtain vegetable (saturated fats) ghee from hydrogenation of oil. [A₂] Electrophlic Addition Reactions:

- **(B) Oxidation Reaction:** Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.
 - (1) Combustion:

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

One mole of alkene requires $\frac{3n}{2}$ moles of O_2 for complete combustion.

- (2) Ozonolysis : (A test for unsaturation in molecule)
 - (i) The addition of ozone on the double bonds and subsequent a reductive hydrolysis of the ozonide formed is termed as ozonolysis.
 - (ii) Ozonides are explosive compound.
 - (iii) On warming with Zn and H_2O , ozonides cleave at the site of the double bond, the products are carbonyl compound (aldehyde or ketone) depending on the nature of the alkene.

Ex.
$$CH_3 \xrightarrow{-} C = CH \xrightarrow{-} CH_3 \xrightarrow{Ozonolysis} CH_3 \xrightarrow{-} C = O + CH_3CHO$$

(iv) Ozonolysis of alkenes helps in locating the position of double bond in an alkene. It can be achieved by joining together the carbon atoms of the two carbonyl compounds formed as the products of ozonolysis with double bond.



It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond.

- hydroxylation.
- (a) Oxidation by Baeyer's reagent (A test for unsaturation) : Alkenes on passing through dilute alkaline 1% cold $\rm KMnO_4$ (i.e., Baeyer's reagent) decolourise the pink colour of $\rm KMnO_4$ and gives brown ppt of ${\rm MnO}_{\rm 2}.$ The reaction involves syn addition.

$$C = C \langle H_2O + [O] \xrightarrow{OH^-}_{KMnO_4} \rightarrow C \xrightarrow{-C}_{I} \langle Glycol \\ \downarrow I \\ OH OH (syn-addition)$$

(b) By OsO_4 : R-CHR-CH $+ OsO_4 \longrightarrow R-CH-O$ $R-CH-O \longrightarrow Os \longrightarrow Os \longrightarrow R-CH-OH$ R-CH-OH $+ H_2OsO_4$ $+ H_2OsO_4$

(c) By peracid :
$$>C=C<+H-C-O-H\xrightarrow{-HCOOH}>C\xrightarrow{-C}<\xrightarrow{H_2O/H^{\oplus}}>C\xrightarrow{-C}<\downarrow_{I_1}$$

(Anti-addition)(glycol)

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(d) By Ag_2O/Δ :

(a) Alkenes reacts with oxygen in the presence of Ag catalyst at 250° - 400° C to form epoxide.



Syn addition on alkene \longrightarrow H₂, Baeyer's reagent, OsO₄ / H₂O Antiaddition on alkene \longrightarrow X₂, HOX, RCOOOH / H₃O^{\oplus}, Ag₂O / H₃O⁺





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(4) Oxidation by strong oxidising agent (Oxidative cleavage): The alkenes themselves are readily oxidised to acid or ketone by means of acid permagnate. If HCOOH is formed, it further oxidized to CO_2 and H_2O . Keep it in mind that no further oxidation of ketones will takes place.

$$CH_{2} = CH_{2} + 4[O] \longrightarrow 2HCOOH _ 2|O] \rightarrow 2CO_{2} + H_{2}O$$

$$CH_{3}CH = CH_{2} _ 5|O] \rightarrow CH_{3}COOH + CO_{2} + H_{2}O$$

$$CH_{3}CH = CHCH_{3} _ 4|O] \rightarrow 2CH_{3}COOH$$

$$CH_{3} \rightarrow C = CH_{2} _ 4|O| \rightarrow CH_{3} \rightarrow C = O + CO_{2} + H_{2}O$$

(C) Substitution Reaction (Allylic Substitution):

When alkenes are treated with low concentration of Cl_2 or Br_2 at high temperature or with NBS/hv one of their allylic hydrogen is replaced by halogen atom. Allylic position is the carbon adjacent to one of the unsaturated carbon atoms. It is free radical substitution.

 $CH_{3}-CH=CH_{2} + Cl_{2} \xrightarrow{500^{0}C} CICH_{2}-CH=CH_{2} + HCl$

Allyl chloride

(3-Chloro-1-propene)

N-Bromosuccinimide (NBS) is an important reagent used for allylic bromination and benzylic substitution.

Substitution reaction is not given by ethene.



3° (more stable)

(D) Polymerization:

- (i) Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecule having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.
- (ii) Molecular weight of polymer is simple multiple of monomer.
- (iii) Polymerization can be carried out by free radical or ionic mechanism.

(iv) The presence of oxygen initiates free radical mechanism.

- (v) Addition polymerization can also be carried out by ionic mechanism by using Ziegler Natta Catalysts $(R_3Al+TiCl_4)$
 - **Ex.** $nCH_2 = CH_2 \longrightarrow (-CH_2 CH_2)n$ ethene Poly ethene used in the manufacture of insulating Coating,

sheeting and moulded products.

$$nCH_{3} - CH = CH_{2} \xrightarrow{R_{3}AI+TiCl_{4}} (-CH - CH_{2} -)_{n}$$

Polypropene or Koylene (Plastic)

(E) Isomerisation :

Alkene on heating to 500° to 700 °C or on heating in presence of catalyst $[AlCl_3 \text{ or } Al_2(SO_4)_3]$ undergo isomerisation.

$$CH_{3}CH_{2} - CH = CH_{2} \xrightarrow{Catalyst}{\Delta} CH_{3} - CH = CH - CH_{3} + CH_{3} - C = CH_{2}$$

1–Butene

2–Butene

- **Uses:** (1) In plastic formation.
 - (2) In oxy ethylene welding
 - (3) As food preservatives and ripening fruits.
 - (4) As general anaesthetic (C_2H_4 with 10% O_2)
 - (5) In preparation of mustard gas

$$\begin{array}{c} CH_2\\ \parallel\\ CH_2\\ CH_2\\ \end{array} + \begin{array}{c} S_2Cl_2\\ H_2\\ \end{array} + \begin{array}{c} CH_2\\ H_2\\ \end{array} - \begin{array}{c} CH_2Cl\\ H_2\\ CH_2\\ \end{array} + \begin{array}{c} CH_2Cl\\ H_2\\ CH_2\\ CH_2\\ \end{array} + \begin{array}{c} CH_2Cl\\ H_2\\ CH_2\\ CH_2\\$$

2,2' or (β, β') dichloro diethyl-sulphide

Isobutylene

(mustard gas)

BEGINNER'S BOX-3

- 1. The treatment of $(CH_3)_2$ C=CHCH₃ with boiling KMnO₄ produces (1) $CH_3COCH_3 + CH_3COOH$ (2) CH₃COCH₃ + CH₃CHO (3) $CH_3CHO + CO_2$ (4) CH₃COCH₃ only 2. An alkene on treating with hot acidified $KMnO_4$ gives 4 - oxopentanoic acid. The alkene is (1) Pentene (2) 2-Pentene (4) 1, 2- Dimethyl cyclopropene (3) 1–Methyl cyclobutene 3. The addition of Br₂ to cis-2-butene produces (1) (+) -2, 3-dibromobutane only (2) (-) -2, 3-dibromobutane only (3) racemic-2, 3-dibromobutane (4) meso -2, 3-dibromobutane 4. The addition of HCl to 3, 3, 3-trichloropropene gives (1) Cl₂CCH₂CH₂Cl (2) Cl₃CCH(Cl)CH₃ (3) Cl₂CHCH(Cl)CH₂Cl (4) Cl₂CHCH₂CHCl₂ 5. When ethene reacts with bromine in aqueous sodium chloride Solution. The product(s) obtained is (are) (1) Ethylene dibromide only (2) Ethylene dibromide and 1-bromo-2-chloro ethane
 - (3) 1–bromo–2–chloroethane only
 - (4) Ethylene dichloride only

160



5.3 ALKYNES

5.5 ALKINLS

5.3.1 Introduction of Alkynes

Alkynes are unsaturated hydrocarbons and characterised by the presence of a triple bond between the two carbon atoms ($C \equiv C$). The carbon-carbon triple bond is also called acetylenic bond. It consists of a strong σ and two weak π bonds. Alkynes are isomers of alkadienes and cycloalkenes.

5.3.2 General Methods of Preparation

(1) From Gem dihalides (by dehydrohalogenation) : Dehydrohalogenation agents are : NaNH₂ (Sodamide) or Alc. KOH or ROH + RONa.

$$R \xrightarrow[H]{} X \xrightarrow[-HX]{} R \xrightarrow[-HX]{}$$

(Stable by resonance)

(Vinyl halide)

(2) From Vicinal dihalides (by dehydrohalogenation) :



(a) Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.

(3) Dehalogenation of tetrahalo alkane : By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



(4) From Kolbe's electrolysis : By the electrolysis of aqueous Solution. of sodium or potassium fumarate or maleate, acetylene is formed at anode.

$$\begin{array}{ccc} CH-COOK & CH \\ \parallel \\ CH-COOK & Electrolysis & CH \\ (Aqueous) & \\ \end{array} \\ \begin{array}{c} CH-COOK \\ \parallel \\ CH-COOK \\ (Aqueous) & \end{array} \\ \begin{array}{c} CH-COO^{-} \\ \parallel \\ CH-COOK \\ (Aqueous) & \end{array} \\ \begin{array}{c} CH-COO^{-} \\ \parallel \\ CH-COO^{-} \end{array} + 2K^{+} \\ \end{array}$$

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at anode (Alkyne and CO_2 gas is formed)



at cathode (KOH and H_2 gas is formed)

$$2K^{+} + 2HQ_{\overline{J}}H \xrightarrow{2e^{-}} 2KOH + H_{2}\uparrow$$

(5) **Preparation of higher alkynes by Grignard reagent :** By this method lower alkyne is converted in to higher alkyne

$$CH \equiv \bigvee_{CH}^{\delta^{-}} \stackrel{\delta^{+}}{H} \stackrel{\delta^{-}}{CH_{3}} - \stackrel{\delta^{+}}{Mg} - Br \longrightarrow \bigcup_{CH}^{C} \stackrel{MgBr}{H} + CH_{4} \xrightarrow{R-1} R - C \equiv CH + Mg_{I}$$

$$R - C \equiv CH + CH_{3}Mg - Br \longrightarrow \bigcup_{\substack{I \\ C - R}}^{C - MgBr} + CH_{4} \xrightarrow{R'I} R' - C \equiv C - R + Mg I$$

(6) Preparation of Ethyne or Acetylene:

(a) From Metal carbide [Laboratory method] : Acetylene is prepared in the laboratory by the action of water on calcium carbide.

 $CaC_{2} + 2H_{2}O \longrightarrow CH \equiv CH + Ca(OH)_{2}$ $[Ca^{+2} + \overset{\Theta}{C} \equiv \overset{\Theta}{C} + 2H^{+} + 2OH^{-} \longrightarrow CH \equiv CH + Ca(OH)_{2}]$

(b) From haloform [CHI₃, CHCI₃] : Pure acetylene is obtained when iodoform or chloroform is heated with Silver powder

 $CHI_{3} + 6Ag + I_{2}CH \xrightarrow{\Lambda} CH \equiv CH + 6AgI$

5.3.3 Physical & Chemical Properties of Alkynes

Physical Properties

- (i) First three members $[C_2 \text{ to } C_4]$ are gases, from C_5 to C_{12} are liquid and after that they are solid.
- (ii) Alkynes are slightly soluble in H_2O but soluble in CCl_4 , benzene, acetone and alcohol.
- (iii) B.P., M.P. and densities of alkynes are comparatively more than alkenes and alkanes due to more polarisation.

B.P. \propto mol.wt. $\propto \frac{1}{\text{number of side chains}}$

Chemical Properties

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The chemical properties of alkynes are due to two factors

(a) **Presence of** π **electrons :** Due to presence of loosely bonded π electrons, alkynes like alkenes, undergo easily electrophilic addition reaction.

Carbon-carbon triple bond is less reactive than the carbon-carbon double bond towards electrophilic addition reactions.

In addition to electrophilic additions, alkynes also undergo nucleophilic addition with nucleophiles

(b) Presence of acidic hydrogen atom : The hydrogen atom attached to the triple bonded carbon can be removed by a strong base and hence acetylene and 1-alkynes are considered as weak acids.

Explanation : The amounts of s-character in various types of C-H bonds is as-

$\equiv C - H$	=C-H	—С—Н
50%	33%	25%

Since s electrons are closer to the nucleus than the p electrons, the electrons present in a bond having more s-character will be closer to nucleus. Due to high s-character of the C—H bond in alkyne (s=50%) the electrons constituting this bond are more strongly held by the carbon nucleus, with the result the H present on \equiv C–H can be easily removed as proton.

GOLDEN KEY POINTS

• The acidic nature of the three types of –C–H bonds as

$$\begin{array}{rcl} \hline & C & -H \\ & sp & sp^2 & sp^3 \end{array}$$

• Relative acidic order $H_2O > ROH > HC = CH > HNH_2 > CH_2 = CH_2 > CH_3 - CH_3$

(1) Addition reaction

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(a) Addition of hydrogen : Alkynes reacts with hydrogen in presence of a catalyst. In presence of Pt., Pd or Ni alkynes give alkanes with H₂

$$R - C \equiv CH \quad \xrightarrow{Ni, H_2} \quad R - CH = CH_2 \quad \xrightarrow{Ni, H_2} \quad R - CH_2 - CH_3$$

In presence of Lindlar's catalyst [Pd/CaCO3 + quinoline or Nickle boride] alkynes give cis – alkene

$$R - C \equiv C - R' \xrightarrow{\text{Lindlar's catalyst}}_{H_2} \xrightarrow{R} C = C \begin{pmatrix} R' \\ H \end{pmatrix}$$
 (Stereo specific reaction)

cis - alkene

In presence of Na/NH_3 alkynes give trans-alkene. (Birch Reduction)

 $R - C \equiv C - R' \qquad \xrightarrow{Na/Liq.NH_3} \qquad \begin{array}{c} R \\ H_2 \end{array} \qquad \begin{array}{c} R \\ H \end{array} > C = C \begin{pmatrix} H \\ R' \\ \end{array} \qquad (Stereo \ specific \ reaction) \end{pmatrix}$

trans-alkene

(b) Electrophilic addition : Addition reactions where the addition is initiated by electrophile (positive group). The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in $C \equiv C$, the π electrons are tightly held by carbon nuclei and so they are less easily available for reaction with electrophiles.

Another reasons is : The intermediates when an electrophile attack on alkene and alkynes are :

(i)
$$R-C\equiv C-R \xrightarrow{H^+} R \xrightarrow{H} R \xrightarrow{I} C = \overset{H}{C} - R$$

(ii) $R-CH=CH-R \xrightarrow{H^+} R \xrightarrow{CH} CH \xrightarrow{+} CH - \overset{H}{C} H \xrightarrow{-} R$

Stability of intermediates :

 $R-CH = \overset{\oplus}{C} -R < R-CH_2 - \overset{\oplus}{CH} -R$ (+) ve on more EN more stable

atoms is less stable

So we can say that alkenes are more reactive towards electrophilic addition reaction.

(i) Addition of Halogens : Alkynes react with Cl_2 or Br_2 in dark in presence of metal halide and form di and tetra halo derivatives.

		u u
R—C≡CH	$\xrightarrow{2Cl_2} FeCl_3 \rightarrow$	 R—C—C—H C C

Mechanism :

 $Cl_2 + FeCl_3$

Cl+ + FeCl₄



(ii) Addition of halogen acids (H – X) : Addition according to Markovnikov's Rule.

Reactivity order of H – X :
$$HI > HBr > HCl > HF$$

 $R - C \equiv C - H \xrightarrow{H-X} R - C - C - H$
 $X H$
 $X H$

(Gem dihalides major product)

Mechanism :

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$$R - C \stackrel{\frown}{=} \stackrel{\bullet}{C} H \qquad \xrightarrow{H^+}{[H-X]} \rightarrow \qquad R - \stackrel{+}{C} = C - H$$

(Intermediate is carbocation)

$$R - \stackrel{\oplus}{C} = CH_2 \xrightarrow{X^-} R - \stackrel{X}{C} = CH_2$$

Further

(more stable (only –I of X)

due to +M of X)

so

$$R \xrightarrow{X}_{\oplus} CH_{3} \xrightarrow{X^{\Theta}} R \xrightarrow{X}_{H} CH_{3}$$

(Major Product)

(iii) Addition of HOX : Alkynes react with hypohalous acids according to Markovnikov's rule and form gem diol, which are unstable, lose a molecule of water and form dihalo aldehyde or dihalo ketones.

$$R - C \equiv CH + HOCI \longrightarrow R - C - CHCl_2$$

Mechanism :

$$R-C \equiv CH \xrightarrow[Hocl]{Cl^+} R \xrightarrow{c_{+}} CH \xrightarrow{c_{+}} R \xrightarrow{c_{+}} CH \xrightarrow{c_{+}} R \xrightarrow{c_{+}} CH$$

(more stable due to +M of OH group) (less + M of

Cl - Atom)

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165

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 $3R - C \equiv C - R \xrightarrow{BH_3} (R - C = C -)_3B$

Since BH₃ is not available as monomer so a solvent THF is used for the stability of BH₃.



(2) Oxidation Reactions

(a) Combustion :

$$C_{n}H_{2n-2} + \frac{3n-1}{2}O_{2} \longrightarrow nCO_{2} + (n-1)H_{2}O + Heat$$

2HC = CH + 5O₂ \longrightarrow 4CO₂ + 2H₂O + 312 K.cal

The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000°C) is produced.

(b) Oxidation with acidic $KMnO_4$: In presence of acidic $KMnO_4$, alkynes are oxidised to monocarboxylic acids.

$$\begin{array}{c} R \longrightarrow C \equiv C \longrightarrow R' + 2[O] \longrightarrow R \longrightarrow C \longrightarrow C - C \longrightarrow R' \xrightarrow{H_2O+[O]} RCOOH + R'COOH \\ \parallel & \parallel \\ 0 & 0 \end{array} \xrightarrow{(CH)} RCOOH + R'COOH \xrightarrow{(O)} CO_2 \\ H^{0} \longrightarrow CHO \xrightarrow{(H)} CHO \xrightarrow{(H_2O+[O])} 2HCOOH \xrightarrow{(O)} CO_2 \\ glyoxal \end{array}$$

$$CH_3 \longrightarrow C \equiv CH + 2[O] \longrightarrow CH_3 - C = 0 \xrightarrow{(H_2O+[O])} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(O)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(H)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CH_3COOH + HCOOH \xrightarrow{(H)} CO_2 \\ CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} CHO \xrightarrow{(H)} COOH \xrightarrow{(H)} CO_2 \\ CHO \xrightarrow{(H)} CH$$

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Ex.





In this reaction ${\rm H_2O_2}$ is oxidant which oxidise ${\rm R}-{\rm C}-{\rm C}-{\rm R}$ into acids. $\| \ \| \\ 0 \ 0$

But if we use some amount of Zn as reductant with H_2O then it reduce H_2O_2 so oxidation does not take place $H_2O_2 + Zn \longrightarrow ZnO + H_2O$ Ex.

$$CH_{3}-C \equiv CH \xrightarrow{(i) 0_{3}} CH_{3}-C-C-H+H_{2}0_{2} \longrightarrow CH_{3}-C-OH+HCOOH$$

$$(i) 0_{3} \longrightarrow CH_{3}-C-C-H+ZnO$$

$$(i) 0_{3} \longrightarrow CH_{3}-C-C-H+ZnO$$

$$(i) H_{2}O/Zn \longrightarrow CH_{3}-C-C-H+ZnO$$

(3) Substitution Reaction : (Formation of metallic derivatives)

 $\equiv \overset{\delta^{-}}{C} - \overset{+\delta}{H}$ Only 1-alkynes give substitution reaction and show acidic characters

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two H⁺ where as propyne can give one H⁺.

(a) Formation of sodium acetylides : Acetylene and 1-alkynes react with sodamide to form acetylides

 $\xrightarrow{\text{NaNH}_2} \text{NaC} \equiv \text{CNa}$ $H - C \equiv C - H \xrightarrow{NaNH_2} NaC \equiv C - H$ Mono sodium Disodium acetylide acetylide

(b) Formation of copper and silver acetylides : Copper and silver acetylides are obtained by passing 1-alkynes in the ammonical Solution. of cuprous chloride and silver nitrate (Tollen's reagent) respectively.

$$\begin{array}{ll} R & \longrightarrow C \equiv C & \longrightarrow H + Cu_2Cl_2 + NH_4OH \longrightarrow R & \longrightarrow C \equiv CCu + NH_4Cl + H_2O \\ & & \text{ammonical cuprous-} & \text{copper acetylide} \\ & & \text{chloride} & [Red ppt.] \\ R & & \longrightarrow C \equiv C & \longrightarrow H + AgNO_3 + NH_4OH \longrightarrow R & \longrightarrow C \equiv CAg + NH_4NO_3 + H_2O \\ & & \text{Tollen's reagent} & White ppt. \end{array}$$

These reactions are used for detecting the presence of acetylenic hydrogen. These are test to distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

(4) Isomerisation: When alkyne-1 is heated with alc. KOH alkyne-2 is obtained.

$$CH_{3} - CH_{2} - C \equiv CH \xrightarrow{alc.KOH} CH_{3} - C \equiv C - CH_{3}$$

When alkyne -2 is heated with $NaNH_2$ alkyne -1 is obtained

$$CH_{3} - C \equiv C - CH_{3} \xrightarrow{\text{NaNH}_{2}} CH_{3} - CH_{2} - C \equiv CH$$
2-Butvne
1-Butvne

(5) Polymerisation :

(a) Linear polymerisation :

Dimerisation : When two molecules of acetylene passed through a Solution. of Cu_2Cl_2 and NH_4Cl a vinyl acetylene is obtained.

$$2\text{HC} \equiv \text{C}-\text{H} \xrightarrow{\text{Cu}_2\text{Cl}_2} \text{NH}_4\text{Cl} \rightarrow \text{CH}_2 = \text{CH}-\text{C} \equiv \text{C}-\text{H}$$

mono vinyl acetylene (butenyne)

When vinyl acetylene react with HCl then chloroprene is obtained.

 $CH_2 = CH - C \equiv C - H \xrightarrow{HCl} CH_2 = CH - C = CH_2 \xrightarrow{Polymerisation} Neoprene (Synthetic rubber)$

2-chloro-1,3-butadiene

[chloroprene]

Trimerisation : 3 molecules of acetylene.

$$3CH \equiv CH \xrightarrow{Cu_2Cl_2} CH_2 = CH - C \equiv C - CH = CH_2$$

Divinyl acetylene

(b) Cyclic polymerisation : When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound

$$3 \text{ CH}_3 - \text{C} \equiv \text{CH} \xrightarrow{\text{Red hot}} \text{iron tube}$$

$$3 \text{ CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3 \xrightarrow{\text{Redhot}} \text{iron tube}$$

Mesitylene

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array}$$

Hexa methyl benzene

Uses of Acetylene

- (i) Oxyacetylene flame used in welding and cutting
- (ii) Acetylene is used as an illuminant
- (iii) Acetylene is used for artificial ripening of fruits
- (iv) Used for manufacture of acetaldehyde, acetic acid, ethyl alcohol, westron, westrosol, PVC, PVA, Chloroprene, butadiene, Lewisite etc.
- (v) It is used as a general anaesthetic.

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Test for alkynes :

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- (i) Decolourization of Br_2 in CCl_4 Solution..
- (ii) Decolourisation of 1% alkaline $KMnO_4$ Solution..
- (iii) 1- alkynes give white ppt. with ammonical $AgNO_3$ and red ppt with ammonical cuprous chloride Solution...

Note : (i) and (ii) tests are used for determination of unsaturation (i.e, presence of double or triple bond in any compound). (iii) Test is used for distinguish between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.

Separation of ethane, ethene and ethyne :



BEGINNER'S BOX-4

Propyne and HCl in presence of peroxide gives :
 (1) 1,1-dichloro propane
 (2) 1,2-dichloro propane
 (3) 1,3-dichloro propane
 (4) 2,2-dichloro propane

5.4 AROMATIC HYDROCARBONS [ARENES]

5.4.1 Introduction of Arenes

- Arenes are cyclic, planar and follow Huckel's rule.
- There should be cyclic resonance in Arenes.
- General formula of Arenes are $C_n H_{2n-6v}$ where n = Number of carbons

y = Number of rings

- Characteristic reaction of arenes is Electrophilic substitution reaction (ESR).
- Arenes are cyclic unsaturated compounds but do not give test of unsaturation with Br_2/CCl_4 or alk. $KMnO_4$.
- Main source of Arenes is coaltar.
- They have higher precentage of carbon so burn with smoky flame.

5.4.2 General Methods of Preparation

(i) From alkanes (By cyclisation or Aromatisation) Hydroforming or catalytic reforming

n – Hexane
$$\xrightarrow{Cr_2O_3/Al_2O_3}$$
 Benzene + $4H_2$

(ii) From alkyne (By cyclic polymerisation) When acetylene is passed through red hot metallic tube cyclic polymerisation takes place and benzene is formed.

$$3CH \equiv CH \longrightarrow Red hot iron tube \bigcirc$$

(iii) From Phenolic compounds (By deoxygenation) :

$$\bigcirc \overset{OH}{\longrightarrow} + Zn \qquad \xrightarrow{\Lambda} \qquad \bigcirc \overset{H}{\longrightarrow} + ZnO$$

$$\overset{CH_{3}}{\bigcirc} \overset{OH}{\longrightarrow} + Zn \qquad \xrightarrow{Fe/H_{2}O} \qquad \bigcirc \overset{CH_{3}}{\bigcirc} \overset{H}{\longrightarrow} + ZnO$$

(iv) From carbonyl compounds (By reduction) :



(v) From carboxylic acids (By decarboxylation) :



(vi) From sulphonic acids (By hydrolysis) :



(vii)By diazonium salts :

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(viii) By Grignard reagent :



(ix) By Wurtz fittig reaction :



(x) From petroleum :

Petroleum $\xrightarrow{\text{high temp.}}$ Mixture of lower $\xrightarrow{\text{Seperate}}$ $CH_2 = CH_2 + CH_2 = CH - CH = CH_2$





171

5.4.3 Physical & Chemical Properties of Arenes

Physical properties :

- (i) Benzene is colourless liquid [B.P. is 80°C]
- (ii) Benzene is insoluble in $\mathrm{H_2O}$ and density less than $\mathrm{H_2O}$
- (iii) Benzene is used as a solvent and it is soluble in organic solvents.
- (iv) It is highly inflammable and burns with smoky flame.
- Chemical properties : Benzene show following types of reaction -
- (A) Addition reactions (B) Electrophilic substitution reactions

(A) Addition reaction :

(i) Addition of X_2





Alicyclic compound ($C_6H_6Cl_6$) or Benzene hexachloride BHC or 666 or Gammexene or lindane *BHC is used as powerful insecticide

(C) Oxidation reactions

Formation of BHC from C_6H_6 is an example of free radical addition reaction.



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$\begin{array}{c} & & CH_{3} \\ & & \underbrace{O_{3}/H_{2}O}_{Zn} \xrightarrow{CH_{3}} \begin{array}{c} CH_{3} - C - CHO \\ \parallel \\ O \end{array} + 2 \begin{array}{c} CHO \\ HO \end{array}$

Addition of 3 mole Cl_2 or 3 mole H_2 or 3 mole O_3 on benzene show presence of 3 double bonds in benzene. Benzene does not give addition reaction with Br_2/CCl_4 or alkaline KMnO₄

(C) Oxidation reactions :

ALLEN

(i) Combustion :

$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$$

(ii) Catalytic Oxidation :



(iii) Side chain Oxidation : Atleast one benzylic –H containing alkyl benzene gives benzoic acid in presence of strong oxidising agent.



Note : t-butyl benzene does not give benzoic acid in presence of $H^{\oplus}/KMnO_4$, since t-butyl benzene does not contain benzylic-H

$$O - C \xrightarrow{CH_3}_{CH_3}$$
 [Absence of benzylic -H]

ANSWER KEY

REGINNER'S BOX-1	Que.	1	2	3	4	5	6	7		
DLOIMALK S DOX-1	Ans.	2	4	3	3	2	2	1		
DECININED'S DOV 9	Que.	1	2	3	4	5	6			
DEGINNER 5 DUA-2	Ans.	4	1	1	3	3	1			
REGINNER'S ROX-3	Que.	1	2	3	4	5				
DLOIMALK S DOX-3	Ans.	1	3	3	1	2				
REGINNER'S BOY	Que.	1	2	3	4	5				
DEGINNER 5 DUA-4	Ans.	4	3	4	4	3				
						•	-			

E	XERCISE-I (Conceptual Questions)		Build Up Your Understanding				
1.	ALKANES The order of reactivity of alkyl halides in Wurtz reaction is	8.	(A) CH_3 — CH — $COOH$ $\xrightarrow{\text{Red P/HI}}$ B \downarrow OH				
	(1) $R-I > R-Br > R-CI$ (2) $R-I < R-Br < R-CI$ (3) $R-Br > R-I < R-CI$ (4) $R-I > R-CI > R-Br$		'B' looses its optical activity because of(1) Chirality of the molecule destroyed(2) Symmetry of molecule is destroyed(3) Spatial arrangement is changed				
2.	 Kolbe's electrolysis of a mixture of pot. Propanoate and pot. 3-Methylbutanoate gives (1) Butane and isobutane (2) Butane and 2,5-dimethylhexane (3) Butane, 2,5-dimethylhexane and isohexane (4) Butane and isohexane 	9.	(4) Racemic mixture is formed $CH_{3} - CH MgCl + CH_{3} - CH_{3} \longrightarrow 'Q';$ $CH_{3} + CH_{3} - CH_{3} + CH_{3} \longrightarrow 'Q';$				
3.	The Corey-House alkane synthesis is carried out by treating an alkyl halide with (1) Lithium metal (2) Copper metal		What is 'Q' ? (1) isobutane (2) isopropane (3) tert. butyl chloride (4) propane				
	(3) Lithium metal followed by reaction with cuprous iodide and then treating the product with an alkyl halide(4) Cuprous iodide followed by reaction with alkyl halide	10.	\bigcirc = 0 can not be converted to \bigcirc by : (1) Red P + HI (2) Wolf Kishner reduction (3) Clemmensen reaction (4) LiAlH ₄				
4.	 Which of the following acids on decarboxylation gives isobutane (1) 2,2–Dimethyl butanoic acid (2) 2,2–dimethyl propanoic acid (3) 3–Methyl pentanoic acid (4) 2–Methyl butanoic acid 	11.	$(CH_{3})_{3}C-Br \xrightarrow{(i) \text{ Li}}_{(ii) \text{ Cul}} A \xrightarrow{CH_{3} \text{ CH}_{2} \text{ CH}_{2} \text{ Br}} B;$ 'B' is $(1) \text{ CH}_{3}(CH_{2})_{2}C(CH_{3})_{3} \qquad (2) (CH_{3})_{3}C-C (CH_{3})_{3}$ $(3) \text{ CH}_{3}(CH_{2})_{4}CH_{3} \qquad (4) (CH_{3})_{2}CH_{2}C(CH_{3})_{3}$ Which of the following reactions does not involve				
5.	Which of the following compound is not suitableto obtain from wurtz reaction ?(1) ethane(2) butane(3) isobutane(4) hexane		 a C—C bond formation (1) Hydrolysis of a Grignard reagent (2) Combination of two alkyl free radicals (3) Corey-House synthesis of alkanes 				
6.	When ethyl chloride and n-propyl chlorideundergoes wurtz reaction which is not obtained(1) n-butane(2) n-pentane(3) n-hexane(4) isobutane	13.	 (4) KNa + K−Br → K−K + NaBr The highest boiling point is expected for (1) Isooctane (2) 2,2,3,3-tetramethylbutane 				
7.	Which of the following reagent can be used for following conversion		(3) n-octane (4) n-butane				
	HO \longrightarrow CCH ₃ $\xrightarrow{?}$ HO \longrightarrow CH ₂ CH ₃ (1) Zn - Hg/HCl (2) Red P + HI (3) NH ₂ - NH ₂ / $^{\Theta}$ OH (4) All of them	14.	Pyrolysis of alkanes is a(1) Nucleophilic addition reaction(2) Free radical substitution reaction(3) Electrophilic addition reaction(4) Free radical elimination reaction				
174	•		•				

Pre-Medical : Chemistry

- The antiknocking compound is 15. (2) Diethylzinc (1) TEL (3) Dimethylcadmium (4) Tetramethyl tin
- **16**. Which of the following reactions of methane is incomplete combustion :-

(1)
$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm.} 2CH_3OH$$

(2)
$$CH_4 + O_2 \xrightarrow{M_{O_2}O_3} HCHO + H_2O$$

(3) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O(\ell)$

$$(4) \operatorname{CH}_4 + 2\operatorname{O}_2 \longrightarrow \operatorname{CO}_2(g) + 2\operatorname{H}_2\operatorname{O}(\ell)$$

ALKENE

- **17.** Ozonolysis of 3–Methyl–1–butene gives a mixture of
 - (1) Propanal and ethanal
 - (2) Propanone and ethanal
 - (3) 2-Methylpropanal and methanal
 - (4) Butanone and methanal
- 18. Which alkene gives acetone only on ozonolysis (1) Isobutylene
 - (2) 2,3–Dimethyl–1–butene
 - (3) 2,3-Dimethyl-2-butene
 - (4) 3,3–Dimethyl–1–butene
- **19.** Oxidation of isobutylene with acid potassium permanganate gives
 - (1) Acetone + CO_{2}
 - (2) Acetic acid
 - (3) Acetic acid + CO_{2}
 - (4) Acetic acid + acetone
- 20. Which of the following reactions is used for locating the position of double bond in an alkene (1) Hydroboration (2) Hydroxylation (3) Chlorohydroxylation (4) Ozonolysis

21. CH₃CH₂CH₂Br $\xrightarrow{\text{alc.KOH}} A \xrightarrow{(i)O_3} B + C$

In the above reaction A, B and C are given by the set

- (1) Propylene, acetone, formaldehyde
- (2) Propene, ethanal, methanal
- (3) Propyne, acetaldehyde, formaldehyde
- (4) Propylene, propionaldehyde, formaldehyde
- **22.** Which one of the following has the smallest heat of hydrogenation per mole

(1) 1-butene (2) Trans-2-butene (4) Propene

(3) Cis-2-butene

- **23**. An alkene "A" contains three C-C, eigth C-H σ -bonds and one C–C π -bond. "A' on ozonolysis gives two moles of an aldehyde of molar mass 44. Which of the following is the IUPAC name of A. (1) But-1-ene (2) But-2-ene (3) Pent-2-ene (4) But-2-yne
- **24**. The molecules having dipole moment are :-(1) 2,2-dimethylpropane (2) trans pent-2-ene (3) cis-hex-3-ene
 - (4) 2 and 3
- **25**. Which of the following alkenes on ozonolysis give a mixture of ketones only?

(a)
$$CH_3-CH=CH-CH_3$$
 (b) $CH_3-CH-CH=CH_2$
 CH_3
(c) $\sum = C \begin{pmatrix} CH_3 \\ CH_3 \end{pmatrix}$ (d) $(CH_3)_2C=C \begin{pmatrix} CH_3 \\ CH_3 \end{pmatrix}$
(1) a and b (2) b and c
(3) b and d (4) c and d
ALKYNES

26. Kolbe's electrolysis of sodium maleate at anode gives. (1) Only acetylene (2) Only CO₂

(3) Acetylene + CO_{2}

(4) $CO_{2} + H_{2}$

- 27. The pH of solution in Kolbe's electrolysis (1) increase with time (2) decrease with time (4) nothing can be said (3 remains constant
- 28. Which of the following compound will not give a precipitate with Tollen's reagent
 - (2) 1-butyne (1) ethyne
 - (3) 3-methyl -1-butyne (4) 1-pentene
- $-CH_{3}-C \equiv CH \xrightarrow{H_{g}SO_{4}/H_{2}SO_{4}} A,$ 29. B← H₂O₂/OH A and B are (1) CH₂CH₂CHO, CH₂COCH₂ (2) CH₃COCH₃, CH₃CH₂CHO (3) CH₂COCH₂ both (4) CH₃COCH₃, CH₃CH₂CH₂OH
- MeCH_aC \equiv CH $\xrightarrow{NH_3/NaNH_2}$ A $\xrightarrow{Et Br}$ B, **30**. A and B are (1) MeCH₂C \equiv CNa, MeCH₂C \equiv C-Et (2) MeCH₂CH=CH₂, MeCH₂-CHEt-CH₂ (3) MeCH₂CH=CHNH₂,MeCH₂CH=CH-NHBr (4) $MeCH_{2}C \equiv C - NH_{2}$, $MeC \equiv C - NH - Br$



- 32. To distinguish between propene and propyne, the reagent would be -(1) Bromine (2) Alkaline KMnO₄ (3) Ammonical silver nitrate (4) Ozone
- 33. When treated with ammonical cuprous chloride, which one among the following forms red precipitate ? (1) $C_{2}H_{6}$ (2) $C_{2}H_{4}$ $(3) C_{2}H_{2}$ (4) $C_{6}H_{6}$

34. In which of the following reactions benzene is obtained



respectively are

- (1) o-bromo styrene, benzoic acid
- (2) p-bromostryrene, benzaldehyde
 (3) m-bromostyrene, benzaldehyde
 (4) Styrene dibromide, benzoic acid.

EXERCISE-I (Conceptual Questions)

is/are :-(1) Only $CH_3 - C - C - CH_3$ (2) $CH_3 - C - C - H + CH_3 - C - C - CH_3$ (3) $H-C-C-H+CH_3-C-C-CH_3$ $\begin{array}{cccccccc} (4) & CH_{3}C-CCH_{3}+HC-CH+CH_{3}C-C-H\\ \parallel & \parallel & \parallel & \parallel & \parallel\\ & 0 & 0 & 0 & 0 & 0 \end{array}$ 37. Benzene_ ; A and B resectively are (1) Zn - Hg + HCl , CI, LiAlH Cl. NaBH. Zn—Ha + HC

The ozonolysis product of 1, 2-dimethyl benzene

38. Which of the following reaction does not gives benzoic acid

(1)
$$C_6H_5 - CH_3 \xrightarrow{Acidic} KMnO_4$$

(2) $C_6H_5 - CH_3 \xrightarrow{CrO_2Cl_2} IO \rightarrow IO$
(3) $C_6H_5 C \equiv CH \xrightarrow{Acidic} KMnO_4 \rightarrow IO$
(4) $C_6H_5 - C - CH_3 \xrightarrow{Acidic} KMnO_4 \rightarrow IO$

Z:\NODE02\B0AI-B0\TARGET\CHEM\ENG\MODULE-3\05 HYDROCARBON\02-EXERCISE.P65 Ε

ANSWER KEY

Que Ans Que Ans Que Ans

36.

EXERCISE-II (Previous Year Questions)

AIPMT 2007

- 1. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
 - (1) Cope reduction

ALLEN

- (2) Dow reduction
- (3) Wolf-kishner reduction
- (4) Clemmensen reduction
- 2. Which of the compounds with molecular formula $C_5 H_{10}$ yields acetone on ozonolysis
 - (1) 3-Methyl-1-butene
 - (2) Cyclopentene
 - (3) 2-Methyl-1-butene
 - (4) 2-Methyl-2-butene

AIPMT 2010

- 3. Liquid hydrocarbons can be converted to a mixture of gasesous hydrocarbons by :-
 - (1) Hydrolysis
 - (2) Oxidation
 - (3) Cracking

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Ε

(4) Distillation under reduced pressure

AIIMS 2013



AIPMT/NEET & AIIMS (2006-2018)

AIIMS 2014

5. The product of the following reaction is :-







AIPMT 2015

6. A single compound of the structure :-

(3

$$OHC \underbrace{C}_{H_2} \underbrace{H}_{H_2} \underbrace{C}_{H_2} \underbrace{C}_$$

is obtainable from ozonolysis of which of the following cyclic compounds ?



7. 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid ?

(1)
$$(CH_3)_2C = CH - CH_2 - CH_3$$

(3) $(CH_3)_2CH-CH-CH=CH_2$ ĊΗ₃

(4) (CH₃)₃C–CH=CH₂

177

Pre-Medical : Chemistry

- 8. The oxidation of benzene by V_2O_5 in the presence of air produces :
 - (1) benzoic acid (2) benzaldehyde
 - (3) benzoic anhydride (4) maleic anhydride
- 9. Which of the following is not the product of



10. Identify product of the reaction

$$\begin{array}{c} \text{CH=O} \\ \text{(CHOH)}_3 \xrightarrow{\text{HI}} \\ \text{CH}_3 \end{array} \rightarrow$$

(1) n-Pentane (2) 2-Pentane

(3) 1,3 Pentadiene (4) 3-Pentene

NEET(UG) 2018

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

(1)
$$CH = CH$$
 (2) $CH_2 = CH_2$

- (4) CH₄ (3) $CH_3 - CH_3$
- 12. The compound C_7H_8 undergoes the following reactions :

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The product 'C' is

- (1) m-bromotoluene
- (2) o-bromotoluene
- (3) 3-bromo-2,4,6-trichlorotoluene
- (4) p-bromotoluene

of their boiling point CH₃CH₂CH₂CH₂CH₃ I. III. CH₃-CH-CH₂-CH₃ L CH₃ CH₃ II. CH₂ (1) I > II > III(2) II > I > III (3) I > III > II(4) III > I > II $Ph-CH_2-C=C-CH_3 \xrightarrow{Na} A \xrightarrow{Cl_2/hv} B$ 14. The final product 'B' is :- $C=C \xrightarrow{H}_{CH}$ (1)

AIIMS 2018

Arrange the following alkanes in decreasing order

(2)
$$Ph-CH_2 \rightarrow C=C \stackrel{H}{\sim} C=C \stackrel{H}{\sim} CH_2-Cl$$

(3)
$$Ph-CH_{2}$$
 $C=C \begin{pmatrix} CH_{3} \\ H \end{pmatrix}$
Ph-CH_{2} $C=C \begin{pmatrix} CH_{3} \\ H \end{pmatrix}$

(4)
$$Ph-CH_2 C=C CH_2-Cl$$

15. Benzene is :-

13.

- (1) Weakly attracted in the magnetic field
- (2) Strongly attracted in the magnetic field
- (3) Strongly repelled in magnetic field
- (4) Weakly repelled in magnetic field

16. Br
$$NO_2 \xrightarrow{2HBr}{\Delta}$$
 Product.

Product of reaction is :-









EXERCISE-II (Previous Year Questions)													ANSV	VER	KEY
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	4	3	4	2	4	4	4	4	1	4	1	3	1	4
Que.	16					-			-		-		-		
Ans.	1														
178		•								-					



EXERCISE-III (Analy	ions)					ANSWER KEY		
	Que.	1	2	3	4	5	6	
	Ans.	2	2	4	4	2	4	
								179

E	XERC	ISE-I	IV (As	sertic	on & R					Tar	get AIIMS			
Directions for Assertion & Reason questions														
These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.														
(A)	(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.													
(B)	(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.													
(C)	(C) If Assertion is True but the Reason is False.													
(D) If both Assertion & Reason are false.														
1 . 2 .	Asser decarbo CH ₃ —C Reaso interme (1) A Assert distingu Reaso	tion $Dxylatic DH_2DH_$:- T on is COOH Reactiv carboca 2) B - Baeye clopent Baeyer's	he rea > CH ₃ ity dep ition. (3) er's reagent cane from s reagent	activity 	orde -COOF n stabi (4) n be u pene. ccolouris	r for H lity of D sed to sed by	6. 7.	Asse treate Reas of Cu (1) A Asse distin Reas while (1) A	ertion ed with son :- F a. ertion guished son :- 1 2-alkyr	:- Ace ammon Red ppt (2) B :- 1-al by Ba L-alkyne ne does (2) B	lkyne eyers e deco s not o	e gives F Cu ₂ Cl ₂ . tained du (3) C and 2-a reagent. blourise B decolouri (3) C	Red ppt when (4) D alkyne can be aeyers reagent se. (4) D
3.	propene but not by cyclopentane (1) A (2) B (3) C (4) D Assertion :- Increasing order of heat of hydrogenation is $CH_2=CH-CH_3 < CH_3-CH=CH-CH_3 < CH_3-C=C-CH_3$ $CH_3-C=C-CH_3$ $CH_3 CH_3$								 Assertion :- Benzene does not decolouris Br₂-water. Reason :- Benzene is stabilized by aromaticity and no addition of Br₂. (1) A (2) B (3) C (4) D Assertion :- Benzene reacts with Cl₂ in presence of light to form BHC. Reason :- Reaction undergoes electrophility is the stabilized of the stabilized of the stabilized of the stabilized by aromaticity and no addition of Br₂. 					
Α	stability (1) A	. ()	2) B	(3)) C	(4)	D	10.	(1) A Asse	ertion	(2) B :-		(3) C	(4) D
H. Assertion :- In the following reaction $CH_2 = CH_2 + NaNH_2 \rightarrow CH_2 = CH Na + NH_3$ reaction is always in forward direction. Reason :- Ethene is stronger acid than ammonia. (1) A (2) B (3) C (4) D									CH_3 + Cl_2 <u>Catalyst</u> product. In product benzene ring is remain unchanged. Reason :- Hexachloro benzene is an aromat compound.					
 Assertion :- Ethyne and its derivatives give white precipate with ammonical silver nitrate solution. Reason :- Alkynes gives white ppt with ammonical silver nitrate solution due to nucleophilic substitution reaction. (1) A (2) B (3) C (4) D 								11.	Assertion :- Acetylene gives glyoxal on reductive ozonolysis while benzene does not give glyoxal. Reason :- Benzene does not show reductive ozonolysis reaction. (1) A (2) B (3) C (4) D					
E	KERC	SE-I	V (As	sertio	n & R	eason)						ANS	NER KEY
		Que. Ans.	1 3	2 1	3 4	4 4	5 4	6 3	7 4	8 1	9 3	10 2	11 4	

- Allen

180