Fill Ups of Hydrocarbons

Q.1. .... is most acidic. (Ethane, Ethene, Ethyne) (1981 - 1 Mark)

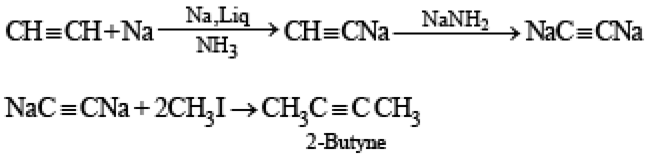
Ans. ethyne

Sol. Ethyne, because of the high s character of the – C ≡ H bond in ethyne (sp hybridisation).

Q.2. Acetylene is treated with excess sodium in liquid ammonia.
The product is reacted with excess methyl iodide. The final product is .... (1983 - 1 Mark)

Ans. 2-butyne

Sol. 2-butyne



$$CH\equiv CH + Na \xrightarrow[NH_3]{Na, Liq} CH\equiv CNa \xrightarrow{NaNH_2} NaC\equiv CNa$$

$$NaC\equiv CNa + 2CH_3I \rightarrow \underset{\text{2-Butyne}}{CH_3C\equiv CCH_3}$$

Q.3. Th e starting material for the manufacture of polyvin yl chloride is obtained by reacting HCl with .... (1983 - 1 Mark)

Ans. C_2H_2

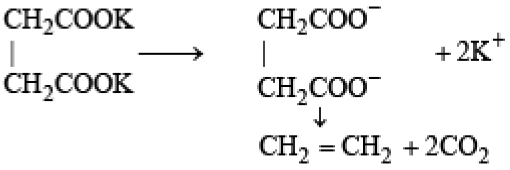
Sol. C_2H_2

$$CH\equiv CH + HCl \longrightarrow CH_2 = CHCl \longrightarrow PVC$$

Q.4. Kolbe electrolysis of potassium succinate gives CO_2 and .... (1993 - 1 Mark)

Ans. ethylene

Sol. ethylene



$$\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array} \longrightarrow \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \\ \quad\downarrow \\ CH_2 = CH_2 + 2CO_2 \end{array} + 2K^+$$

Q.5. Addition of water to acetylenic compounds is catalyzed by.........and........... (1993 - 1 Mark)

Ans. H_2SO_4, $HgSO_4$

Sol. H_2SO_4, $HgSO_4$

Q.6. The bond dissociation energy needed to form the benzyl radical from toluene is........than the formation of the methyl radical from methane. (1994 - 1 Mark)

Ans. less

Sol. less;

NOTE :

$$\text{Stability of free radical} \propto \frac{1}{\text{Bond dissociation energy}}$$

Benzyl $(C_6H_5\dot{C}H_2)$ free radical is more stable than methyl $(\dot{C}H_3)$ free radical because of hyperconjugation (no bond resonance).

Q.7. 1, 3-Butadiene with bromine in molar ratio generates predominantly .... (1997 - 1 Mark)

Ans. 3, 4-dibromo-1-butene-1 (at low temperature) or 1, 4-dibromo-2-butene (at high temperature)

Sol. 3, 4-dibromo-1-butene (at low temperature) or 1, 4- dibromo2-butene (at high temperature

True False of Hydrocarbons

Q.1. Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1982 - 1 Mark)

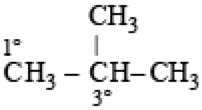
Ans. F

Sol. False : Ethylene reacts with sulphuric acid to form ethyl hydrogen sulphate. It can be dried by passing it through phosphorus pentoxide.

Q.2. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio of 9: 1. (1993 - 1 Mark)

Ans. F

Sol. False : Bromine is less reactive, hence it is more selective and thus 3° hydrogen will be removed more easily than the 1° hydrogen leading to 2-bromo-2-methylpropane as the main product.



$$\overset{1^\circ}{CH_3} - \underset{3^\circ}{\overset{\overset{CH_3}{|}}{CH}} - CH_3$$

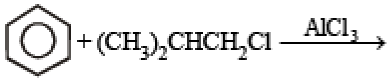
Subjective questions of Hydrocarbons (Part -1)

Q. 1. Give one characteristic test which would distinguish. CH_4 from C_2H_2 (1979)

Ans. Sol. Bromine water test : C_2H_2 decolourises bromine water while CH_4 does not decolourises bromine water.

Q. 2. Write the structural formula of the major product in each of the following cases : (i) the compound obtained by the hydration of ethyne is treated with dilute alkali (1981 - ½ Mark) (ii) ethene mixed with air is passed under pressure over a silver catalyst at 250°C. (1981 - ½ Mark)

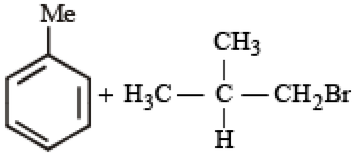
(iii)



(iv) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

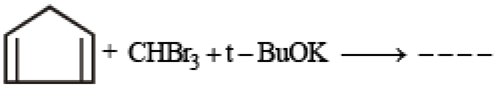
(v) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1.Br_2,\ Heat, Light}$

(vi)



$+ \text{Anhyd. } AlCl_3 \longrightarrow$ ---

(vii)



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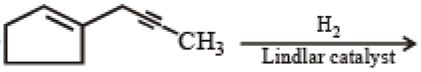
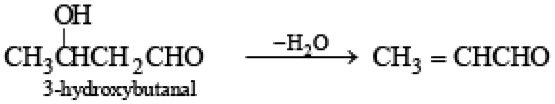


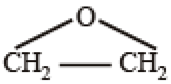
(2000 - 1 Mark)

Ans. Sol.

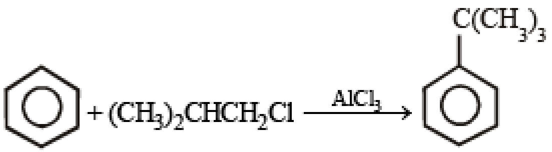
(i) $\underset{\text{ethyne}}{CH \equiv CH} \xrightarrow{\text{hydration}} CH_3CHO \xrightarrow[\text{aldol cond.}]{OH^-}$



$\underset{\text{3-hydroxybutanal}}{CH_3\overset{OH}{C}HCH_2CHO} \xrightarrow{-H_2O} CH_3 = CHCHO$

(*ii*) 

Ethylene oxide

(*iii*) 

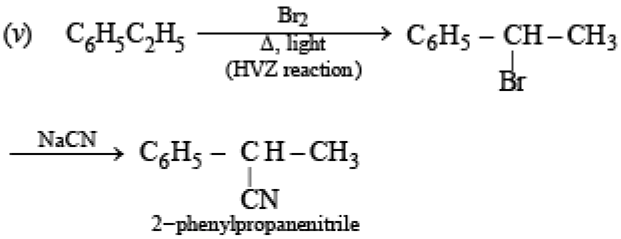
NOTE : that the 1° carbocation, $(CH_3)_2CH\overset{+}{C}H_2$ formed during reaction rearranges to the more stable, 3° carbocation, $(CH_3)_3\overset{+}{C}$ and hence the above product isformed.] (see also ix part)b

(*iv*) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} \underset{tert\text{−Butylbenzene}}{C_6H_5(CH_3)_3}$

Explanation :

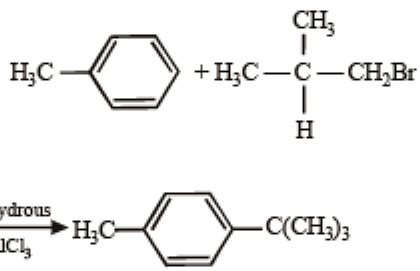
$$(CH_3)_2CHCH_2OH \xrightarrow{H^+} \underset{1^\circ\text{ carbocation}}{(CH_3)_2CH\overset{+}{C}H_2}$$

$$\xrightarrow[\text{to}]{\text{rearranges}} \underset{3^\circ\text{ carbocation}}{(CH_3)_3C^+} \xrightarrow{C_6H_6} C_6H_5C(CH_3)_3$$

(*v*) 

$$C_6H_5C_2H_5 \xrightarrow[\substack{\Delta,\text{ light}\\ \text{(HVZ reaction)}}]{Br_2} C_6H_5-\underset{\substack{|\\ Br}}{CH}-CH_3$$

$$\xrightarrow{NaCN} \underset{\text{2−phenylpropanenitrile}}{C_6H_5-\underset{\substack{|\\ CN}}{CH}-CH_3}$$

(*vi*) 

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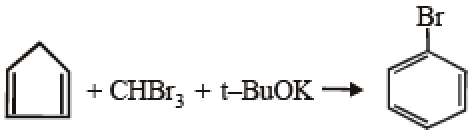

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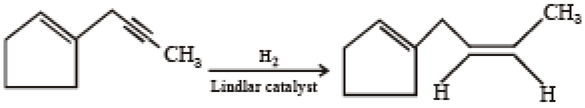
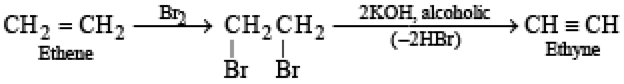


(Partial reduction of triple bond in syn-manner)

Q. 3. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). (1981 - 1 Mark)

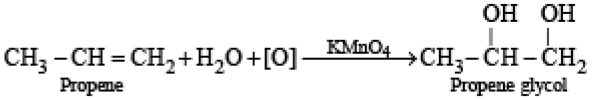
Ans. Sol.



$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{Br_2} \underset{Br\quad Br}{CH_2CH_2} \xrightarrow[(-2HBr)]{2KOH,\ alcoholic} \underset{\text{Ethyne}}{CH\equiv CH}$$

Q. 4. State with balanced equations, what happens when propene is bubbled through a hot aqueous solution of potassium permanganate. (1982 - 1 Mark)

Ans. Sol.



$$\underset{\text{Propene}}{CH_3-CH=CH_2}+H_2O+[O] \xrightarrow{KMnO_4} \underset{\text{Propene glycol}}{CH_3-\overset{OH}{CH}-\overset{OH}{CH_2}}$$

[**NOTE :** Colour of $KMnO_4$ is discharged]

Q. 5. Give reasons for the following : (i) Methane does not react with chlorine in the dark. (1983 - 1 Mark)

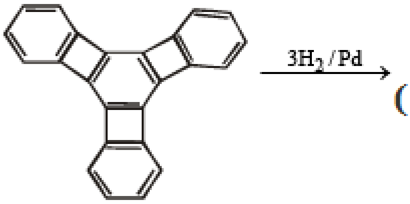
(ii) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide. (1983 - 1 Mark)

(iii) Although benzene is highly unsaturated, normally it does not undergo addition reaction. (1983 - 1 Mark)

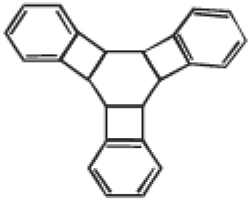
(iv) Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives p-bromotoluene. Give explanation for the above obser vations. (1996 - 2 Marks)

(v) The central carbon-carbon bond in 1, 3 – butadiene is shorter than that in n-butane. (1998 - 2 Marks)

(vi) tert-Butylben zen e does n ot give ben zoic acid on treatment with acidic $KMnO_4$. (2000 - 1 Mark)

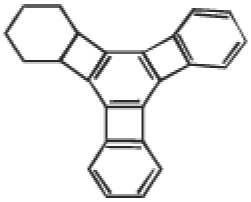
(vii) 

(2005 - 1 Mark)



but not

(A)



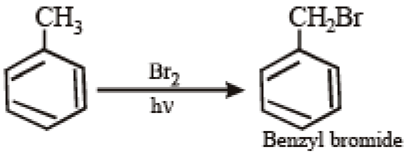
(B)

Ans. Sol. (i) **TIPS/Formulae :** Chlorination of methane is a free radical substitution reaction.
In dark, chlorine is unable to be converted into free radicals, hence the reaction does not occur.

(ii) **TIPS/Formulae :** Addition of unsymmetrical addendum (HBr in present case) to unsymmetrical olefin ($CH_3CH = CH_2$, in present case) takes place according to Markownikoff rule.

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \rightarrow \underset{\textit{iso}\text{-Propyl bromide}}{CH_3.CHBr.CH_3}$$

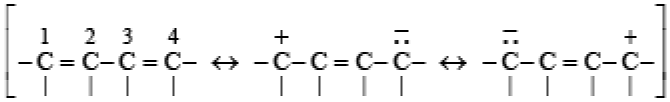
(iii) Unlike olefins, p-electrons of benzene are delocalised (resonance) and hence these are unreactive towards addition reactions. Moreover, addition reaction leads to destruction of the benzenoid ring. (iv) In presence of light, toluene undergoes side chain bromination through a free radical mechanism.



Benzyl bromide

[NOTE :–CH_3 is o-, p-directing]

(v) **TIPS/Formulae** : 1, 3 - Butadiene is a conjugated diene and is a reasonance hybrid:



$$\left[\overset{1}{\underset{|}{-C}}=\overset{2}{\underset{|}{C}}-\overset{3}{\underset{|}{C}}=\overset{4}{\underset{|}{C}}- \leftrightarrow -\overset{+}{\underset{|}{C}}-\underset{|}{C}=\underset{|}{C}-\overset{\cdot\cdot}{\underset{|}{C}}- \leftrightarrow -\overset{\cdot\cdot}{\underset{|}{C}}-\underset{|}{C}=\underset{|}{C}-\overset{+}{\underset{|}{C}}-\right]$$

Thus resonance induces some double bond character in the central C-C bond leading to the shortening of this bond. Alternatively, all the four C atoms of 1, 3– butadiene are sp^2 hybridised and thus their C – C bond length will be lower than that of n-butane in which all the four C atoms are sp^3 hybridised.

(vi) tert-Butyl benzene does not give benzoic acid on treatment with acidic $KMnO_4$ because it does not contain any hydrogen atom on the key carbon atom.

(vii) Reduction of cental ring to form A involves reduction of all the three cyclobutadiene rings (which are antiaromatic as they have 4p electrons each), i.e. antiaromatic rings are converted into nonaromatic rings.

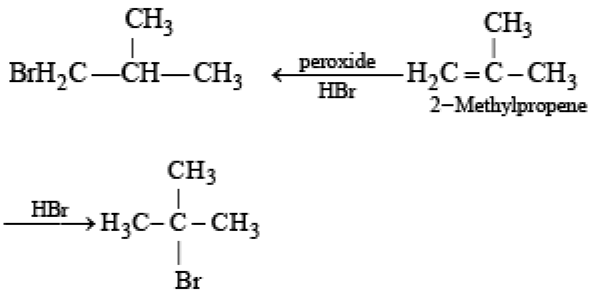
On the other hand, reduction of the terminal ring to form B involves reduction of only one antiaromatic ring.

Remember that antiaromatic rings impart unstability.

Q. 6. (i) 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide, is true under what conditions? (1984 - 1 Mark)

(ii) 'Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution', is true under what conditions. (1984 - 1 Mark)

Ans. Sol. (i) **NOTE :** Under normal conditions, ter-butyl bromide is formed, isobutyl bromide is formed in presence of peroxide.

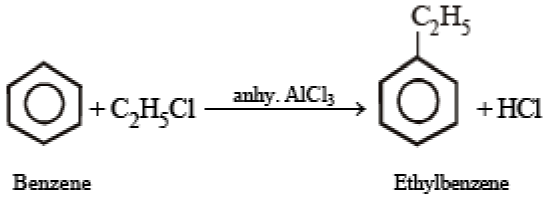


$$BrH_2C-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xleftarrow[\text{HBr}]{\text{peroxide}} \underset{\text{2-Methylpropene}}{H_2C=\overset{\overset{CH_3}{|}}{C}-CH_3}$$

$$\xrightarrow{\text{HBr}} H_3C-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(ii) Ethyne (HC ≡ CH) and only those derivatives which have at least one acetylenic hydrogen atom (≡ C – H) i.e. terminal alkynes will give white precipitate with ammonical silver nitrate solution.

$[C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl]$



Q. 8. A certain hydrocarbon A was found to contain 85.7 percent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.00 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by weight) of Br_2 in CCl_4. Compound A, on oxidation with concentrated $KMnO_4$, gave compound C (molecular formula C_4H_8O) and acetic acid. Compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2- butyne. Determine the molecular formula of A and deduce the structure of A, B and C. (1984 - 6 Marks)

Ans. Sol. Calculation of molecular formula of A.

Element	Percentage	Relative No. of atoms	Simplest whole ratio
C	85.7	85.7/12 = 7.14	7.14/7.14 = 1
H	14.3	14.3/1 = 14.3	14.3/7.14 = 2

∴ Empirical formula of A = CH_2 Determination of molecular weight of A

1g of A consumes = 38.05 g of 5% Br_2 (in CCl_4)

$$= \frac{38.05 \times 5}{100} \text{ g of } 100\% \ Br_2$$

$= 1.90$ g of 100% Br_2.

Now since 1.90 g of Br_2 is consumed by 1 g of compound A

∴ 160g (1 mole) of Br_2 will be consumed by

$= \frac{1}{1.90} \times 160 = 84.2$ g of A = 84.0 (app.)g of A

∴ Molecular weight of A = 84

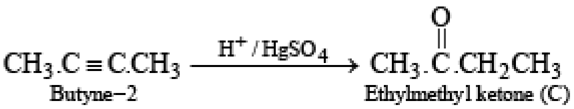
$$\text{Hence, } n = \frac{84}{12+2} = 6$$

∴ Molecular formula of A = $(CH_2)_6 = C_6H_{12}$

Since the hydrocarbon A consumes 1 molar equivlaent of hydrogen, it must contain one double bond. Oxidation of compound A with $KMnO_4$ to form compound C (C_4H_8O) and acetic acid indicates = $CH.CH_3$ fragment in A, i.e.

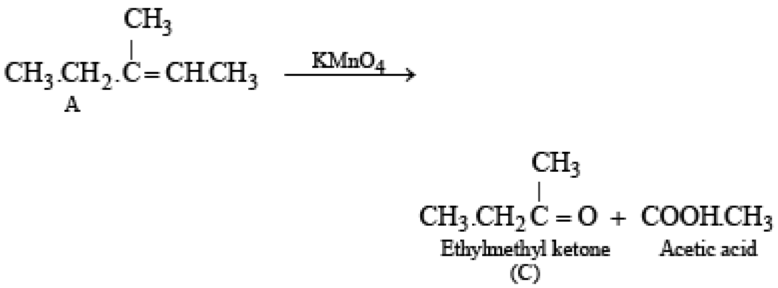
$$\underset{A}{C_4H_8 = CHCH_3} \xrightarrow{KMnO_4} \underset{C}{C_4H_8O} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Now the fragment C_4H_8 of A on oxidation forms the compound 'C' (C_4H_8O) which may be easily obtained from butyne-2 and acidic aq. $HgSO_4$, the compound 'C' must be ethylmethyl ketone.



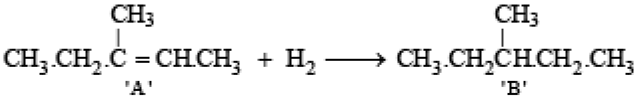
$$\underset{\text{Butyne}-2}{CH_3.C \equiv C.CH_3} \xrightarrow{H^+/HgSO_4} \underset{\text{Ethylmethyl ketone (C)}}{CH_3.\overset{\overset{O}{\|}}{C}.CH_2CH_3}$$

The formation of ketone 'C' from C_4H_8 fragment of 'A' can be explained by the following structure of A



$$\underset{A}{CH_3.CH_2.\overset{\overset{CH_3}{|}}{C} = CH.CH_3} \xrightarrow{KMnO_4} \underset{\substack{\text{Ethylmethyl ketone}\\ \text{(C)}}}{CH_3.CH_2\overset{\overset{CH_3}{|}}{C} = O} + \underset{\text{Acetic acid}}{COOH.CH_3}$$

Hence formation of 'B' can be represented as below.



$$\underset{'A'}{CH_3.CH_2.\overset{\overset{CH_3}{|}}{C} = CH.CH_3} + H_2 \longrightarrow \underset{'B'}{CH_3.CH_2\overset{\overset{CH_3}{|}}{C}H.CH_2.CH_3}$$

Q. 9. How would you distinguish between (i) 2-butyne and 1-butyne. (1985 - 1 Mark) (ii) cyclohexane and cyclohexene. (1988 - 1 Mark)

Ans. Sol. (i) By amm. $AgNO_3$ or by acidic-H tests : Terminal alkynes give white precipitate with amm. $AgNO_3$ or red ppt. with amm. Cu_2Cl_2 (H atom attached on sp hybridized carbon is acidic). $2CH_3CH_2C \equiv CH + Ag_2O \rightarrow 2CH_3CH_2C \equiv CAg + H_2O$
$CH_3 - C \equiv C - CH_3 + Ag_2O \rightarrow$ No reaction

NOTE : Only terminal alkynes respond to these reactions. (ii) Cyclohexene gives positive response to bromine water test and Baeyer's test while cyclohexane does not respond to these reagents.

Q. 10. n-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g n-butane, if the bromination takes place with 90 per cent yield and the Wurtz reaction with 85 per cent yield. (1989 - 3 Marks)

Ans. Sol. $2C_2H_6 \xrightarrow{\text{monobromination}} 2C_2H_5Br$ (yield 90%) (given)

$2C_2H_5Br \xrightarrow[\text{reaction}]{\text{Wurtz}} C_4H_{10} + 2HBr$ (yield 85%) (given)Moles of n-butane to be produced

$= \dfrac{55\text{ g}}{58\text{ g mol}^{-1}} = 0.948$ mol ($\because$ molecular mass of $C_4H_{10} = 58$)

Amount of C_2H_5Br required to obtain 0.948 mol. of $C_4H_{10} = 2 \times 0.948$ mol.

Hence, the amount of C_2H_5Br required

$= \dfrac{2 \times 0.948 \times 100}{85}$ mol. ...(1) [$\because$ yield is 85% only]

Further 1 mole of C_2H_6 gives one mole of C_2H_5Br, hence number of moles of C_2H_6 reqd. for C_2H_5Br in (1)

$= \dfrac{2 \times 0.948 \times 100 \times 100}{85 \times 90}$ mol. $= 2.48$ mol [$\because$ yield is 90%]

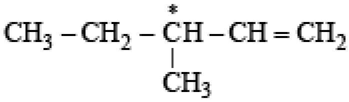
$\therefore$ Required volume of ethane at NTP = 22400 × 2.48 = 55552 ml. = 55.55 litres

Q. 11. Identify, B(C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br. (1993 - 1 Mark)

Ans. Sol. TIPS/Formulae : A symmetric alkene does not follow Markovnikoff and antiMarkovnikoff 's rule (Peroxide effect).
B has to be a symmetric alkene (butene-2) $CH_3CH = CHCH_3$ as it will give the same product $CH_3 - CH(Br) - CH_2 - CH_3$ in presence /absence of peroxide.

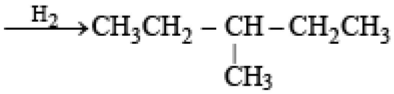
Q. 12. Identify, D(C_6H_{12}), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, C_6H_{14}. (1993 - 1 Mark)

Ans. Sol. An optically active hydrocarbon will have an asymmetric C-atom. This means D(C_6H_{12}) should have an asymmetric C-atom & C_6H_{14} will have no asymmetric C-atom, hence D would be 3-methylpentene-1,



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{*}{C}H}-CH=CH_2$$

(D) Optically active (C_6H_{12})



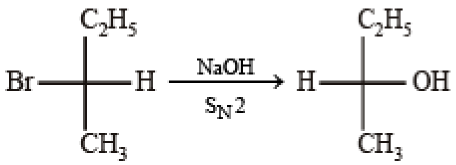
$$\xrightarrow{H_2} CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3$$

Optically inactive (C_6H_{14})

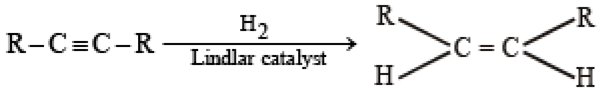
Q. 13. Draw the stereochemical structures of the products in the following reactions : (1994 - 4 Marks)

$$R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2}$$

Ans. Sol. (i) SN_2 reaction leads to inversion in configuration.



(ii)



(*cis*-alkene)

NOTE :

(i) Lindlar's catalyst is Pd supported over $CaCO_3$ which is partially poisoned by $(CH_3COO)_2Pb$. It can restrict the hydrogenation of alkyne to alkene stage. It yields a cis-alkene. (ii) Reduction of alkynes to alkene stage can also be carried out with sodium or lithium in liquid NH_3. Here transalkene is major product.

Subjective questions of Hydrocarbons (Part -2)

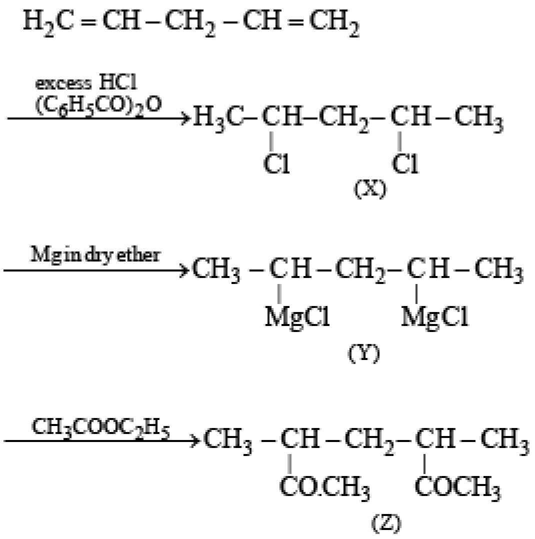
Q. 14. 1, 4–Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound X which upon reaction with excess of Mg in dry ether forms Y. Compound Y on treatment with ethyl acetate followed by dilute acid yields Z. Identify the structures of compounds X, Y and Z. (1995 - 4 Marks)

Ans. Sol. TIPS/Formulae : (i) 1, 4-Pentadiene reacts with HCl in presence of benzoyl peroxide in Markownikoff's way.

NOTE : : Peroxide effect applies to HBr only.

(ii) Gr ignard reagent reacts with ethyl acetate to form ketones, or ter-alcohol if Grignard reagent is taken in excess.

Thus the given reactions can be written as below.



$$H_2C=CH-CH_2-CH=CH_2$$

$$\xrightarrow[(C_6H_5CO)_2O]{\text{excess HCl}} \underset{(X)}{H_3C-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_3}$$

$$\xrightarrow{\text{Mg in dry ether}} \underset{(Y)}{CH_3-\underset{MgCl}{\underset{|}{CH}}-CH_2-\underset{MgCl}{\underset{|}{CH}}-CH_3}$$

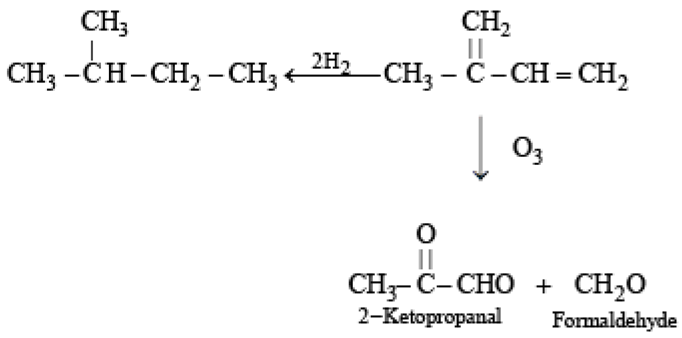
$$\xrightarrow{CH_3COOC_2H_5} \underset{(Z)}{CH_3-\underset{CO.CH_3}{\underset{|}{CH}}-CH_2-\underset{COCH_3}{\underset{|}{CH}}-CH_3}$$

Q. 15. An organic compound E(C_5H_8) on hydrogenation gives compound F(C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E. (1995 - 2 Marks)

Ans. Sol. Summary of the given reactions

$$\underset{(F)}{C_5H_{12}} \xleftarrow{H_2} \underset{(E)}{C_5H_8} \xrightarrow{\text{ozonolysis}} HCHO + \underset{\text{2–Ketopropanal}}{CH_3-\overset{O}{\overset{||}{C}}-CHO}$$

Since hydrogenation of (E) to (F) takes up two molecules of hydrogen, it indicates the presence of two double bonds in E which is further supported by its ozonolysis to form two products having three carbonyl groups. Further structure of ozonolysis product leads to following structure to compound (E).

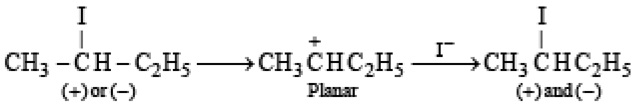


$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3 \xleftarrow{2H_2} CH_3-\overset{CH_2}{\overset{||}{C}}-CH=CH_2 \xrightarrow{O_3} \underset{\text{2-Ketopropanal}}{CH_3-\overset{O}{\overset{||}{C}}-CHO} + \underset{\text{Formaldehyde}}{CH_2O}$$

Q. 16. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. (1995 - 2 Marks)

Ans. Sol. TIPS/Formulae : In SN_1 reaction racemization as well as inversion is observed.

Reaction of optically active 2-iodobutane with NaI in acetone is an SN_1 reaction which involves formation of carbocation as intermediate.

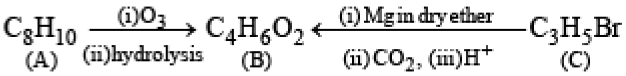


$$\underset{(+)\text{ or }(-)}{CH_3-\overset{I}{\overset{|}{C}}H-C_2H_5} \longrightarrow \underset{\text{Planar}}{CH_3\overset{+}{C}HC_2H_5} \xrightarrow{I^-} \underset{(+)\text{ and }(-)}{CH_3\overset{I}{\overset{|}{C}}HC_2H_5}$$

Thus the product, being a racemic mixture will be optically inactive.

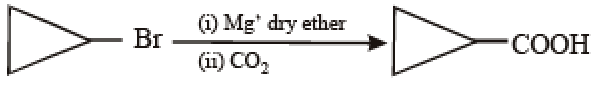
Q. 17. A hydrocarbon A, of the formula C_8H_{10}, on ozonolysis gives compound $B(C_4H_6O_2)$ only. The compound B can also be obtained from the alkyl bromide, $C(C_3H_5Br)$ upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B and C and also give equations for the reactions. (1996 - 3 Marks)

Ans. Sol. Summary of the given facts



$$\underset{(A)}{C_8H_{10}} \xrightarrow[\text{(ii)hydrolysis}]{\text{(i)}O_3} \underset{(B)}{C_4H_6O_2} \xleftarrow[\text{(ii)}CO_2,\ \text{(iii)}H^+]{\text{(i) Mg in dry ether}} \underset{(C)}{C_3H_5Br}$$

Since compound (B) is obtained from compound (C) C_3H_5 Br through reaction with Mg and CO_2, it seems that compound (B) is a carboxylic acid formed via the formation of Grignard reagent. Hence compound (C) should be an alkyl halide having three carbon atoms. The alkyl halide (C) is unsaturated (indicated by number of hydrogen atoms) which is present in the form of ring and thus (C) should be bromocyclopropane.

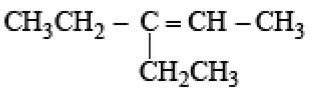


(C) C_3H_5Br (B) $C_4H_6O_2$

(A) C_8H_{10} (B) $C_4H_6O_2$

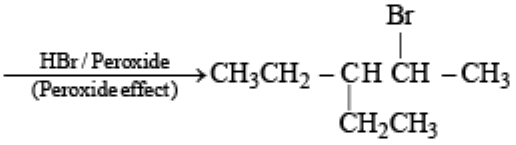
Q. 18. Give the structures of the major organ ic products from 3-ethyl-2-pentene under each of the following reaction con ditions. (1996 - 3 Marks) (a) HBr in the presence of peroxide (b) Br_2/H_2O (c) $Hg(OAc)_2/H_2O$; $NaBH_4$

Ans. Sol.

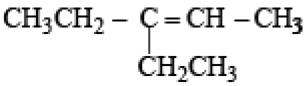
(a) 

$$CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CH_3$$

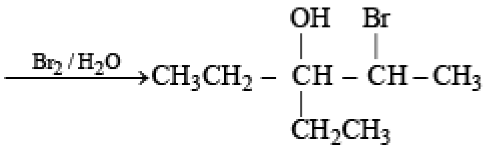
(unsymmetrical)



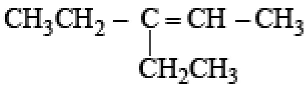
$$\xrightarrow[\text{(Peroxide effect)}]{\text{HBr / Peroxide}} CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}\overset{\displaystyle Br}{\overset{|}{CH}}-CH_3$$

(b) 

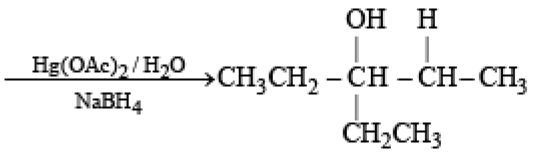
$$CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CH_3$$



$$\xrightarrow{Br_2/H_2O} CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{CH}}}}-\overset{\displaystyle Br}{\overset{|}{CH}}-CH_3$$

(c) 

$$CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}=CH-CH_3$$



$$\xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} CH_3CH_2-\underset{CH_2CH_3}{\overset{OH}{C}H}-\overset{H}{C}H-CH_3$$

Q. 19. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidized vigorously with KMnO₄, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. (1997 - 2 Marks)

Ans. Sol. TIPS/Formulae : (i) It should be an alkene as it adds one mole of H_2. (ii) The C_6 alkene should be symmetrical because on oxidation it gives a single carboxylic acid having three carbon atoms.

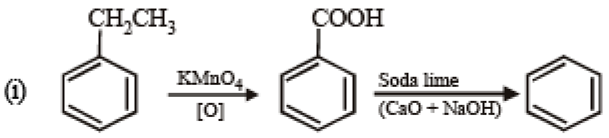
$$\underset{n\text{–Hexane}}{CH_3(CH_2)_4CH_3} \xleftarrow{H_2} \underset{(A)}{CH_3CH_2CH=CHCH_2CH_3}$$

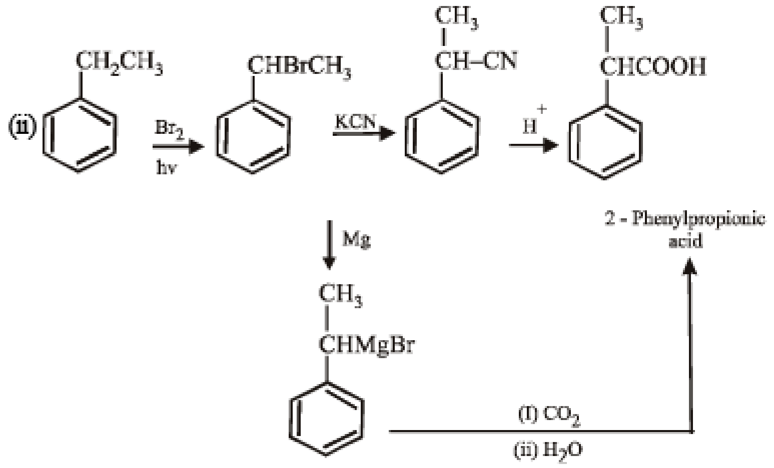
$$\xrightarrow[KMnO_4]{(O)} 2CH_3CH_2COOH$$

Q. 20. Show the steps to carry out the following transformations.

(i) Ethylbenzene → benzene (1998 - 2 Marks)
(ii) Ethylbenzene → 2- phenylpropionic acid. (1998 - 3 Marks)

Ans. Sol.

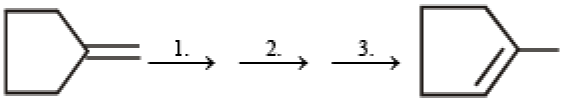




Q. 21. Complete the following reactions with appropriate structures of products/reagents.

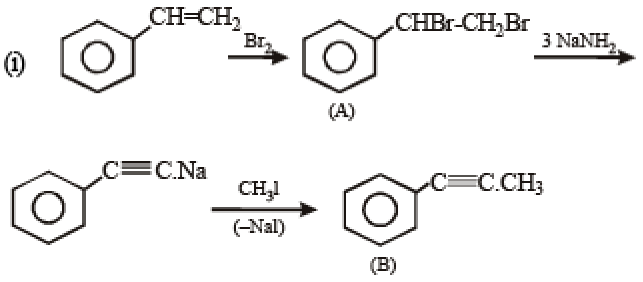
(i) $C_6H_5CH=CH_2 \xrightarrow{Br_2} [A]$

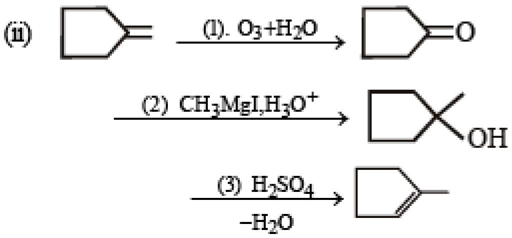
$\xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3.0 equiv.)}} [B\}$ **(1998 - 2 + 2 Marks)**



(1999 - 3 Marks)

Ans. Sol.



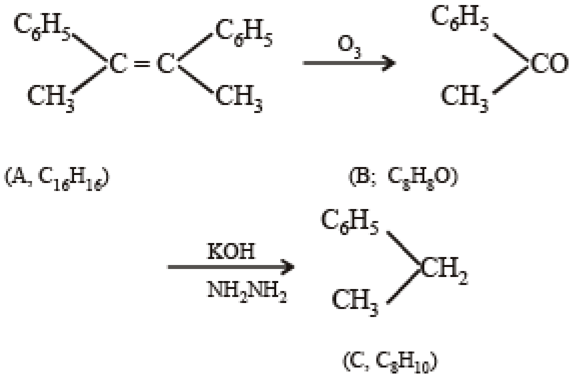


Q. 22. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compund (B) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information, two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation ($H_2/Pd – C$) gives a racemic mixture. (2001 - 5 Marks)

Ans. Sol.

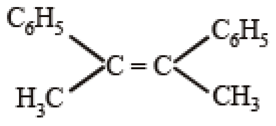
$$\begin{tikzcd}
\underset{\text{(A)}}{\underset{\text{(an alkene)}}{C_{16}H_{16}}} \arrow[r, "O_3"] & \underset{\text{(B)}}{\text{only } C_8H_8O} \arrow[r, "NaOH/I_2"] \arrow[d, "KOH / NH_2NH_2"] & C_6H_5COONa \\
& \underset{\text{(C)}}{C_8H_{10}} &
\end{tikzcd}$$

(i) Conversion of (B) to (C) involves iodoform reaction, hence (B) must contain –$COCH_3$ group leading to $C_6H_5COCH_3$ (C_8H_8O) as its molecular formula. (ii) Since the given alkene gives only one product on ozonolysis, so the given alkene must be a symmetrical alkene containing a double bond in centre. Thus the alkene (A) must have following structure

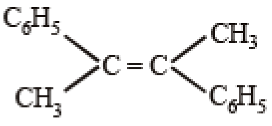


(A, $C_{16}H_{16}$) (B; C_8H_8O) (C, C_8H_{10})

Isomeric structures of A



cis



trans

NOTE : Since catalytic hydrogenation of alkenes takes place in cis -(syn-) manner; hence recemic mixture will be formed by the trans-isomer.

Q. 23. Write down the heter ogeneous catalyst in volved in the polymerisation of ethylene. (2003 - 2 Marks)

Ans. Sol. Ziggler – Natta catalyst ($R_3Al + TiCl_4$)

Q. 24.

$A(C_6H_{12}) \xrightarrow{HCl} \underset{(C_6H_{13}Cl)}{B + C}$ **(2003 - 4 Marks)**

$B \xrightarrow{alc.\ KOH} D$ **(isomer of A)**

$D \xrightarrow{ozonolysis} E$ **(it gives negative test with Fehling solution but responds to iodoform test).**

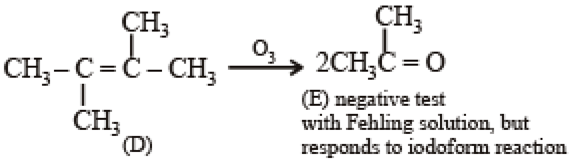
$A \xrightarrow{Ozonolysis} F + G$ **(both gives positive Tollen's test but do not give iodoform test).**

$F + G \xrightarrow{conc.\ NaOH} HCOONa + A$ **primary alochol.**

Identify from A to G.

Ans. Sol. (i) Formation of HCOONa and a primary alcohol due to Cannizzaro reaction of F and G indicate that either F or G should be HCHO. Thus the alkene A should have CH_2 = grouping. The remaining 5 C's of A should have grouping = HCC_4H_9.

(ii) Formation of only E by the ozonolysis of D (C_6H_{12}) indicates that D should have following structure



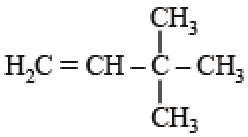
$$CH_3-\underset{CH_3}{C}=\overset{CH_3}{C}-CH_3 \xrightarrow{O_3} 2CH_3\overset{CH_3}{C}=O$$

(D)

(E) negative test with Fehling solution, but responds to iodoform reaction

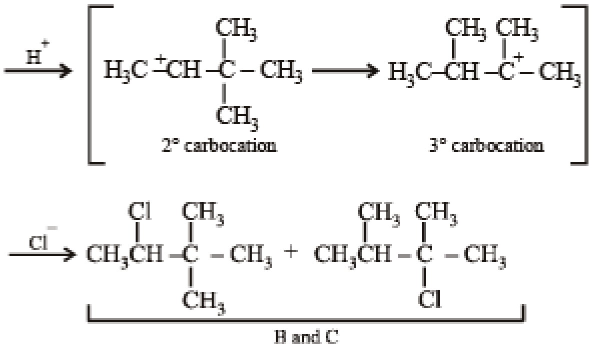
NOTE : Fehling's test is given by aldehydes and not ketones.

(iii) Since A is isomer of D, former should have following structure.



$$H_2C=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

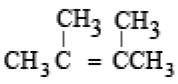
(A) (C_6 H_{12}, alkene)



$$\xrightarrow{H^+}\left[H_3C\overset{+}{C}H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow H_3C-\overset{CH_3}{CH}-\overset{CH_3}{\overset{+}{C}}-CH_3\right]$$

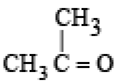
2° carbocation   3° carbocation

$$\xrightarrow{Cl^-}\underbrace{CH_3\overset{Cl}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + CH_3\overset{CH_3}{CH}-\underset{Cl}{\overset{CH_3}{C}}-CH_3}_{\text{B and C}}$$



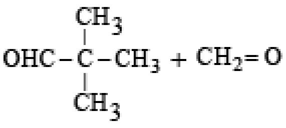
$$CH_3\overset{CH_3}{C}=\overset{CH_3}{C}CH_3$$

(D)



$$CH_3\overset{CH_3}{C}=O$$

(E)

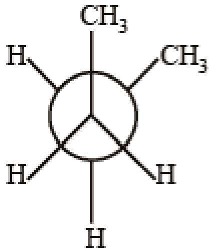


$$OHC-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + CH_2=O$$

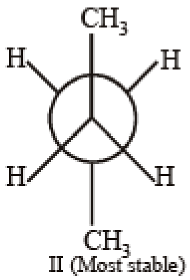
(F) & (G)

Q. 25. Draw Newmann projection of relatively less stable staggered form of n-butane. The reason of low stability of this form is van der Waal's repulsion, torsional strain, or both. (2004 - 2 Marks)

Ans. Sol.



I (Less stable)



II (Most stable)

Newmann projection formulae II is the most stable because the bulky groups (CH_3) are at maximum possible distance from each other. Structure I is relatively less stable because the two CH_3 groups are close to each other leading to vander Waal's repulsion between the two methyl groups.