22

Hydrocarbons

TOPIC 1 Alkanes

01 Which of the following alkane cannot be made in good yield by Wurtz reaction? [NEET 2020]

(a) 2, 3-dimethylbutane (b)n-heptane (c)n-butane (d)n-hexane

Ans. (b)

In Wurtz reaction, an alkyl halide (R - X)give a symmetrical alkane (R - R) of even number of carbon atom with 100% yield.

> $2R \longrightarrow X \xrightarrow{2Na/ether} R \longrightarrow R(100\%)$ -2NaX

An unsymmetrical alkane (R - R') with odd number of carbon atom can be obtained with 33% yield only, if we take a mixture of two different alkyl halides, R—X and R'—X.

$$R \longrightarrow X + R' \longrightarrow X \longrightarrow \underbrace{R \longrightarrow R + R' - R'}_{67\%} + \underbrace{R - F}_{33\%}$$

So, here *n*-heptane (C_7H_{16}) cannot be obtained with good yield. Hydrocarbons in options (a), (c) and (d) have even number of carbon atom (symmetrical, alkanes).

02 The alkane that gives only one mono-chloro product on chlorination with Cl₂ in presence of diffused sunlight is

[NEET (Odisha) 2019]

- (a) 2, 2-dimethylbutane
- (b) neopentane
- (c) n-pentane
- (d) isopentane

Ans. (b)

Key Idea Alkanes which contain all equivalent hydrogen atoms forms only one monochloro derivative on halogenation.

$$CH_3$$

|
Neo-pentane, H_3C — C — CH_3 contains all
|
 CH_3

equivalent hydrogen atoms. So, it will give only one monochloro derivative on halogenation.

03 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 [NEET 2018]

(a) $CH_3 - CH_3$ (b) $CH_2 = CH_2$ (c) CH≡CH (d) CH4

Ans. (d)

R'

The given reaction takes place as follows

$$CH_4 \xrightarrow{Br_2 / hv} CH_3Br \xrightarrow{Na / dry ether} Wurtz reaction (Step 2)$$

CH₃-CH₃

Step | Alkyl halide is formed by free radical halogenation of alkane in the presence of UV-light.

Step II The formed alkyl halide reacts with sodium in presence of dry ether to form alkane containing double number of carbon atoms present in alkyl halide.

This reaction is known as Wurtz reaction.

From the above mechanism, it is concluded that option (d) is correct as in all other cases the hydrocarbon formed in step 2 will contain more than four carbon atoms.

04 The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is

[NEET 2016, Phase I]

- (a) The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
- (b) The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
- (c) The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
- (d) The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain

Ans. (c)

Due to the absence of torsional strain staggered conformation of ethane is more stable than eclipsed conformation of it



05 The compound that will react most readily with gaseous bromine has the formula [NEET 2016, Phase II] (a) C_3H_6 (b) C₂H₂ (d) $C_2 H_4$ (c) C₄H₁₀

Ans. (c)

In gaseous state, Br_2 forms free radicals and saturated hydrocarbons are more prone to have free radical substitutions. As C_4H_{10} reacts most readily with gaseous bromine via free radical mechanism as shown below:

 $\label{eq:c4} \begin{array}{c} C_4 H_{10} + Br_2 \longrightarrow C_4 H_9 Br + HBr \\ \mbox{Therefore, option(c) is correct.} \end{array}$

06 Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by

[CBSE AIPMT 2010]

- (a) oxidation
- (b) cracking
- (c) distillation under reduced pressure(d) hydrolysis

Ans. (b)

Key Idea Lower hydrocarbons exist in gaseous state while higher ones are in liquid state or solid state.

On cracking or pyrolysis, the hydrocarbon with higher molecular mass gives a mixture of hydrocarbons having lower molecular mass. Hence, we can say that by cracking a liquid hydrocarbon can be converted into a mixture of gaseous hydrocarbons.

07 In the following the most stable conformation of *n*-butane is [CBSE AIPMT 2010]





Ans. (b)

Key Idea The conformation in which the heavier groups are present at maximum possible distances, so that the forces of repulsion get weak, is more stable. Among the given conformations of *n*-butane, the conformation shown in option (b), i.e. anti conformation is most stable as in it the bulkier group, i.e. $--CH_3$ group are present at maximum possible distance and get lower energy. Which of the following reactions is expected to readily give a hydrocarbon product in good yields? [CBSE AIPMT 1997]
 (a) RCOOK _ Electrolytic >

(b)
$$RCOOAg \xrightarrow{I_2}$$

(c) $CH_3CH_3 \xrightarrow{CI_2}$

Ans. (a)

Electrolysis of sodium or potassium salt of carboxylic acid gives good yield of hydrocarbon

$$2RCOOK \xrightarrow{\text{Electrolytic}} 2RCOO^{-}_{\text{Anode}} + 2K^{+}$$

$$2 RCOO^{-} \longrightarrow 2 RCOO^{+} + 2 e^{-}$$

Cathode

$$2 RCOO \longrightarrow R \longrightarrow R + 2CO_2$$

At cathode $2K^+ + 2e^- \longrightarrow 2K$ $2K + H_20 \longrightarrow 2KOH + H_2\uparrow$

09 In the commercial gasolines, the type of hydrocarbons which is more desirable, is **[CBSE AIPMT 1997]**

(a) branched hydrocarbon

- (b) straight chain hydrocarbon(c) linear, unsaturated hydrocarbon
- (d) toluene

Ans. (a)

On increasing the number of branches, knocking is decreased and octane number is increased. So, branched chain hydrocarbons have less knocking and is more desirable.

10 The most stable configuration of *n*-butane will be **[CBSE AIPMT 1997]**

(a) skew boat (c) gauche

Ans. (d)

Conformations of *n*-butane are as under

(b) eclipsed

(d) staggered-anti



H H H CH₃ (Structure III) Gauche or

Staggered conformation has minimum repulsion, so it is the most stable. The order of stability is

Skew form

staggered > gauche > eclipsed Energy order eclipsed > gauche > staggered

11 The distance between two adjacent carbon atoms is largest in [CBSE AIPMT 1994]

Ans. (c)	
(c)butane	(d)ethyne
(a) benzene	(b)ethene

The C–C bond length is maximum for single bond, butane have largest C–C bond length because it contains carbon-carbon single bond.

12 In the free radical chlorination of methane, the chain initiating step involves the formation of [CBSE AIPMT 1994]
(a) chlorine free radical
(b) hydrogen chloride

- (c) methyl radical
- (d) chloromethyl radical

Ans. (a)

 $CH_4 + CI_2 \xrightarrow{hv} CH_3CI$

Chain initiation step involves the fission of Cl₂ molecule into chlorine free radical.

 $Cl_2 \xrightarrow{hv} Cl^{\bullet} + Cl^{\bullet}$

13 Which of the following compounds has the lowest boiling point? [CBSE AIPMT 1994]

Ans. (d)

Boiling points of alkanes increase as the number of carbon atom increases or molecular mass increases. Alkenes have high boiling point, so $CH_3CH_2CH_2CH_3$ has the lowest boiling point.



(a) tertiary > primary > secondary
(b) primary > secondary > tertiary
(c) Both (a) and (b)

(d) tertiary > secondary > primary

Ans. (d)

Tertiary alkanes are more reactive as they form tertiary free radical which is more stable. On the other hand, primary alkanes are less reactive because they form 1° free radicals which are less stable.





TOPIC 2 Alkenes

15 The correct structure of 2,6-dimethyl-dec-4-ene is



Ans. (a)

Structure of 2,6-dimethyl-dec-4-ene is



The structure can be identified with the help of branches at 2 and 6 positions and a double bond at 4 position.

16 An alkene on ozonolysis gives methanal as one of the product. Its structure is **[NEET (Sep.) 2020]**



(c) $CH_2CH_2CH_3$ $CH = CH - CH_3$ (d) $CH = CH - CH_3$

Ans. (b)

Let us identity the ozonolysis [(i)O_2/THF, (ii)Zn/H_2O] products from each of the following :



We get, methanal from the hydrocarbon in option (b) only.

17 An alkene 'A' on reaction with O_3

and Zn $-H_2O$ gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene 'A' gives 'B' as the major product. The structure of product 'B' is **[NEET (National) 2019]** CH₂Cl

$$(a) H_{3}C - CH_{2} - CH_{-}CH_{3}$$

$$(b) H_{3}C - CH_{2} - C - CH_{3}$$

$$(c) H_{3}C - CH_{2} - C - CH_{3}$$

$$(c) H_{3}C - CH_{-}CH_{-}$$

$$(c) H_{3}C - CH_{-}CH_{-}CH_{-}$$

Ans. (b)

The given road map problem is



The products of first reaction, i.e. ozonolysis can give an idea about the probable alkene as $\sum_{C=0}$

group of these arose from the $\pi\text{-}\text{bonds}$ of alkene. Thus, most probable alkene will be

 $\begin{array}{c} H_{3}C \\ H_{3}C \\ \end{array} \xrightarrow{C \neq 0 \\ H_{3}C \\ \end{array} \xrightarrow{C = 0} C = C \\ H_{3}C \\ \end{array} \xrightarrow{H_{3}C \\ H_{3}C \\ C = C \\ CH_{3} \\ H_{3}C \\ \end{array}$

The reaction taking place will be



18 Which of the following molecules represents the order of hybridisation sp^2 , sp^2 , sp, sp from left to right atoms? [NEET 2018] (a) $CH_2 = CH - CH = CH_2$ (b) $CH_2 = CH - CH = CH_2$ (c) CH = C - C = CH(d) $CH_3 - CH = CH - CH_3$ Ans. (b)

Key Idea While judging the hybridisation in the given type of organic molecules always look for the number of σ and π bonds formed by C-atom involved.

The hybridisation of the given molecules are. (i) $CH_2 = CH - CH = CH_2$ (ii) $CH_2 = CH - CH = CH_2$ (iii) $CH_2 = CH - C \equiv CH$ (iii) $CH \equiv C - C \equiv CH$ (iv) $CH_3 - CH = CH - CH_3$ Therefore, the correct option is (b).

19 2,3-dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid? **[NEET 2016, Phase I]** (a)(CH₃)₂ CH—CH—CH —CH = CH₃ $|_{CH_3}$ (b)(CH₃)₃C —CH = CH₂ (c)(CH₃)₂C = CH — CH₂ — CH₂

(d)
$$(CH_3)_2CH - CH_2 - CH = CH_2$$

Ans. (b)

, (*b*)



20 Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction?

[NEET 2016, Phase II] (a) H₂C ,____,CH₂

(b)
$$H_3C = C = 0$$

(c) $H_2C = C = 0$

(d)
$$H_3C$$
— C — CH_2Br

Ans. (c)

CH

The said reactions can be visualised as

$$H_{2}C \xrightarrow{C} CH_{2} \xrightarrow{HBr} CH_{3} \xrightarrow{H} CH_{2} \xrightarrow{H} C \xrightarrow{H} CH_{2} \xrightarrow{H} CH_{2}$$

$$\stackrel{\qquad }{\longleftrightarrow} H_3C - C - E$$

 CH_3 —CH= CH_2 Thus, option (c) is correct.

21
$$H_3C \longrightarrow CH \longrightarrow CH \implies CH_2 + HBr \longrightarrow A$$

 \downarrow
 CH_3
A (predominantly) is
[CBSE AIPMT 2008]
(a) $CH_3 \longrightarrow CH \longrightarrow CH \longrightarrow CH_2Br$
 \downarrow
 CH_3
(b) $CH_3 \longrightarrow CH \longrightarrow CH_2CH_3$
 \downarrow
 CH_3
(c) $CH_3 \longrightarrow CH \longrightarrow CH_2CH_3$
 \downarrow
 CH_3
 $CH \longrightarrow CH \longrightarrow CH_2CH_3$
 $CH \longrightarrow CH \longrightarrow CH_2CH_3$
 $CH \longrightarrow CH_3CH \longrightarrow CH_2CH_3$
 $CH \longrightarrow CH \longrightarrow CH_2CH_3$
 $CH \longrightarrow CH \longrightarrow CH_2CH_3$
 $CH \longrightarrow CH \longrightarrow CH_3CH \longrightarrow CH_2CH_3$
 $CH \longrightarrow CH_3CH \longrightarrow CH \longrightarrow CH_3CH \longrightarrow$

Ans. (b)

CH3

$$H_3C$$
— CH — CH = CH_2 + HBr — Br =

$$CH_{3} \xrightarrow{H} CH_{3}$$

$$\begin{array}{c} \overset{H-shift}{\longrightarrow} CH_{3} \overset{\oplus}{\longrightarrow} CH_{2} & -CH_{2} & -CH_{3} & \xrightarrow{Br^{-}} \\ CH_{3} & & \\ & CH_{3} & \\ & &$$

22 Which of the following compounds with molecular formula, C₅H₁₀ yields acetone on ozonolysis? [CBSE AIPMT 2007]

(a)2-methyl-2-butene (b)3-methyl-1-butene (c)Cyclopentane (d)2-methyl-1-butene

Ans. (a)

2-methyl-2-butene (molecular formula C_5H_{10}) yields acetone on ozonolysis.

Which one of the following alkenes will react faster with H₂ under catalytic hydrogenation conditions?
 (R = alkyl substituent)

$$[CBSE AIPMT 2005]$$
(a) $\stackrel{R}{\underset{R}{\longrightarrow}}$
(b) $\stackrel{R}{\underset{R}{\longrightarrow}}$
(c) $\stackrel{R}{\underset{H}{\longrightarrow}}$

Ans. (a)

Stability of alkene

∞ <u>1</u> Heat of hydrogenation of alkene

Greater the number of alkyl groups attached to the double bonded carbon atoms, more stable is the alkene. Hence, given alkene follow the following order of stability.





24 Reaction of HBr with propene in the presence of peroxide gives [CBSE AIPMT 2004]

(a) *iso*-propyl bromide(b) 3-bromo propane(c) allyl bromide

(d) *n*-propyl bromide

Ans.

(d) Reaction of HBr with propene in the presence of peroxide gives *n*-propyl bromide. This addition reaction is an example of anti-Markownikoff's addition reaction.

(i.e. it is completed in form of free radical addition)

$$CH_3$$
— CH = CH_2 + HBr $\xrightarrow{Peroxide}$

Mechanism of this reaction is represented asfollows :

Step I Formation of free radical of peroxide by means of decomposition.

$$C_6H_5$$
 — C—O—O—C—C₆H₅ \xrightarrow{A}
 \parallel \parallel \parallel \square
Benzoyl peroxide
 $2C_6H_5$ — COO
Benzoate free radical

Step II Benzoate free radical forms bromine free radical with HBr.

$$C_6H_5COO + H - Br \rightarrow C_6H_5COOH + Br$$

Step III Bromine free radical attacks on C = C of propene to form intermediate free radical.

CH₃—CH==CH₂ + Br → CH₃ — CH — CH₂ +

$$|$$

 Br
(less stable)
CH CH Pr

Hence, $CH_3 - \overset{\bullet}{C}H - CH_2Br$ is the major product of this step.

Step IV More stable free radical accept hydrogen free radical from benzoic acid and give final product of reaction. i.e. *n*-propyl bromide.

$$CH_3 - CH - CH_2Br + C_6H_5COOH \rightarrow$$

$$CH_3 - CH_2 - CH_2Br + C_6H_5COO$$

n-propyl bromide

Step V Benzoate free radicals are changed into benzoyl peroxide for the termination of free radical chain.

$$C_6H_5COO + C_6H_5COO \rightarrow (C_6H_5COO)_2$$

$$CH_3 - C = CH - CH_3$$
 on reaction

with NalO₄ in the presence of KMnO₄ gives [CBSE AIPMT 2003] (a) $CH_3COCH_3 + CH_3CHO$ (b) $CH_3CHO + CO_2$ (c) CH_3COCH_3 (d) $CH_3COCH_3 + CH_3COOH$

Ans. (d)

$$H_{3}C \longrightarrow C = CH - CH_{3} + 3[0] \xrightarrow{\text{NalO}_{4}} H_{3}C \longrightarrow C = 0 + CH_{3}COH$$

26 Which alkene on ozonolysis gives
$$CH_3CH_2CHO$$
 and CH_3CCH_3 ?

(b)
$$CH_3CH_2CH = CHCH_2CH_3$$

(c) $CH_3CH_2CH = CHCH_3$
(d) $CH_3 - C = CHCH_3$
 $|$
 CH_3

Ans. (a)

When O_3 reacts with alkene, it forms ozonide, which on reaction with Zn and acid or H_2 /Ni gives aldehydes and/or ketones. These products helps in locating the position of a double bond as

$$CH_{3}-CH_{2}-CH = C \xrightarrow{CH_{3}} + 0_{3} \xrightarrow{CH_{3}} + 0_{3} \xrightarrow{CH_{3}} + 0_{3} \xrightarrow{CH_{3}} + CH_{3}-CH_{2}-CH_{3} \xrightarrow{CH_{3}-CH_{2}-CH_{3}} \xrightarrow{CH_{3}-CH_{2}-CH_{3}} \xrightarrow{CH_{3}-CH_{2}-CH_{3}} \xrightarrow{CH_{3}-CH_{2}-CH_{3}} \xrightarrow{CH_{3}-CH_{2}-CH_{3}} \xrightarrow{CH_{3}-CH_{2}-CH_{3}} \xrightarrow{CH_{3}-CH_{3$$

the decreasing order of stability is [CBSE AIPMT 2000]

a) > >	(b) > >
c) > >	(d) > >

Ans. (b)

(

Stability of alkene

Therefore, lower the heat of hydrogenation of alkene. Therefore, lower the heat of hydrogenation of an alkene. Therefore, lower the heat of hydrogenation of an alkene, higher will be stability. Order of stability is

trans-but-2-ene > *cis*-but-2-ene > but-1-ene.

Heat of hydrogenation (kJ/mol) are 115.5, 119.6 and 126.8 respectively.

28 In a reaction,

$$CH_2 = CH_2 \xrightarrow{Hypochlorous} M$$

$$\xrightarrow{R} | CH_2OH$$

$$\xrightarrow{R} CH_2OH$$

M = molecules, R = reagent. M and R are [CBSE AIPMT 1997]

(a) CH_3CH_2CI and NaOH (b) $CH_2CI \cdot CH_2OH$ and aq. NaHCO₃ (c) CH_3CH_2OH and HCI (d) CH_2 — CH_2 and heat

29 In the presence of platinum catalyst, hydrocarbon *A* adds hydrogen to form *n*-hexane. When hydrogen bromide is added to *A* instead of hydrogen only a single bromo compound is formed. Which of the following is *A*?

[CBSE AIPMT 1996]

(a)CH₃—CH₂—CH=CH—CH₂—CH₃ (b)CH₃—CH₂—CH₂—CH=CH—CH₃



30 When 3,3-dimethyl-2-butanol is heated with conc. H₂SO₄, the major product obtained is

[CBSE AIPMT 1995]

- (a) 2,3-dimethyl-2-butene
- (b) 3,3-dimethyl-2-butene
- (c) 2,3-dimethyl-1-butene
- (d) *cis* and *trans*-isomers of 2,3-dimethyl-2- butene

Ans. (a)





31 The alkene R-CH=CH₂ reacts readily with B₂H₆ and formed the product B which on oxidation with alkaline H₂O₂ produces

(a) *R*—CH₂—CHO (b) *R*—CH₂—CH₂—OH

$$\begin{array}{c} (c) R - C = 0 \\ | \\ CH_3 \end{array} \quad \begin{array}{c} (d) R - CH - CH_2 \\ | \\ | \\ OH \end{array}$$

Ans. (b)

Here, $\frac{1}{2}$ mole of B_2H_6 react with alkene by

Markownikoff's addition and form trialkylborone called Hydroboration, H_2O_2 / OH^- gives oxidation. So, trialkyborone oxidise in alcohols and reaction is also called Hydroboration-oxidation.

$$3R - CH = CH_2 \xrightarrow{B_2H_6} (R - CH_2 - CH_2)_3 - B$$

$$\xrightarrow{H_2O_2/H} 3R - CH_2 - CH_2 - OH$$

TOPIC 3 Alkynes

32 How many (i) sp^2 hybridised carbon atoms and (ii) π bonds are present in the following compound?

[NEET (Oct.) 2020]

(a)7,5 (c)7,6 (b)8,6 (d)8,5

Ans. (c)



Number of sp^2 -carbon atom = 7 π -bonds = 6 Hence, option (c) is correct.

33 The most suitable reagent for the following conversion, is [NEET (National) 2019]

H₃C—C≡C—CH₃ —

H₃C H_{cis-2-butene}CH

(a) H_2 , Pd/C, quinoline (b) Zn/HCl (c) Hg^{2+}/H^+ , H_2O (d) Na/liquid NH_3

Ans. (a)

Hydrogenation of alkynes in the presence of Pd/C, quinoline proceeds through *syn* addition of hydrogen and the



34 The number of sigma (σ) and pi (π) bonds in pent-2-en-4-yne is [NEET (National) 2019]

(a) 8σ -bonds and 5π -bonds (b) 11σ -bonds and 2π -bonds (c) 13σ -bonds and no π -bonds (d) 10σ -bonds and 3π -bonds

Ans. (d)

Single bond = 1σ , Double bond = $1\sigma + 1\pi$, Triple bond = $1\sigma + 2\pi$. The structure of pent-2-en-4-yne is

$$H H H$$

$$H - C = C = C - 1\sigma = C - H$$

$$H - C = C + 1\sigma = C - 1\sigma = C - H$$

$$H H H = H$$

:. The number of sigma (σ) bonds are 10 and pi (π) bonds are 3.

35 Which one is the correct order of acidity? **[NEET 2017]**

- (a) $CH_2 = CH_2 > CH_3 CH = CH_2$ > $CH_3 - C \equiv CH > CH \equiv CH$
- (b) $CH \equiv CH > CH_3 C \equiv CH > CH_2 = CH_2 > CH_3 CH_3$
- (c) $CH \equiv CH > CH_2 = CH_2 > CH_3$ $-C \equiv CH > CH_3 - CH_3$ (d) $CH_3 - CH_3 > CH_2 = CH_2 > CH_3$ $-C \equiv CH > CH \equiv CH$

Ans. (b)

Greater the s-character of C-atom in hydrocarbons, greater the electronegativity of that carbon and thus greater the acidic nature of the H attached to electronegative carbon.

	CH≢ CH	$CH_2 = CH_2$	CH3 -CH3
Hybridisation :	sp	sp ²	sp ³
s-character :	50%	33%	25%
Electronegativity:	← ^{Max.}		
Acidic character of terminal H	← ^{Max.}		

Thus, $CH \equiv CH > CH_3C \equiv CH$ > $CH_2 = CH_2 > CH_3 - CH_3$

$$H \longrightarrow C \equiv CH \xrightarrow{(i) \text{ NaNH}_2/\text{liq.NH}_3} (ii) CH_3 CH_2 Br \xrightarrow{(i) \text{ NaNH}_2/\text{liq.NH}_3} Y$$

X and Y are [NEET 2016, Phase I]

(a) X = 2 -butyne; Y = 3 -hexyne (b) X = 2 -butyne; Y = 2 -hexyne (c) X = 1-butyne; Y = 2-hexyne (d) X = 1-butyne; Y = 3-hexyne

Ans. (d)

Since, NaNH₂/lig.NH₃ behaves as a base, so it abstracts proton from acetylene to form acetylide anion followed by alkylation to give compound (X) i.e. 1-butyne. (X) further reacts with NaNH₂/liq.NH₃ followed by alkylation with ethyl bromide yields 3-hexyne (Y).

$$H \longrightarrow C \equiv C \longrightarrow H (1)$$

$$\xrightarrow{NaNH_2/Liq.NH_3} H - C \equiv C^{\ominus}$$

$$\xrightarrow{(2) CH_3CH_2-Br}$$

$$HBr + H - C \equiv C - CH_2CH_3$$

$$\xrightarrow{(2) CH_3CH_2-Br}$$

$$\xrightarrow{S} C \equiv C - CH_2CH_3$$

$$H_3CH_2C - C \equiv C - CH_2CH_3 + HBr$$

$$\xrightarrow{(Y)}$$

$$\xrightarrow{(Y)}$$

$$\xrightarrow{(Y)}$$

$$\xrightarrow{(Y)}$$

37 Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne?

> [CBSE AIPMT 2012] (b) HCI (d)Br₂

(c)0₂ Ans. (a)

(a)NaNH₂

NaNH₂ is used to distinguish between 1-butyne and 2-butyne.

CH₃CH₂C=CH → CH₃CH₂CH₂C=CNa $+\frac{1}{2}H_{2}\uparrow$

$$CH_3 \longrightarrow C \implies C \longrightarrow H \xrightarrow{NaNH_2} No reaction$$

38 Predict the product *C* obtained in the following reaction of butyne-1. [CBSE AIPMT 2007]

$$CH_3CH_2 \longrightarrow C \Longrightarrow CH + HCI \longrightarrow B \xrightarrow{HI}$$



Ans. (d)

Followed by Markownikoff's rule.

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{C}\equiv\mathrm{CH}+\mathrm{HCI}\longrightarrow\\ \mathrm{CH}_{3}\mathrm{CH}_{2}-\mathrm{C}=\mathrm{CH}_{2}\xrightarrow{\mathrm{HI}}\\ & & & & \\ \mathrm{CI}\\ \mathrm{CH}_{3}-\mathrm{CH}_{2}-\overset{\mathrm{I}}{\mathrm{C}}-\mathrm{CH}_{3}\\ \mathrm{CI}\\ \mathrm{2\text{-chloro-2-iodobutane}}\end{array}$$

39 Products of the following reaction [CBSE AIPMT 2005]

$$CH_{3}C \equiv C \cdot CH_{2}CH_{3} \xrightarrow{(i)0_{3}} \rightarrow$$

... are

(a)CH₃CHO + CH₃CH₂CHO
(b)CH₃COOH + CH₃COCH₃
(c)CH₃COOH + HOOC
$$\cdot$$
CH₂CH₃
(d)CH₃COOH + CO₂

Ans. (c)



40 When acetylene is passed through $dil \cdot H_2SO_4$ in presence of $HgSO_4$, the compound formed is

[CBSE AIPMT 1999]

(a) ether (b) ketone (c) acetic acid (d) acetaldehyde

С

Hydration of alkyne,
CH=CH + H₂0
$$\xrightarrow{\text{Hg}^{2+}/\text{H}^+}$$
 CH₂ = CH
I
OH
Unsaturated
alcohol

Ans (d)

ÒН

CH---СНО

41 The cylindrical shape of an alkyne is due to [CBSE AIPMT 1997]

- (a) three sigma C—C bonds
- (b) three π C–C bonds
- (c) two sigma C–C and one π C–C bonds
- (d) one sigma C–C and two π C–C bonds

Ans. (d)

In alkynes C = C is present, out of these three bonds one sigma and two π -bonds are present. Sigma bond is formed by *sp*-hybrid orbitals whereas π -bonds are formed by unhybridised orbitals. Hence, it shows cylindrical shape.

42 A compound is treated with NaNH₂

to give sodium salt. Identify the compound. [CBSE AIPMT 1993] $(a)C_2H_2$ $(b)C_6H_6$ $(c)C_2H_6$ $(d)C_2H_4$ Ans. (a)

Sodamide is strong base. Therefore it attracts the more acidic hydrogen and gives sodium salt

 $H - C \equiv C - H + NaNH_2 \longrightarrow$ $H \stackrel{2}{\longrightarrow} C \equiv C^{-}Na^{+} + \frac{1}{2}H_{2}$ Sodium ethynide

43 Reduction of 2-butyne with sodium in liquid ammonia gives

predominantly [CBSE AIPMT 1993]

(a) cis-2-butene (c) no reaction

(b) trans-2-butene (d) n-butane

Ans. (b)

In presence of Na and liquid NH_{z} lig $\cdot NH_{z}$. Trans addition of hydrogen on alkene occurs.



44
$$R-CH_2 - CCI_2 - R \xrightarrow{\text{Reagent}}$$

 $R-C \equiv C - R$. The reagent is
[CBSE AIPMT 1993]
(a) Na (b) HCl in H₂0
(c) KOH in C₂H₅OH (d) Zn in alcohol
Ans. (c)
Dehydrohalogenation reaction,
 CI
 $RCH_2 - C - R \xrightarrow{C_2H_5OH + KOH}_{-KCI, -H_2O}$
 $RCH = C - R \xrightarrow{KOH + C_2 H_5OH}_{-KCI, -H_2O}$

D - - - - +

45 Select the true statement about benzene amongst the following. [CBSE AIPMT 1992]

CI

- (a) Because of unsaturation benzene easily undergoes addition
- (b) There are two types of C-C bonds in benzene molecule
- (c) There is cyclic delocalisation of pi-bonds in benzene
- (d) Monosubstitution of benzene gives three isomeric products

Ans. (c)

According to the orbital concept, each carbon atom in benzene is sp^2 -hybridised and one *p*-orbital of each carbon remains unhybridised. The π -electron charge in benzene is not confined to space between two carbon atoms as in ethylene, but is spread over a greater area. This is known as the delocalisation of the electron charge.

46 Which one of the following has the shortest carbon-carbon bond length?

[CBSE AIPMT 1992]
(b)Ethene
(d) Ethane

Ans. (c)

Ethyne (acetylene) have shortest C-C bond length because it have C = Ci.e.triple bond. The bond length follows the following order

C = C < C = C < C - C

47 The shortest C–C bond distance is found in [CBSE AIPMT 1991] b) ethane (c)

(a) diamond	(b) ethane (c
benzene	(d)acetylene

Ans. (d)

Acetylene have shortest C-C bond length because it have C = C triple bond. The bond length follows the following order

0 = 0 < 0 = 0 < 0 = 0

48 Which is the most suitable reagent among the following to distinguish compound (III) from rest of the compounds? [CBSE AIPMT 1989]

I.
$$CH_3 \rightarrow C \equiv C \rightarrow CH_3$$

II. $CH_3 \rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_3$
III. $CH_3 \rightarrow CH_2 \rightarrow C \equiv CH$
IV. $CH_3 \rightarrow CH \equiv CH_2$
(a) Br_2 / CCI_4 (b) Br_2 / CH_3COOH
(c) Alk. KMnO₄
(d) Ammonia cal AgNO₂

Ans. (d)

It may be noted that only the terminal alkynes react with ammoniacal silver nitrate. Therefore, this reaction can be used to distinguish between 1-alkynes and others such as alkane, alkenes and non-terminal alkynes.

 CH_{z} — CH_{z} — $C\equiv CH + 2[Ag(NH_{z})_{2}]NO_{z}$ → CH_zCH₂C = CAg↓

White ppt-

- **49** Acetylenic hydrogens are acidic because [CBSE AIPMT 1989]
 - (a) sigma electron density of C–H bond in acetylene is nearer to carbon which has 50% s-character
 - (b) acetylene has only one hydrogen on each carbon
 - (c) acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons
 - (d) acetylene belong to the class of alkynes with molecular formula C_nH_{2n-2}

Ans. (a)

Acidic character of alkynes can be explained on the basis of sp-hybridisation state of the carbon atom in alkynes. We know that an electron in s orbital is more tightly held than in a p orbital because s-electrons are more closer to the nucleus. In sp-hybridisation, s-character is more (50%) as compared to sp^2 -(33%) or sp³-(25%) hybrid orbitals. Due to very large s-character, the electrons in sp-hybrid orbitals are held tightly by the nucleus and are quite electronegative. Consequently, the electron pair of F—C≡ bond gets displaced more

towards the carbon atom and help in the release of H⁺ ions.

For a example ethyne react with sodium metal and release the H⁺ ions. $CH \equiv CH + Na \longrightarrow HC \equiv C^{-}Na^{+}$

TOPIC 4 Aromatic Hydrocarbons

50 In the following reaction,

 $H_3C \longrightarrow C \Longrightarrow CH \xrightarrow{\text{Red hot iron tube}} A.$ 873 K

the number of sigma (σ) bonds present in the product A is [NEET (Odisha) 2019]

a)21	(b)9
c)24	(d)18

Ans. (a)

Key Idea Single bond = 1σ , Double bond = 1σ , 1π ; Triple bond = 1σ and 2π . Alkynes form aromatic compounds when their vapours are passed over red hot copper or iron tubes.

3CH₃—C≡CH _____Red hot iron tube 873 K



The number of sigma (σ) bonds present in the product (A) is 21.



51 In the given reaction



the product P is







Ans. (c)

Key Idea It is an example of Friedel-Craft reaction. First π -electrons of cyclohexene attack at H⁺ ion of HF and form carbocation. This carbocation further reacts with benzene and forms addition product.



Thus, the correct option is (c).

52 In the reaction with HCl, an alkene reacts in accordance with the Markownikoff's rule, to give a product 1-chloro-1- methylcyclohexane. The possible alkapa is product a product a product a product according to product a product a product a product according to product a product according to product a product according to product according

alkane is [CBSE AIPMT 2015]



Ans. (c)

For structure A,



For structure B, The rearrangement of carbocation occur because 3° -carbocation is more stable than 2° -carbocation.







The enthalpy of hydrogenation of these compounds will be in the order as **[CBSE AIPMT 2015]**

order as (a) | > || > ||| (c) || > ||| > |

(b) ||| > || > | (d) || > | > |||

Ans. (b)

The enthalpy of hydrogenation of given compounds is inversely proportional to stability of alkene.



(c) Nitrobenzene (d) Toluene

Ans. (c)

Nitro group being electron withdrawing, deactivates the benzene nucleus to such an extent . that an electrophile cannot attack on benzene ring easily due to deactivation of benzene ring. Hence becomes incapable to give Friedel-Craft's reaction.

NOTE Nitrobenzene because of its unreactivity towards Friedel-Craft's reaction is used as a solvent for this reaction.

55 Some *meta*-directing substituents in aromatic substitution are given. Which one is most deactivating? [NEET 2013]

(a)—C≡N	(b)—SO₃H
(c)—COOH	(d)—NO ₂

Ans. (d)

The deactivating tendency of given groups follows the order

Thus, — NO_2 is the most deactivating group.

56 The reaction of toluene with Cl_2 in the presence of FeCl₃ gives X' and reaction in presence of light gives Y'. Thus, X' and Y'' are

[CBSE AIPMT 2010]

- (a) X = benzal chloride,Y = o-chlorotoluene
- (b) X = m-chlorotoluene, Y = p-chlorotoluene
- (c) X = o and *p*-chlorotoluene, Y = trichloromethyl benzene
- (d) X = benzyl chloride,
 - Y = m-chlorotoluene

Ans. (c)

Key Idea In the presence of halogen carrier, electrophilic substitution occurs while in the presence of sunlight, substitution, occurs at the side chain.



Cl p-chlorotoluene

 $FeCl_3 + Cl_2 \longrightarrow FeCl_4^- + Cl^+$ Electrophile attacking species (:----CH₃ is an o/p-directing group.) In presence of hv_i , reaction is free radical substitution reaction.



57 Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 . In the mixture, nitric acid acts as a/an [CBSE AIPMT 2009]

(a) reducing agent (b) acid (c)base (d) catalyst

Ans. (c)

Conc. H_2SO_4 and conc. HNO_3 react in the following manner $HNO_3 + H_2SO_4$ \rightarrow H₂NO_z⁺ + HSO_z⁻ Base Acid H₂NO₃⁺ $NO_{2}^{+} + H_{2}O$

Nitronium ion Attacking species (electrophile)

Hence, in this reaction HNO₃ acts as a base and H_2SO_4 as an acid.



presence of anhy. AICl₃ to form [CBSE AIPMT 2009]

(a)toluene (b) chlorobenzene (c) benzylchloride (d) xylene

Ans. (a)



This reaction is known as Friedel-Craft's alkylation of benzene.

59 Using anhy. AICl₃ as catalyst, which one of the following reactions produce ethylbenzene (PhEt)? [CBSE AIPMT 2004]

(a) H_3C — $CH_2OH + C_6H_6$ (b) CH_3 —CH= $CH_2 + C_6H_6$

(c)
$$H_2C == CH_2 + C_6H_6$$

(d) $H_3C == CH_3 + C_6H_6$

Ans. (c)

From the reaction of benzene with ethylene in the presence of anhy. AICl₃, ethylbenzene isproduced.



60 In Friedel-Craft's synthesis of toluene, the reactants in addition to anhydrous AICI₃ are [CBSE AIPMT 2000]

 $(a)C_{B}H_{E}CI + CH_{4}$ $(c)C_{6}H_{6} + CH_{4}$

 $(b)C_6H_5CI + CH_3CI$ $(d)C_{6}H_{6} + CH_{3}CI$

Ans. (d)

Friedel-Craft's alkylation of benzene $(\Delta r - H)$

Mechanism of this reaction is represented as follows :

Step I

ĊH₃ + AICI4 $CH_3CI + AICI_3 \rightarrow$ Electrophilie





С



+ AICI3 + HCI

Thus, $C_{B}H_{B}$ and $CH_{3}CI$ are required in addition to AICI3.

61 In Friedel-Craft's alkylation, besides AICI₃ the other reactants are

[CBSE AIPMT 1999] $(a)C_6H_6 + NH_2$ $(b)C_{6}H_{6} + CH_{4}$

 $(c)C_6H_6 + CH_3CI$ $(d)C_{6}H_{6} + CH_{3}COCI$ Ans. (c)

Friedel-Craft's alkylation When benzene reacts with alkyl halide in presence of anhy. AlCl₃, toluene is obtained. It is called Friedel-Craft's alkylation reaction. Friedel-Craft's reaction is type of an electrophilic substitution reaction.

$$_{8}H_{6} + CH_{3}CI \xrightarrow{Anhy. AlCl_{3}} C_{6}H_{5}CH_{3} + I$$

Toluene

62 Which one of these, is not compatible with arenes? (a) Greater stability [CBSE AIPMT 1998] (b) Delocalisation of π -electrons (c) Electrophilic additions (d) Resonance

Ans. (c)

Arenes gives an electrophilic substitution reactions. They do not give electrophilic addition reaction in normal state due to resonance stabilisation.

63 Which is the correct symbol relating the hetero Kekule structure of benzene? **[CBSE AIPMT 1993]**

$$(a) \rightleftharpoons (b) \longrightarrow (c) \equiv (d) \longleftrightarrow$$

Ans. (d)

Kekule in 1865 proposed a ring structure for benzene in which the position of the three double bonds are not fixed. He suggested that the double bond keeps on changing their position and this is called **resonance**. According to Kekule, benzene is a resonance hybrid of two structures (a) and (b) and the hybrid structure may be represented as (c). The (a) and (b) are called resonating structures and are represented by putting (\longleftrightarrow) double headed arrow between them.



64 Benzene reacts with *n*-propyl chloride in the presence of anhydrous AICI₃ to give [CBSE AIPMT 1993]

(a) 3-propyl-1-chlorobenzene (b) n-propyl benzene (c) no reaction (d) iso-propyl benzene Ans. (d)

Electrophilic substitution reaction of benzene ring yields iso-propyl benzene.

