

Aliphatic Hydrocarbons (Alkanes)

INTRODUCTION

- + These are the hydrocarbons in which carbon-carbon contains single bond. (saturated hydrocarbon).
- + These are also called as 'Paraffins' (Parum + Affinis i.e. less reactive).
- + General reagents such as dil. and conc. HCl, dil. and conc. H₂SO₄, dil. and conc. HNO₃, acidic and basic KMnO₄ and K₂Cr₂O₇ usually does not react with alkane.
- ✦ General formula is CnH_{2n+2}.(n = 1, 2, 3, 4)
- + Hybridisation state of carbon is sp³
- + Bond angle on sp^3 carbon is 109°28′ and geometry is tetrahedral.
- + Number of bond angles in methane are six, while in ethane they are twelve.



+ Nature of bonding

Type of bond	Bond length	Bond energy
C–C	1.54 Å	84 Kcal/mole
С–Н	1.12 Å	98 Kcal/mole

+ Alkanes have following isomerisms with given minimum number of carbons.

Isomerism	Minimum Number of carbons
Chain isomerism	4
Position isomerism	6
Conformational isomerism	2
Optical isomerism	7

+ In alkane if chiral carbon or unsymmetrical carbon is present, then it shows optical isomerism.

PHYSICAL PROPERTIES

- (i) Alkanes are colourless, odourless and tasteless.
- (ii) Physical state:
 - $C_1 \rightarrow C_4$ Gaseous state

 $C_5 \rightarrow C_{17}$ Liquid state (except neo pentane)

 C_{18} & above \rightarrow solid like wax

- (iii) Alkanes are lighter than water, so they floats over water.
- (iv) Solubility: [Like dissolves like]

Alkanes are non-polar or weakly polar compounds so these are soluble in non-polar solvents (benzene, ether, chloroform, carbon tetrachloride etc.)

(v) **Boiling point:**

For homologues boiling point \propto Molecular weight For isomeric alkanes

boiling point $\propto \frac{1}{\text{Number of branches}}$

(vi) Melting point:

The melting point of alkanes depends upon molecular weight as well as packing in crystal lattice





Number of carbon atoms

 \uparrow M.P. (odd to even) > \uparrow M.P. (even to odd)

METHODS OF PREPRATION OF ALKANE

DCOOL	NaOH + CaO/ Δ	
KCOOH-	Soda lime]
RCOONa -	Kolbe's electrolysis	-
R-X-	Na/ether	
	Wurtz reaction	
P Y-	Zn/Ether	-
K-A	Frankland's reaction	
D V	(i) Li (ii) CuX (iii) R-X	
K-A-	Corey–House synthesis	
D V	Zn/HCl or LiAIH ₄	R–H
R-X-	Reduction	$\Box_{\mathbf{R}}^{\text{Or}}$
R-Mg-X-	HOH or ROH	
	Or NH ₃ or RNH ₂	
PCOOL of POU of P C P of PCUO	HI/red P/140°C	
	Reduction	
Ö	Zn-Hg/HCl	
R–C–R or R–C–H –	Clemmensen's reduction	-
Ö Ö	H ₂ N–NH ₂ /KOH	
R–C=O or R–C=O-	Wolff Kishner-reduction	-
Ŕ H	200–300°C, H ₂ /Ni	
$R-C=CH \text{ or } R-CH=CH_2 -$	Sabatier–Senderen's reaction	J

CHEMICAL PROPERTIES OF ALKANES

1. Substitution Reaction:

(i) Halogination The characteristics reaction of alkanes are free radical substitution reaction (F.R.S.R)

$$R-H \xrightarrow[]{X_2/hv} or X_2/\Delta R-X+ HX (F.R.S.R)$$

Mechanism:

- (1) Initiation step $X_2 \xrightarrow{hv} 2X^{\bullet}$
- (2) Propogation step
- $R H + X^{\bullet} \longrightarrow R^{\bullet} + HX$ $R^{\bullet} + X X \longrightarrow R X + X^{\bullet}$
- (3) Termination step

$$\begin{array}{c} \mathbf{R}^{\bullet} + \mathbf{R}^{\bullet} \longrightarrow \mathbf{R} - \mathbf{R} \\ \mathbf{X}^{\bullet} + \mathbf{X}^{\bullet} \longrightarrow \mathbf{X}_{2} \end{array}$$

$$R^{\bullet} + X^{\bullet} \longrightarrow R - X$$

Important Points

- (i) It is 3-step process.
- (ii) It is also known as chain reaction.
- (iii) propagation step is rate determination step (r.d.s.).
- (iv) Rate of radical substitution or rate of H[•] radical abstraction \propto stability of carbon-free radical.
- (v) Bond dissociation energy (B.D.E) $\propto \frac{1}{\text{Stability of carbon free radical}}$
- (vi) Reactivity of X_2 $F_2 > Cl_2 > Br_2 > I_2$ $10^{15} : 10^6 : 10^3 : 1$ (relative rate order)
- (vii) Fluorination is very fast and explosive so carried out in dark. $(CH_4 + F_2 \xrightarrow{dark} CH_3F + HF)$
- (viii) Iodonation very slow and reversible so carried out in presence of strong oxidant like HNO₃, HgO, HIO₃ etc. $CH_4 + I_2 \rightleftharpoons CH_3 - I + HI$
 - $2\mathrm{HI} + \mathrm{HgO} \longrightarrow \mathrm{HgI}_2 + \mathrm{H_2O}$
- (ix) Relative rate for abstraction of per H by Cl'/Br is-

Radical	1 <mark>+</mark>	2 <mark>•</mark> H	3 <mark>•</mark>
Cl•	1	3.8	5.0
Br•	1	82	1600

% of product (p) \propto number of similar type hydrogen atoms (n) \times selectivity (s)

$$\frac{\mathbf{P}_1}{\mathbf{P}_2} = \frac{\mathbf{n}_1}{\mathbf{n}_2} \times \frac{\mathbf{s}_1}{\mathbf{s}_2}$$

(x) Regents:

For chlorination – Cl_2/hv , Cl_2/Δ , SO_2Cl_2/hv , $(CH_3)_3C$ –OCl etc.

For bromination – Br_2/hv , Br_2/Δ , – $(CH_3)_3C$ –OBr

(xi) In excess of alkane mono halo product is major product.

- (xii) In excess of halogen most halogenated product is major product.
- (xiii) Number of monohalo products (structural isomers) = Type of H in alkane.

Note: For total mono halo isomer (including stereoisomer).

(ii) Nitration of alkanes:

Alkane on reactin with HNO_3 gives nitroalkane in vapor phase at 400° to 500°. In case of alkane containing more than one carbon atom, all possible mono nitroalkanes are formed.

 $R-H + HNO_3 \xrightarrow{\Delta} R-NO_2 + H_2O$

$$\begin{array}{cccc} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}_{3} + \mathrm{HNO}_{3} & \xrightarrow{400-500^{\circ}\mathrm{C}} & \mathrm{CH}_{3}-\mathrm{NO}_{2} + \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{NO}_{2} \\ & & \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NO}_{2} + \mathrm{CH}_{3}-\mathrm{CH}_{-}\mathrm{CH}_{3} \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ \end{array}$$

• In nitration breaking of C-C and C-H bond takes place at high temperature so all possible nitro alkane are formed

(iii) Sulphonation of Alkanes:

- For sulphonation n-Alkane must have minimum 6C
- Reagent: Fuming sulphuric acid (oleum)

$$R-H + H_2SO_4 \xrightarrow{fumin g}{High temp} R-SO_3H + H_2O$$

(iv) Chlorosulphonation of Alkanes (Reed reaction): The chlorosulphonation of organic compounds with chlorine and sulphur dioxide in called the Reed reaction.

$$RH + SO_2 + Cl \xrightarrow{hv} RSO_2Cl$$

Na-salt of Sulphonic acid called as detergent.

(v) Nitrososation: Alkane give free radical substitution reaction with nitrosyl chloride. The product of the reaction is nitroso compound. This compound, on tautomerisation, gives oxime.



2. Isomerisation: Normal alkane when heated (200°C) in the presence of AlCl₃ and HCl gives branched alkanes



3. Aromatisation or Reforming or Hydroformation: n-Hexane and onwards on aromatisation in the presence of Cr_2O_3 or Al_2O_3 or MoO_3 at 500°C and 15 atm gives benzene and its derivatives.



4. Carbene Insertion:

- The lower alkanes are converted into higher homologues.
- Reagent: diazomethane or ketene acts as insertion reagent.



5. Oxidation



6. Pyrolysis or Cracking: The decomposition of a compound by heat is called pyrolysis. When pyrolysis occurs in alkanes, the process is termed cracking.

$$C_{2}H_{6} \xrightarrow{500^{\circ}C} H_{2}C=CH_{2} + H_{2}$$
Ethane
$$\Delta \rightarrow CH_{3}CH=CH_{2} + H_{2}(C-H \text{ fission})$$

$$C_{3}H_{8} \xrightarrow{\Delta} H_{2}C=CH_{2} + CH_{4}(C-C \text{ fission})$$

Special Points

- LPG is called as liquefied petroleum gas or kitchen gas which is a mixture of propane and butane.
- CNG (compressed natural Gas) mainly contains CH₄.
- A mixture of n-butane and isobutene is called as Calore gas.
- Methane reacts with ozone to make formaldehyde.
- When methane is heated (at about 1500°C) in presence of nickel it makes acetylene.
- Sabetier Senderen's reaction:

$$CO + 3H_2 \xrightarrow{Ni/200^{\circ}C} CH_4 + H_2O$$
$$CO_2 + 3H_2 \xrightarrow{Ni/200^{\circ}C} CH_4 + 2H_2O$$

• Preparation of synthesis gas:

$$CH_4 + H_2O \xrightarrow{Ni/1000^{\circ}C} CO + 3H_2$$

• Methane can be prepared by aluminum carbide

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

 Which of following reagents does not give isobutane when reacted with isobutyl magnesium bromide?
 (1) CH₂-C≡CH

$$(2) \quad CH_3 - C - CH_2 - C - O - CH_3$$

$$(3) CH_3-CH_2-OH$$

(4) PhOCH₃

Sol. [4]

 $Ph-O-CH_3 \rightarrow don't have acidic H$

So can not be takes part in acid base reaction

$$\begin{array}{c} CH_{3} \\ | \\ CH_{3}-CH-CH_{2}-MgBr \xrightarrow{Acidic H} CH_{3}-CH_{3}-CH-CH_{3} \end{array}$$

- **2.** Methane as well as ethane can be obtained in one step (in two separate reactions) from
 - (1) CH_3OH (2) C_2H_5OH (3) CH_3I (4) CH_3CH_3I
- Sol. [3]

$$\begin{array}{c} CH_{3}\text{-}I \xrightarrow{\text{reduction}} CH_{4} \\ Wurtz \text{ reaction} & \\ & \\ Va/ether \\ CH_{3}\text{-}CH_{3} \end{array}$$

- **3.** An alkane of molecular weight 86 gives on monochlorination two product. The alkane is
 - (1) 2-Methylbutane
 - (2) n-butane
 - (3) 2, 2-Dimethyl propane
 - (4) 2, 3-Dimethyl butane

Sol. [4]

 $C_nH_{2n+2} = 86$ 12n + 2n+2 = 86 14n = 84 n = 6

$$I = 0$$

$$\mathrm{m.f} = \mathrm{C_6H_{14}}$$

for two monochloro product alkane must have 2-type H

$$\begin{array}{c} \overset{1^{\circ}}{\overset{}{\operatorname{CH}_{3}}} \overset{1^{\circ}}{\underset{}{\operatorname{CH}_{3}}} \\ \overset{1}{\underset{}{\operatorname{CH}_{3}}} \\ \overset{1}$$

4. Which of the following alkanes will give a single product with a methylene insertion?

(1) Me₄C

- (2) CH₃CH₂CH₃
- (3) $Me_2CHCHMe_2$
- (4) MeCH₂C(Me)₂CH₂CH₃
- Sol. [1]

Number of methylene insertion product = Type of C-H

$$CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

5. $C_5H_{10} \xrightarrow{H_2/Ni} (X) \xrightarrow{Cl_2/h\nu} 3$ monochloro structural isomers for compound C_5H_{10} how many pairs of geometrical isomers are possible?

$$C_5H_{10} \xrightarrow{H_2/Ni} C_5H_{12} \xrightarrow{Cl_2/h\upsilon} 3M.C.P.$$

 (X) must have 3-type of H, so it is n-pentane Possible structure of C₅H₁₀ is CH₃-CH₂-CH₂-CH=CH₂ no GI CH₃-CH=CH-CH₂-CH₃ GI

Only one pair of GI is possible (cis/trans)

6. $(CH_3)_2 CHBr \xrightarrow{(1) \text{ Li/ether}} A$

This is Corey–House method of synthesis of A which is

- (1) $(CH_3)_2CH(CH_2)_2CH(CH_3)_2$
- (2) (CH₃)₂CHCH₂CH₂CH₃
- (3) $(CH_3)_2CHCH_2CH_2CH_2CH_3$

(4)
$$(CH_3)_2$$
-CH-CH₂-CH(CH₃)₂

Sol. [1]

- $\begin{array}{rcl} (CH_3)_2 CH-Br & \xrightarrow{Li/ether} & [(CH_3)_2 CH]_2 LiCu \\ (CH_3)_2-CH-(CH_2)_2-Br & + & [(CH_3)_2 CH]_2 LiCu \\ & \xrightarrow{SN_2} & (CH_3)_2 CH-(CH_2)_2-CH(CH_3)_2 \end{array}$
- **7.** An alkyl bromide reacts with sodium to form 4, 5-diethyloctane. The alkyl bromide is
 - (1) $CH_3(CH_2)_2CH_2Br$ (2) $CH_3(CH_2)_4CH_2Br$
 - (3) $CH_3(CH_2)_3CHBrCH_3$
 - (4) $CH_3(CH_2)_2CHBrCH_2CH_3$

 $R-X \xrightarrow{Na/ether} R-R$

so given alkane divided by half and gets corresponding alkyl halide as following:

- 8. Iodine practically does not react with ethane in the presence of light of heat because
 - (1) the dissociation of I_2 into iodine radicals is more difficult compared to that of F₂, Cl₂ or Br₂
 - (2) the reaction $CH_3^{\bullet} + I_2 \rightarrow CH_3I + I^{\bullet}$ is endothermic
 - (3) the hydrogen abstraction step $(I^{\bullet} + CH_4 \rightarrow CH_3^{\bullet})$ + HI) is highly endothermic which makes the overall reaction also endothermic
 - (4) the reaction $CH_3^{\bullet} + I_2 \rightarrow CH_3I + I^{\bullet}$ is exothermic

Sol. [3]

$$I^{\bullet} + CH_4 \longrightarrow HI + CH_3^{\bullet} \quad \Delta H^{\circ} = +142$$

$$CH_3^{\bullet} + I_2 \longrightarrow CH_3I + I^{\bullet} \quad \Delta H^{\circ} = -89$$

Overall $\Delta H^{\circ} = +53$ endothermic

- 9. Monochlorination of ethylbenzene (PhCH₂CH₃) with Cl₂ under heat produces
 - (1) PhCH₂CH₂Cl
 - (2) PhCHClCH₃
 - (3) both (1) and (2) in equal amounts
 - (4) more of (2) and less (1)

 $Ph-CH_2-CH_3 \xrightarrow{CI'} Ph-\dot{C}H-CH_3 + Ph -CH_2-\dot{C}H_2$ Resonance stable Less stable C-free radical

$$\begin{array}{c} \text{Ph-CH-CH}_{3} \xrightarrow{\text{Cl}_{2}/\Delta} \text{Ph-CH-CH}_{3} \\ & | \\ & \text{Cl} \\ & (\text{major}) \end{array}$$

$$Ph-CH_2-CH_2 \xrightarrow{Cl_2/\Delta} Ph-CH_2-CH_2-Cl$$
(Minor)



Sol. [1]



- 11. In the reaction $Br_2 + CH_3Br \xrightarrow{hv} CH_2Br_2 + HBr$ which of the following mechanism steps is productive, but relatively unlikely to occur?
 - (1) $Br' + CH_3Br \longrightarrow HBr + CH_2Br$
 - (2) $Br' + CH_2Br \longrightarrow CH_2Br_2$

$$(3) Br' + Br_2 \longrightarrow Br_2 + Br$$

(4) $Br' + CH_3 \longrightarrow CH_3Br$

Sol. [3]

Br
$$-Br \xrightarrow{hv} 2 Br'$$

Propogation step

(option 1)
$$CH_3$$
-Br + Br $\longrightarrow CH_2$ -Br + H - Br
 CH_2 - Br + Br $\longrightarrow CH_2Br_2$ + Br $\xrightarrow{\bullet}$

Termination step

(option 2)
$$CH_2 - Br + Br' \longrightarrow CH_2 - Br_2$$

 $Br^{\bullet} + Br^{\bullet} \longrightarrow Br_{2}$ (option 3) $CH_{3} + Br^{\bullet} \longrightarrow CH_{3}$ -Br Thus option (3) $Br^{\bullet} + Br_{2} \longrightarrow Br + Br^{\bullet}$ is relatively unlike.

12. Compare the heats of combustion of the following compounds:

(i)
$$(ii)$$
 (ii) (ii) (iii) (iii) (iii) (1) (i) (1) (i) (1) (i) (2) II > I > III
(3) III > I > II (4) II > III > I

Sol. [2]

Heat of combustion \propto number of carbon

13. (A) + Cl₂ \xrightarrow{hv} monochloro product

To maximise the yield of monochloro product in the above reaction?

- (1) Cl_2 must be added in excess
- (2) Reactant (A) must be added in excess
- (3) Reaction must be carried out in dark
- (4) Reaction must be carried out with equimolar mixture of Cl₂ and A

Since intermediate is C-free radical so when alkane taken in excess then maximum collision between (A) and Cl radical takes place thus monochloro product obtained as major product

- 14. How much volume of oxygen will be needed for complete combustion of 10 lit. of ethane:
 - (1) 135 lit. (2) 35 lit.
 - (3) 175 lit. (4) 205 lit.

Sol. [2]

v

$$C_{2}H_{6} + \frac{7}{2}O_{2} \longrightarrow 2CO_{2} + 3H_{2}O$$

Making mole equation
Mole $C_{2}H_{6} = \frac{2}{7}$ mole O_{2}
vol $C_{2}H_{6} = \frac{2}{7}$ vol O_{2}
 $10 = \frac{2}{7}$ vol O_{2}

vol of $O_2 = 35$ lit

- 15. The most volatile alkane is-
 - (1) n-pentane (2) isopentane
 - (3) neopentane (4) n-hexane

Sol. [3]

volatile nature $\propto \frac{1}{\text{boiling point}}$

boiling point \propto molecular weight

$$\propto \frac{1}{\text{branching (for isomer)}}$$

So neo pentane have least boiling point, thus most volatile

- 16. Arrange the following in the correct order of reactivity towards Cl₂/hv-
 - (A) CH₄ (B) CH₃CH₃ CH₃ (C) $CH_3CH_2CH_3$ (D) CH_3 – $\dot{C}H$ – CH_3 (1) A >> C > D(2) D > C > B > A(3) B > C > A > D(4) C > B > D > A
- Sol. [2]

Reactivity for radical substitution ∝ stability of C-free radical

(A) $CH_3-H \longrightarrow CH_3 \ 0\alpha-H$ (least stable)

(B)
$$CH_3$$
- CH_2 - $H \longrightarrow CH_3$ - $CH_2 3\alpha$ - H

(C) CH_3 -CH-CH₃ \longrightarrow CH₃-CH-CH₃ 6 α -H ĊH₂

(D)
$$CH_3 \xrightarrow[]{} CH_3 \xrightarrow[]{} CH_3$$

(D) $CH_3 \xrightarrow[]{} CH_3 \xrightarrow[]{} CH_3 \xrightarrow[]{} CH_3 \xrightarrow[]{} CH_3$
(D) $CH_3 \xrightarrow[]{} CH_3 \xrightarrow[]{} CH_3 \xrightarrow[]{} CH_3$
(D) $CH_3 \xrightarrow[]{} CH_3$
(C) CH_3
(C) CH_3

17. The best retrosynthetic set of reactant used for the preparation of 2-methyl butane by the Corey-House synthesis СН

(2)
$$CH_3-Br + (CH_3-CH-CH_2)_2-LiCu$$

(3) $CH_3-CH-Br + (CH_3-CH_2)_2-LiCu$
(4) $CH_3-CH-CH_2-Br + (CH_3)_2-LiCu$

Sol. [2]

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

$$CH_{3}-Br + (CH_{3}-CH-CH_{2})_{2}-LiCu \xrightarrow{SN_{2}} CH_{3}-CH-CH_{2}+CH_{3}$$

since corey house synthesis taking place by SN₂ Reaction rate of SN₂ reaction 1 ∞

steric hindrance of
$$R-X$$

18. Which of the following reaction would be most exothermic?

(1)
$$H^{\bullet} + (CH_3)_3CH \longrightarrow H_2 + (CH_3)_3C^{\bullet}$$

(2) $CH_3 \rightarrow CH_3 \rightarrow 2\dot{C}H_3$

(3)
$$\dot{CH}_3 + CH_3 - CH_3 \longrightarrow CH_4 + CH_3 - \dot{CH}_2$$

(4)
$$2CH_3CH_2 \longrightarrow CH_3-CH_2-CH_2-CH_3$$

Sol. [4]

It involves association of two free radicals without breaking any old bonds of reactant hence, highly exothermic

- 19. Which of the following reaction pairs constitutes the chain propagation step in chlorination of methyl chloride-
 - (1) $^{\circ}CH_3 + Cl_2 \rightarrow CH_3Cl + ^{\circ}Cl$
 - $CH_3Cl + Cl \rightarrow CH_2Cl + HCl$
 - (2) $CH_3Cl + Cl \rightarrow CH_2Cl + H$ $^{\circ}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + ^{\circ}Cl$
 - (3) $CH_3Cl + Cl \rightarrow CH_2Cl + HCl$ $^{\circ}CH_{2}Cl + Cl_{2} \rightarrow CH_{2}Cl_{2} + ^{\circ}Cl_{2}$
 - (4) $^{\circ}CH_{2}Cl + ^{\circ}CH_{2}Cl \rightarrow CH_{2}Cl CH_{2}Cl$ $^{\circ}CH_{2}Cl + ^{\circ}Cl \rightarrow CH_{2}Cl_{2}$

- Sol. [3] $P_1: CH_3-Cl + \dot{C}l \rightarrow \dot{C}H_2-Cl + HCl$ P_2 : $CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl_2$
- 20. [4] The major product formed by monobromination of methylcyclopentane is



Sol. Relative reactivity for the abstraction on of different H[•] by bromination is $3^{\circ}_{H} > 2^{\circ}_{H} > 1^{\circ}_{H}$



3. The Grignard reagent derived from an alkyl halide (A) forms propane on treatment with water. Which one among the following could be the structures of (A)?

(1)
$$CH_2=CHCH_2Br$$
 (2) $HC=C-CH_2Br$
(3) Br (4) $CH_3CHBrCH_3$

4. Which product is obtained at the anode by the electrolysis of sodium butyrate:

(1) Butane +
$$CO_2$$
 (2) Pentane + CO_2
(3) Hexane + CO_2 (4) Hexane

5.
$$\underbrace{\overset{\text{Br}}{\underset{\text{Cl}}{\overset{\text{Mg/ether}}{\longrightarrow}}} \xrightarrow{D_2\text{O}} \underbrace{\overset{\text{Na/ether}}{\underset{\text{Na/ether}}{\overset{\text{Mg/ether}}{\longrightarrow}}}}(X)$$

The compound (X) is:

EXERCISE 1

1. In which of the following reactions, alkanes containing the same number of carbons as the substrate are obtained?

(a)
$$CH_3CH_2COOH \xrightarrow{\text{soda lime}} \Delta$$

- (c) $(CH_3)_2CHCOOH \frac{Hl/P}{reduction}$
- (d) $CH_3CH_2Br \frac{Zn-Cu \ couple}{EtoH}$
- Na and dry ether (e) CH_3CH_2Br –
- Code is:
- (1) b, c, d (2) c, d, e
- (3) a, d, e (4) a, e, c

2. Cl
$$\xrightarrow{O} \xrightarrow{Zn+DCl} (A) \xrightarrow{NaOH} ? \xrightarrow{NaOD+CaO} (B)$$

The compounds (A) and (B) in the equation given above are:

	(A)	(B)
(1)	CH ₃ COOH	CH ₃ CH ₃
(2)	DCH ₂ -COOD	CH_4
(3)	DCH ₂ -COOH	CH_2D_2
(4)	CH ₃ -COOD	CH ₃ D



7. Nitration of propane with nitric acid vapour at about 430°C is expected to yield-

(1)
$$CH_3CH_2CH_2-NO_2$$

(2)
$$CH_3$$
 CH-NO₂

(3)
$$CH_3CH_2-NO_2$$

(4) A mixture of all the above

8.
$$\xrightarrow{\text{AlCl}_3.\text{HCl}} \text{Product is}$$

(1) (2) (2) (4) (4)

- **9.** How many alkene react with H_2 in presence of platinum or nickel catalyst to yeild 2-methyl butane
 - (1) Only one (2) Two
 - (3) Three (4) None of these
- **10.** (A) +(CH₃-CH₂)₂-CuLi \longrightarrow Deduce the structure of A



11. (A) $\xrightarrow{Zn/H^{\oplus}}$ neopentane

Suggest the most suitable structure of A.



12. CH_3 -CH-COOH $\xrightarrow{\text{RedP/HI}}$ Product looses its OH (B) (A)

optical activity because of-

- (1) chirality of the molecule destroyed
- (2) Symmetry of molecule is destroyed
- (3) Spatial arrangement is changed
- (4) Racemic mixture is formed
- 13. An alkane C_5H_{12} is produced by the reaction of lithium di (2propyl) cuprate with ethyl bromide. The alkane is:
 - (1) n-pentane (2) 2-Ethylpropane
 - (3) 3-Methylbutane (4) 2-methyl butane

- **14.** Which of the following compounds may be decarboxylated most easily?
 - (1) CH₃COOH
 - (2) CH₃CH₂-COOH
 - (3) Ph-COOH
 - (4) HOOC-CH₂-COOH
- **15.** An organic compound $A(C_4H_9Cl)$ on reaction with Na/ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then A is
 - (1) t-butyl chloride (2) sec-butyl chloride
 - (3) iso butyl chloride (4) n-butyl chloride
- **16.** Which of the following may yield racemic monochlorinated product?
 - (1) n-Butane
 - (2) 2, 2-Dimethylpropane
 - (3) Isobutane
 - (4) 2, 2, 3, 3-Tetramethylbutane
- **17.** Monochlorination of monodeuterioethance (CH₃CH₂D) yields:
 - (1) chloroethane only
 - (2) monodeuteriochloroethance only
 - (3) equal amounts of (1) and (2)
 - (4) a large amount of (2) and a small amount of (1)
- **18.** The addition of oxygen gas to a reaction mixture of methane and chlorine undergoing photochemical chlorination will:
 - (1) accelerate the reaction
 - (2) retard the reaction for some time
 - (3) rate of the reaction not effect
 - (4) accelerate or retard the rate of the reaction depending upon the amount of oxygen
- 19. Consider the following reaction:

$$CH_{3} \xrightarrow[]{CH_{3}-CH_{-}CH_{3}+CCl_{4}} \xrightarrow{SO_{2}Cl_{2}} \xrightarrow{heat}$$

The major products formed in this reaction are:

- (1) $(CH_3)_3CCl$ and $CHCl_3$
- (2) (CH₃)₃COH and CH₃Cl
- (3) (CH₃)₃C-C(CH₃)₃ and (CH₃)₃COH
- (4) No reaction
- **20.** Photochemical fluorination is explosive while iodination is too slow to occur. The reason for this is:
 - (1) Bond dissociation energy of I_2 is minimum
 - (2) Formation of CH₃-F is most exothermic
 - (3) Formation of H–F is most exothermic while formation of HI is endothermic

- (4) F_2 has lower bond dissociation energy than Cl_2 and Br_2
- **21.** An alkane with the formula C_6H_{14} can be prepared by reduction with Zn^{2+} and H^+ of only two isomeric alkyl chloride ($C_6H_{13}Cl$) what is the systematic name of this alkane
 - (1) 2, 2-dimethyl butane (2) 2, 3-dimethyl butane
 - (3) 3-methyl pentane (4) 2-methyl pentane
- **22.** An alkane will form a single monochloro derivative if
 - (1) it possesses only primary hydrogens
 - (2) it possesses only primary hydrogens which are all equivalent
 - (3) both (1) and (2) are correct
 - (4) both (1) and (4) are wrong
- 23. Consider the reaction

 $CH_3CH_3 + (CH_3)_3C-O-Cl \xrightarrow{heat} \to$ The major products expected are

- (1) CH_3CH_2OH and $(CH_3)_3C-Cl$
- (2) $CH_3CH_2OC(CH_3)_3$ and HCl
- (3) CH_3CH_2Cl and $(CH_3)_3C-OH$
- (4) CH₃CH₂OCl and (CH₃)₃CH24. Consider the following reaction

$$CH_{3}CH_{2}OH \xrightarrow{CH_{3}SO_{2}Cl}{Et_{5}N} A \xrightarrow{LiaAlH_{4}} B$$

The end product (B) is

- (1) $CH_3CH_2OSO_2CH_3$ (2) CH_3CH_3
- (3) $CH_3CH_2CH_3$ (4) CH_3CH_2Cl
- **25.** A mixture of cyclohexane and sulphuryl chloride (3 : 1 molar ratio) is refluxed in the presence of a small amount of $(C_6H_5CO)_2O_2$. The major product obtained is



EXERCISE 2

1. Mono chlorination reaction of n-pentane takes place n-pentane $\xrightarrow{Cl_2/hv}$ (A) $\xrightarrow{fractional}$ (B). A and B are respectively: (1) 3 3 (2) 4 3

2. Pick the correct statement for monochlorination of R-secbutyl chloride.

$$\begin{array}{c|c} Me \\ Cl & H & \underline{Cl_2} \\ H & \underline{Sl_2} \\ Et \end{array}$$

- (1) There are four possible products; three are optically active one is optically inactive
- (2) There are five possible products; three are optically inactive & two are optically active
- (3) There are five possible products; two are optically inactive & three are optically active
- (4) There are four possible products; two are optically inactive & two are optically inactive



- $(3) \begin{array}{c} Me \\ Me \\ Me \end{array} \begin{array}{c} Br \\ Me \\ Ph \end{array} (4) All$
- 4. The product formed in the reaction is:

 $\begin{array}{ccc} BrCH_2 & CH_2Br & \\ BrCH_2 & CH_2Br & \\ \hline \end{array} \xrightarrow{ Na \\ \hline Ether, heat } \end{array}$

(1) $(BrCH_2)_3CCH_2CH_2C(CH_2Br)_3$





6. In the following halogen substituted hydrocarbon, the hydrogen atom that can be eliminated most readily is:



- (3) H_c (4) H_d
- 7. Select the starting material for following reactions



8. Which of the following is the best way to prepare isopentane?

(1)
$$CH_3 \longrightarrow CH \longrightarrow CH_2 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow Br$$

(2) $CH_3 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow Br \xrightarrow{Li} \xrightarrow{Cul} \xrightarrow{Cul} \xrightarrow{CH_3 \longrightarrow CH_2 \longrightarrow$

(3)
$$CH_2$$
—Br \xrightarrow{Li} \xrightarrow{Cul} \xrightarrow{Cul} \xrightarrow{Br} \xrightarrow{Br}





12. A sample of (R)-2-chlorobutane,

$$CH_3 \xrightarrow{H} Cl Cl CH_2CH_3$$

reacts with Br_2 in the presence of light, and all the products having the formula C_4H_8BrCl were isolated. Two possible isomers are shown below:



- (1) only I was formed
- (2) both I and II were formed in equal amounts
- (3) both I and II were formed in unequal amounts
- (4) only II was formed





Br' will abstract which of the hydrogen most readily?

(1) a (2) b
(3) c (4) d
$$CH_2$$
-Cl



Products obtained in above Wurtz reaction is:



(4) Both (1) and (2)

16. Isobutane on monochlorination with Cl_2 in the presence of UV light gives t-butyl chloride (36%) and isobutyl chloride (64%) (based on the total yield of monochlorinated product). On the basis of this data, relative reactivity of tertiary and primary hydrogens on a per-hydrogen basis is expected to be

$$(1) \ 3.2:1 \qquad (2) \ 5.1:1$$

$$(3) \ 2.5:1 \qquad (4) \ 4.5:1$$

17. In the given reaction Br Br Cl P will be: (1) H_6H_5 -Br (2) C_6H_5 -Cl (3)

(4) Mixture of (1), (2) and (3)

18. In the given reaction (P) will be



19. Consider the following statements:

- (i) In free radical substitution reactions both propagation steps should be exothermic
- (ii) Reaction intermediate is carbon free radical
- (iii) Termination step is always exothermic
- (iv) Initiation step is always exothermic, Select the correct statements and give the answer from the codes given below

Code:

- (1) i, ii and iii (2) i, ii and iv
- (3) ii and iii (4) i, ii, iii and iv
- **20.** Chlorination of methane may proceed according to one of the two alternative mechanism.

Mechanism A: $Cl' + CH_4 \longrightarrow HCl + \dot{C}H_3$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

Mechanism B: Cl' + CH₄ \longrightarrow CH₃Cl + H'

 $H^{\bullet} + Cl_2 \longrightarrow HCl + Cl^{\bullet}$

Which statement about these mechanism is correct?

- (1) Mechanism A is preferred because none of the steps is strongly endothermic
- (2) Mechanism A is preferred because step-II is strongly exothermic

- (3) Mechanism B is preferred because none of the steps is strongly endothermic
- (4) Mechanism B is preferred because step-II is strongly exothermic

EXERCISE 3

One and More Than One Option Correct Type Question

1. Select correct statement:

- (1) Methane cannot be prepared by catalytic hydrogenation of alkene
- (2) All isomers of the formula C_6H_{14} can be prepared by catalytic hydrogenation of alkene
- (3) All isomers of the formula C_5H_{12} can be prepared by catalytic hydrogenation of alkene

(4)
$$D \xrightarrow{D} D \xrightarrow{H_2} product obtained show now D$$

optical rotation

- 2. Which statement is correct?
 - (1) C_2H_6 can be prepared by Wurtz reaction
 - (2) CO₂ gas liberates at anode in Kolbe electrolytes of aqueous CH₃COOK
 - (3) Benzene liberates at anode on Kolbe electrolysis of aqueous Ph–COONa
 - (4) Anhydrous ether should be used in Wurtz reaction
- 3. Which of the following reactions will give propane?

(1)
$$Cl \xrightarrow{Mg/ether}{H_2O}$$

(2) $\xrightarrow{B_2H_6/ether}{CH_3COOH}$
(3) $\xrightarrow{O} P+HI \rightarrow$
(4) $\xrightarrow{O} We \xrightarrow{O} OK \xrightarrow{electrolysis}{H_2O}$

4. Which of the following decarboxylation reaction and their product is/are incorrectly matched?



$$(4) \xrightarrow{\text{COOH}} \xrightarrow{\Delta} \swarrow^{\text{CN}}$$

5. Consider the following bromination reaction

If a pure enantiomer of reactant is taken in the above reaction, the correct statement concerning product bromination is/are

- (1) A racemic mixture is formed
- (2) Two optically active isomers are formed
- (3) A pair of diastereomers in equal amount is formed
- (4) A pair of enantiomers but in unequal amounts is formed

6.
$$C_6H_{14(n-hexane)} \xrightarrow{Al_2O_3/\Delta} (A) \xrightarrow{(CO+HCI)/AlCl_3} (B)$$

Select the correct statement among following:

- Compound 'B' form silver mirror on reaction with [Ag(NH₃)₂]OH
- (2) Molecularity of reaction during conversion from 'A' to 'B' is '3'
- (3) Compound 'A' can also be synthesised by reaction of benzene diazonium chloride with H₃PO₂
- (4) Compound 'B' give grey colour with aq. $HgCl_2$ solution
- 7. Which of the following can't be produced as the single alkene in Wurtz's reaction?



Assertion and Reason Type Question

- (1) If both (A) and (R) are correct and (R) is the correct explanation for (A)
- (2) If both (A) and (R) are correct and (R) is not the correct explanation
- (3) If (A) is correct and (R) is incorrect
- (4) If (A) is incorrect and (R) is correct

8. Statement-1:

$$\begin{array}{c} CH_3 & CH_3 \\ CH_3 - C - CH = CHCOOH \\ CH_3 - C - CH = CHCOOH \\ CH_3 & CH_3 \\ I & II \end{array}$$

Acid (II) will decarboxylate more readily on heating.

Statement-2: Acid (II) is a β - γ unsaturated acid and will decarboxylate easily on heating by a mechanism involving cyclic transition state.

9. Statement-1: iso-butyl bromide, on reaction with sodium in the presence of dry ether, gives 2, 5-dimethylhexane.

Statement-2: In Wurtz reaction, alkyl halides yield hydrocarbon containing double the number of carbon atoms present in the halide.

Comprehension Type Question

Passage (Q. 10–12)

A hydrocarbon with molecular formula $C_{10}H_{18}$, upon catalytic hydrogenation gives $C_{10}H_{20}(X)$. X on free radical chlorination gives two monochloro derivatives with their molecular formula $C_{10}H_{19}Cl$ that are constitutional isomers.

10. Which of the following satisfy the criteria of X?



11. How many different alkenes on hydrogenation, can gives X?

(1)	1	(2)	2
(3)	3	(4)	4

12. Which of the following reactions can synthesise X?





Comprehension (Q. 13-15)

Deutrium (D) is the hydrogen isotope of mass number 2, with a proton and neutron in its nucleus. The chemistry of deuterium is nearly identical to the chemistry of hydrogen, except that the C—D bond is slightly stronger than the C—H bond by 5.0 kJ mol (1.2 kcal mol). Reaction rates tend to be slower if a C—H bond (as opposed to C—H bond) is broken in a rate limiting step.

This effect, called a kinetic isotope effect, is clearly seen in the chlorination of methane, Methane undergoes free radical chlorination 12 times as fast as tetra-deuteriomethane (CD_4)

Faster: $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$, Relative rate = 12 Slower: $CD_4 + Cl_2 \longrightarrow CD_3Cl + DCl$, Relative rate = 1

- **13.** What is true regarding transition state for the rate determining step in the monochlorination of CH_4 and CD_4 ?
 - Transition states have same potential energies for both CH₄ and CD₄
 - (2) Transition state has greater potential energy for CH_4 than for CD_4
 - (3) Transition state has greater potential energy for CD₄ than for CH₄
 - (4) The byproduct HCl is is more stable than DCl
- 14. Monochlorination of deuterioethane (C_2H_5D) leads to a mixture containing 93% (C_2H_4DCl) and 7% (C_2H_5Cl) . Based on these percentages, what is the relative rate of abstraction per hydrogen with respect to D?
 - (1) 93 times greater (2) 18.6 times greater
 - (3) 13.3 times greater (4) 2.7 times greater
- **15.** Consider the thermodynamics of the rate determining step in the chlorinatin of methane and the chlorination of ethane,

 $CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl; \qquad \Delta H = 4 \text{ kJ/mol}$ $CH_3CH_3 + \dot{C}l \longrightarrow \dot{C}H_2 - CH_3 + HCl; \Delta H = -21 \text{ kJ/mol}$

The correct statement is

- (1) Methane shows greater kinetic isotopic effect than ethane
- (2) Ethane shows greater kinetic isotopic effect thane methane
- (3) Both sow the same kinetic isotopic effect
- (4) Kinetic isotopic effect cannot be compared in the above two reactions

Column Matching Type Question

16. Column-(I)



Single Digit Integer Type Question

- **17.** How many different dichlorides, including stereoisomers by Wurtz coupling reaction with ethereal solution of sodium, can give 1,4-dimethyl cyclohexane?
- **18.** If a pure enantiomers of 1, 3-dichloropentane, shown below, is subjected to free radical chlorination to obtain trichloropentane, how many different isomers would be formed?

$$H_{\text{Cl}} \xrightarrow{\text{CH}_2\text{CH}_3} \frac{\text{Cl}_2}{\text{hv}} C_5\text{H}_9\text{Cl}_3$$

$$H_{\text{Cl}} \xrightarrow{\text{Cl}_2\text{CH}_2\text{Cl}} (\text{trichloropentane})$$



19. If the following compound is treated with Pd/C in excess of H_2 gas, how many stereoisomers of the product will be obtained?



20. Haw many type of acids can be used to obtained isopentane by decarboxylation?

EXERCISE 4

1. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be-

[AIEEE-2003]

(1)	Isopentane	(2)	Neopentane
(3)	Propane	(4)	Penetane

2. Butene-1 may be converted to butane by reaction with- [AIEEE-2003]

(1) Zn–Hg	(2) Pd/H_2
(3) Zn–HCl	(4) Sn–HCl

3. Amongst the following compounds the optically acitive alkane having lowest molecular mass is-

[AIEEE-2004]

(1)
$$CH_3-CH_2-CH_2-CH_3$$
 (2) $CH_3-CH_2-CH_-CH_3$

(3)
$$CH_3-C_1$$
 (4) $CH_3-CH_2-C=CH_2$
 C_2H_5

- 4. Alkyl halides react with dialkyl copper reagents to give [AIEEE-2005]
 - (1) Alkyl copper halides (2) alkenes
 - (3) alkenyl halides (4) alkanes
- 5. Phenyl magnesium bromide reacts with methanol to give- [AIEEE-2006]

- (1) a mixture of benzene and Mg(OMe)Br
- (2) a mixture of toluene and Mg(OH)Br
- (3) a mixture of phenol and Mg(Me)Br
- (4) a mixture of anisole and Mg(OH)Br
- 6. The treatment of CH₃MgX with CH₃C≡C−H produces [AIEEE-2008]

CH | |

(1)
$$CH_3C=C-CH_3$$
 (2) $CH_3-CH_2-CH-CH_3$
(3) CH_4 (4) $CH_3-CH=CH_2$

- Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide? [AIEEE-2012]
 - (1) Neopentane
 - (2) Isohexane
 - (3) Neohexane
 - (4) Tertiary butyl chloride
- **8.** The major product obtained in the photo catalysed bromination of 2-methylbutane is:

[JEE Main Online-2012, 2014]

- (1) 1-bromo-2-methylbutane
- (2) 1-bromo-3-methylbutane
- (3) 2-bromo-3-methylbutane
- (4) 2-bromo-2-methylbutane
- **9.** 1-Bromo-3-chloro cyclobutane on reaction with 2-equivalent of sodium in ether gives

[IIT Screening-2005]



EXERCISE # 1

1. (1) 6. (1) 11. (3) 16. (1) 21. (2)	2. (3) 7. (4) 12. (1) 17. (4) 22. (2)	3. (4) 8. (3) 13. (4) 18. (2) 23. (3)	4. (3) 9. (3) 14. (4) 19. (1) 24. (2)	5. (2) 10. (2) 15. (1) 20. (3) 25. (4)
EXERCISE #	# 2			
1. (2)	2. (3)	3. (3)	4. (4)	5. (4)
6. (4)	7. (4)	8. (1)	9. (2)	10. (2)
11. (1)	12. (2)	13. (2)	14. (1)	15. (4)
16. (2)	17. (3)	18. (2)	19. (1)	20. (1)



10. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (on the basis of bpt)

[JEE Advance-2014]



- $(3) II > II \qquad (4) III > I > II$
- **11.** In the following monobromination reaction, the number of possible chiral product(s) is (are) _____

[JEE Advance-2016]



ANSWER KEY

1. $(1,2,4)$ 2. $(1,2,4)$ 3. $(1,2,5)$ 4. $(1,2)$ 3.	(2,3)
6. (1,3,4) 7. (1,3) 8. (1) 9. (1) 10.	(3)
11. (1) 12. (4) 13. (3) 14. (14) 15.	(1)
16. (1) 17. (7) 18. (7) 19. (2) 20.	(4)

EXERCISE # 4

EXERCISE # 3

1. (2)	2. (2)	3. (2)	4. (4)	5. (2)
6. (3)	7. (1)	8. (4)	9. (4)	10. (2)
11. (5)				



4. [3]

sodium butyrate
$$CH_3$$
- CH_2 - CH_2 - $COONa$
 $\xrightarrow{electrolysis} CH_2$ - CH_2 - CH_2 - COO^- + Na^+

At cathode $Na^+ + e^- \longrightarrow Na$ 2Na + 2H₂O \longrightarrow 2NaOH + H₂

At Anode

$$CH_{3}-CH_{2}-CH_{2}-COO^{-} CH_{3}-CH_{2}-CH_{2}-COO^{\bullet} + e^{-}$$

$$\downarrow$$

$$CH_{3}-CH_{2}-CH_{2}+CO_{2}$$

$$\downarrow$$

$$coupling$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3}$$

$$n-hexane$$

5. [2]

(C–Br) bond is weaker than (C – Cl) bond, Grignard reagent is formed more predominantly with (C – Br) $\,$





7. [4] At high temprature breaking of both C–C & C–H bond takes place, thus.

$$\begin{array}{cccc} \mathrm{CH}_{3}\text{-}\mathrm{CH}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{H} & \xrightarrow{\mathrm{cone}\,\mathrm{HNO}_{3}(\mathrm{V})} & \mathrm{CH}_{3}\text{-}\mathrm{CH}\text{-}\mathrm{CH}_{3} \\ & & & & & & \\ \mathrm{H} & & & \mathrm{NO}_{2} \\ & & & \mathrm{CH}_{3}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{NO}_{2} \\ & & & \mathrm{CH}_{3}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{NO}_{2} \\ & & & \mathrm{CH}_{3}\text{-}\mathrm{NO}_{2} \end{array}$$

Breaking of C–H and C–C bond takes place 8. [3]

$$\xrightarrow{\text{AlCl}_3.\text{HCl}}$$

It is isomerisation reaction so that branching takes place.

9. [3]

$$C_{1^{\circ}10}^{1^{\circ}CH_{3}}H_{3}-C_{2^{\circ}}^{CH}-C_{1^{\circ}}^{CH_{2}}H_{3}$$
 (2-methylbutane)

number of alkene = type of C - C having H in alkane

Type of C – C
$$\rightarrow$$
 1° and 3°
 \rightarrow 2° and 3°
 \rightarrow 1° and 2°
= 3 type

10. [2]
Br + (CH₃-CH₂)₂CuLi
$$\xrightarrow{SN_2}$$
 \xrightarrow{I}
Corey-House synthesis

11. [3]

 $Zn/H^{\oplus} \Rightarrow$ Reducing agent

(1)
$$\begin{array}{ccc} CH_3 & CH_3 \\ | \\ CH-C-Br & \xrightarrow{Zn/H^+} & CH_3-C-H \\ | \\ CH_3 & CH_3 \end{array}$$

$$(4) CH_{3}-CH_{2}-CH_{2}-Br \xrightarrow{Zn/H^{+}} CH_{3}-C-CH_{3}$$

$$(3) CH_{3}-C-CH_{2}-Br \xrightarrow{Zn/H^{+}} CH_{3}-C-CH_{3}$$

$$(4) CH_{3}-CH_{2}-C-Br \xrightarrow{Zn/H^{+}} CH_{3}-CH_{2}-CH-CH_{3}$$

12. [1]

$$\begin{array}{ccc} CH_3-CH-COOH & \xrightarrow{\text{Red P/HI}} & CH_3-CH-CH_3 \\ & & & | \\ OH & & H \\ Chiral C = 1 & Chiral C = 0 \end{array}$$

13. [4]

$$\begin{array}{c} CH_{3}\\ CH_{3}-CH_{2}-Br + (CH_{3}-CH)_{2}-LiCu\\ Corey-House \\ synthesis \\ CH_{3}\\ CH_{3}-CH_{2}-CH-CH_{3}\\ 2-methyl butane \end{array}$$

14. [4]

Reate of de-corboxylation ∝ stability of carboanion

15. [1]



$$\begin{array}{c} CH_3 & CH_3 \\ | & | \\ CH_2 / hv \rightarrow \\ CH_3 - C - C - C - CH_2 - CH_2 - CH_2 \\ | & | \\ CH_3 & CH_3 \\ (only single product) \end{array}$$

16. [1]

 \rightarrow 1 C chiral \rightarrow Mixture of *d* and *l* isomer possible \rightarrow Racemic mixture

17. [4]

$$\begin{array}{ccc} CH_{3}-CH_{2}-D \xrightarrow{Cl_{2}/hv} & CH_{3}-CH_{2}-Cl+CH_{3}-CH-D \\ & & & & | \\ Minor & & Cl \\ & & Major \end{array}$$

B.E (C - H) < B.E(C-D)

18. [2]

$$CH_4 \xrightarrow{Cl_2/hv} \dot{C}H_3$$

 $\dot{C}H_3 \xrightarrow{O_2} CH_3-O-O^*$

Due to formation of methyl peroxide, rate of reaction retards

$$CH_{3} \xrightarrow{CH_{3}} CH_{3}-CH-CH_{3} + CCl_{4} \xrightarrow{SO_{2}Cl_{2}} CH_{3}-C-CH_{3} + CHCl_{3}$$
Radical substitution Cl

20. [3]

$$F^{\bullet} + CH_{4} \longrightarrow HF + CH_{3}^{\bullet} \qquad \Delta H^{\circ} = -130$$

$$CH_{3}^{\bullet} + F_{2} \longrightarrow CH_{3}F + F^{\bullet} \qquad \Delta H^{\circ} = -302$$

$$Overall \quad \Delta H^{\circ} = -432$$

$$A \text{ Large amount at heat released so that flourination is explosive.}$$

$$I^{\bullet} + CH_{4} \longrightarrow HI + CH_{3}^{\bullet} \qquad \Delta H^{\circ} = +142$$

$$CH_{3}^{\bullet} + I_{2} \longrightarrow CH_{3}I + I^{\bullet} \qquad \Delta H^{\circ} = -89$$

$$Overall \quad \Delta H^{\circ} = +53$$

Heat absorbed so that iodonation is very slow.

21. [2]
$$CH_3 CH_3$$

 $| | | CH_3 - CH - CH_2 - CI$
 $CH_3 CH_3$
 $CH_3 CH_3$
 $CH_3 - CH - CH_2 - CI$
 $CH_3 CH_3$
 $CH_3 - CH_3 - CH_2 - CH_3$
 $CH_3 - CH_3 - CH_2 - CH_3$
 $CH_3 - CH_3 - CH_3 - CH_2 - CH_3$
 $CH_3 - CH_3 -$

Thus the forming alkane prepared by only two isomeric alkyl halide

22. [2]

23. [3]

$$CH_{3}CH_{3}+(CH_{3})_{3}C-O-CI \xrightarrow{heat} CH_{3}-CH_{2}-CI$$
Radical substitution
$$+ (CH_{3})_{3}-C-OH$$

24. [2]

$$CH_{3}CH_{2}OH \xrightarrow{CH_{3}SO_{2}CI} CH_{3}-CH_{2} + O-S-CH_{3}$$

$$\xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{-CH}_3$$

 $\begin{array}{c} CH_{3} & CH_{2}-Cl \\ \hline H & \hline Radical \\ CH_{2} & CH_{2} \end{array} \xrightarrow{} CH_{2}-Cl \\ \hline CH_{2} & Cl \xrightarrow{*} H \\ \hline CH_{2} \end{array}$ Cl--Cl Cl-CH₂ ĊH₃ ĊH₃ ĊH₃ (Optically active) (Optically inactive) CH₂-Cl CH₃ CH₃ $\begin{array}{c} Cl \longrightarrow H \\ H \longrightarrow Cl \end{array}$ Cl----H Cl-Cl--H-H ĊH₂ ĊH₃ ĊH₃ CH₂Cl No POS POS present (Optically active) (Optically active) (Optically inactive) meso



4. [4]

5. [4]

Br CH2

Br/CH₂

COOH

™H

CH₃

COOH

 Δ

 $-CO_{2}$

CH₂/Br

CH₂ Br

Intramolecular Wurtz reaction



 $\xrightarrow[]{Na}{Ether, heat}$

COOH

"Н

ĊH₃

Decarbxylation

2°C

3°C∕

ĊH₃

 $Br_2 | hv$

H I_∞H

Br CH₃

NaOH/CaO

-CO₂

25. [4]



EXERCISE # 2

1. [2]

$$\begin{array}{c} CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{3}\xrightarrow{CL_{2}/hv}CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}\\ (Type of H = 3) \\ CH_{2}-CH_{2}-CH_{2}-CH_{3}\\ (d \& \ell) \\ (Total m.c.p = 4) \\ CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3}\\ CI \\ CI \\ CI \\ \end{array}$$

Total monochloro product = 4

Note: Separation of enantiomeric pair do not takes place by fractional distillation

2. [3]

6. [4]

 \rightarrow Rate of H elimination for halogenation

$$\propto$$
 stability of $-C$

 \rightarrow Removal of H_d gives 3°C radical

7. [4]

Frankland reaction

8. [1]

All above reaction final step completed by SN_2 mechanism

Rate of
$$SN_2 \propto \frac{1}{Steric \text{ hindrance of } RX}$$

Rate of SN₂

$$\begin{array}{c} & \text{Br} & \text{Br} \\ | & \\ \text{CH}_3-\text{Br}>\text{CH}_3-\text{CH}_2-\text{Br}>\text{CH}_3-\text{CH}>\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3\\ | & \\ \text{CH}_3 \end{array}$$

9. [2]

Syn addition takes place so that meso isomer obtained as major product.

10. [2]



11. [1]



12. [2]

Since intermediate is radical which is planner so Br[•] radical attacks from both side.

13. [2]

$$D = N - N = D + H_2O_2 \longrightarrow D + H_2O + D_2O$$



14. [1]

 \rightarrow Br \therefore abstract that hydrogen which forms stable free-radical



15. [4]

Wurtz reaction:



16. [2]

$$\begin{array}{c} CH_3 & CH_3 & CH_3 \\ | \\ CH_3-CH-CH_3 \xrightarrow{Cl_2/vv} & CH_3-C-Cl + CH_3-CH-CH_2-Cl \\ | \\ CH_3 \\ l_H^{\bullet} = 9 \\ 2_H^{\bullet} = 1 \end{array}$$

Let relative reactivity of 1_{H}^{\bullet} and 3_{H}^{\bullet} is n_{1} and n_{2} Contribution of 1° halide = $9 \times n_{1}$ Contribution of 3° halide = $1 \times n_{2}$

% of 1° halide =
$$\frac{9n_1}{9n_1 + n_2} = 64$$
 ...(1)
% of 3° halide = $\frac{n_2}{9n_1 + n_2} = 36$...(2)

Divide equation (2) by equation (1)

$$\frac{36}{64} = \frac{n_2}{9n_1}$$
$$\frac{n_2}{n_1} = \frac{9 \times 36}{64} = \frac{81}{16} = 5.1:1$$

17. [3]

÷

Bu₃SnH is is specific reducing agent

The relative rates of abstraction of halogen by Bu_3Sn radical depend upon the halogen in the order I > Br > Cl > F.





20. [1]

H[•] radical is very less stable than Cl[•]

EXERCISE # 3

1.

[1,2,4]

$$CH_{3}$$

 CH_{3} –C–CH₃ (isomer of C₅H₁₂)
 CH_{3}

It is not prepared by hydrogenation of alkene

 $\begin{array}{c} Ph+C-O-Na \xrightarrow{Electrolysis} Ph-Ph \\ || \\ O \\ (anode) \end{array}$



4. [1,2]

- (1) No such new C-C bond is formed in decarboxylation.
- (2) It is not a β -keto acid, does not undergo decarboxylation on simple heating.
- (3) It is a β -keto acid
- (4) Like β-keto acid, it also forms a resonance stabilised carbanion.
- 5. [2,3]

Reactant has two chiral carbons but reaction occur at only one chiral carbon leaving configuration at other chiral carbon intact.



The product also has two chiral carbons. If configuration at one chiral carbon in the above product in altered leaving configuration at other chiral carbon intact, diastereomers would result. Hence, the two products formed above the diastereomers and in equal amounts.



7. [1, 3]

Unsymmetrical alkane can't produced by wurtz reaction as single product.

Both require reactions of two different alkyl halides. In such situation, multiple products (via self and cross coupling) are always formed.

8. [1]

Rate of decarboxylation \propto stability of carboanion





10. [3]

This compound gives only two monochlorination products as



All other gives more than two monochlorination products.

11. [1]

There is only one position available for double bond in X.



12. [4]

All of the above reaction are Wurtz Coupling reaction. Only reaction (4) can give the expected product as



13. [3]

Since, C—D bond is slightly stronger than C—H bond, hence transition state leading to C—D bond has greater maximum height than the same of C—H bond.

14. [4]

$$H \xrightarrow[H]{} H = H \\ H \xrightarrow[H]{} C \xrightarrow[H]{} C \xrightarrow[H]{} C \xrightarrow[H]{} D \\ H \xrightarrow[H]{} H \xrightarrow[H]{} H \xrightarrow[H]{} C \xrightarrow[H]{} D \\ C \xrightarrow[H]{} D$$

$$x = 7$$
 and $5y = 93$, i.e., $y = 93/5 = 18.6$

$$\frac{y}{x} = \frac{18.6}{7} = 2.7$$

15. [1]

In methane, product is closer to transition state and there is very small difference in potential energies between reactant and product for the rate determining step. Hence, change of C—H by C—D bond will have greater effect on rate here. In ethane, product is much more stable, rate will not be as much affected by change of C—H to C—D bond.

16. [1]





In 1-4-dimethyl cyclohexane, the following indicated bonds can be formed in the given reaction condition



Therefore, following dichlorides can be used for this purpose



(I) has two chiral carbons, hence it has four stereoisomers.



(II) Also has two chiral carbons but there are only three stereoismers as one of them is meso.

18. [7]



Thus 4 type of acid are used to obtained is pentane

EXERCISE #4

1. [2] No of monochloro product = Type of H

$$\begin{array}{ccc} CH_3 & CH_3 \\ | \\ CH_3-C-CH_3 & \longrightarrow CH_3-C-CH_2-Cl \\ | \\ CH_3 & CH_3 \\ (type of H = 1) & Only mono chloro product \end{array}$$

2. [2]

$$CH_{3}-CH_{2}-CH=CH_{2} \xrightarrow{Reduction} CH_{3}-CH_{2}-CH_{2}-CH_{3}$$

3. [2]

For optical octivity, molecule must have is chiral, thus

 $R-X + R_2Cu \xrightarrow{SN_2} R-R$

- 5. [1] Ph-MgBr $\xrightarrow{CH_3-OH}$ Ph-H + Mg(OCH₃)Br
- 6. [3] CH_3 -MgX + CH₃-C=CH $\xrightarrow{\text{Acid-Base}}_{\text{reaction}}$

$$CH_4+CH_3-C\equiv C*\overset{\oplus}{M}gX$$

7. [1]

$$C_n H_{2n+2} = 72$$

 $12n + 2n + 2 = 72$
 $n = 5$
 \therefore M.F = $C_5 H_{12}$

$$\begin{array}{c} CH_{3} & CH_{3} \\ | \\ CH_{3}-C-CH_{3} & \xrightarrow{Cl_{2}/h\nu} & CH_{3}-C-CH_{2}-Cl \\ | \\ CH_{3} & CH_{3} \\ Neo \text{ pentane} \end{array}$$

8. [4]

$$\begin{array}{c} CH_{3} & CH_{3} \\ | \\ CH_{3}-CH-CH_{2}-CH_{3} \xrightarrow{Br_{2}/\Delta} CH_{3}-C-CH_{2}-CH_{3} \\ | \\ Br \\ 2-bromo-2-methyl butane \end{array}$$



10. [2]

This problem is based on boiling point of isomeric alkanes.

As we know more the branching in an alkane, lesser will be its surface area and lesser will be the boiling point.



One moving left to right (III to I)

- branching increase
- surface area decreases
- boiling point decreases

Hence the correct choice is (2)

11. [5]

Given compound undergoes free-radical bromination under given conditions, replacing H by Br. C* is chiral carbon.



(III) has two chiral centres and can have two structures.



(IV) has also two chiral centres and can have two structures.



It has plane of symmetry thus, achiral. Thus, chiral compounds are five. I, III A, III B, IV B and V.

9. [4]