Hydrocarbons

Level - 0	**DTS-0**

1. **(i)** **Initiation :** $Cl_2 \xrightarrow{h\nu} 2\dot{Cl}$

(ii) **Propagation :**

(a) $CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + H-Cl$ **(b)** $\dot{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \dot{C}l$

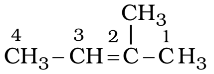
(iii) **Termination :**

(a) $\dot{Cl} + \dot{Cl} \longrightarrow Cl-Cl$ **(b)** $H_3\dot{C} + \dot{C}H_3 \longrightarrow \underset{\text{ethane}}{CH_3-CH_3}$

(c) $H_3\dot{C} + \dot{Cl} \longrightarrow \underset{\text{Chloro methane}}{H_3C-Cl}$

From the above mechanism, it is evident that methyl free radicals are produced during propagation step. If two methyl free radicals combine with each other [as in termination step-(b)], a molecules of ethane is also formed as a side product.

2. **(a)**



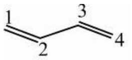
$\overset{4}{CH_3}-\overset{3}{CH}=\overset{\overset{CH_3}{|}}{\underset{2}{C}}-\overset{1}{CH_3}$

2–Methyl but–2–ene

(b) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{CH_3}$

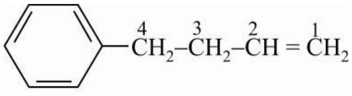
Pent–1–ene–3–yne

(c)



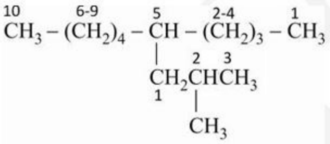
Buta-1, 3-diene

(d)



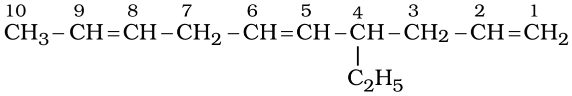
4-phenylbut-1-ene

(e)



5-(2-Methylpropyl)decane

(f)



$\overset{10}{CH_3}-\overset{9}{CH}=\overset{8}{CH}-\overset{7}{CH_2}-\overset{6}{CH}=\overset{5}{CH}-\underset{\underset{C_2H_5}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$

4-Ethyldec-1,5,8-triene

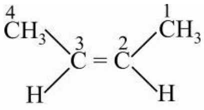
Note: Numbering is done from the side which gives lowest locant to the principal functional group.

3. **(a)** Isomers of C_4H_8 having one double bond are:

(i) $\overset{4}{CH_3}\,\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$

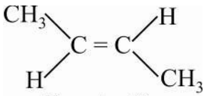
But–1–ene

(ii)



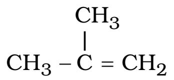
Cis-but-2-ene

(iii)



Trans-but-2-ene

(iv)



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

2-methylprop-1-ene

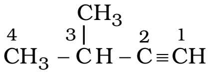
(b) **(i)** $\overset{5}{CH_3}\,\overset{4}{CH_2}\,\overset{3}{CH_2}\,\overset{2}{C}\equiv\overset{1}{CH}$

Pent–1–yne

(ii) $\overset{5}{CH_3}\,\overset{4}{CH_2}-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{CH_3}$

Pent–2–yne

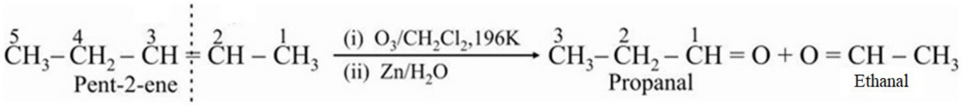
(iii)



$\overset{4}{CH_3}-\overset{\overset{CH_3}{|}}{\underset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{CH}$

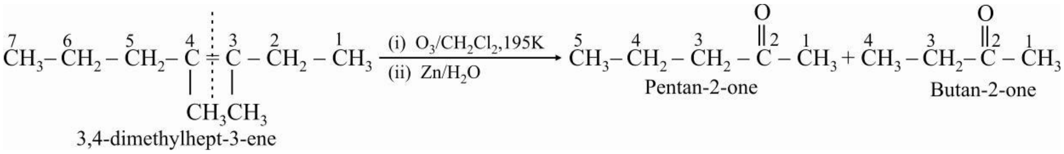
3–methylbut–1–yne

4. **(i)**



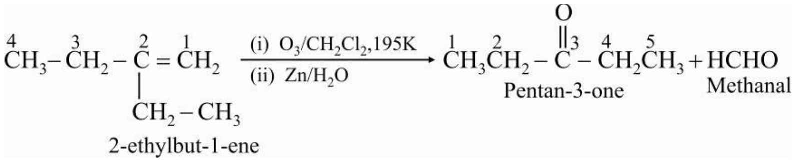
$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2\text{,196K}} \overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H=O+O=CH-CH_3$$

(ii)



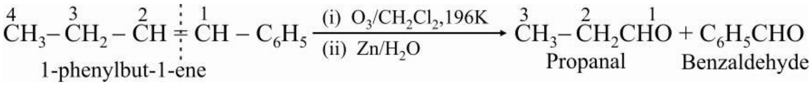
$$\overset{7}{C}H_3-\overset{6}{C}H_2-\overset{5}{C}H_2-\overset{4}{C}(CH_3)=\overset{3}{C}(CH_3)-\overset{2}{C}H_2-\overset{1}{C}H_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2\text{,195K}} \overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}(=O)-\overset{1}{C}H_3+\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}(=O)-\overset{1}{C}H_3$$

(iii)



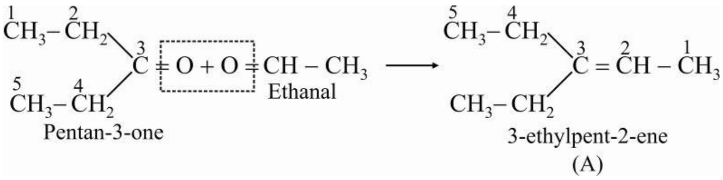
$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}(CH_2-CH_3)=\overset{1}{C}H_2 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2\text{,195K}} \overset{1}{C}H_3\overset{2}{C}H_2-\overset{3}{C}(=O)-\overset{4}{C}H_2\overset{5}{C}H_3+HCHO$$

(iv)

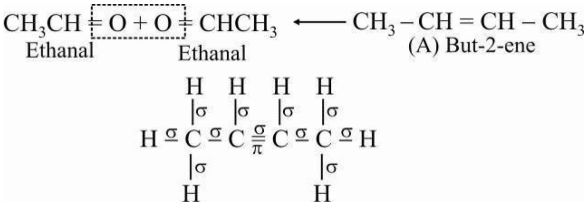


$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H-C_6H_5 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2\text{,196K}} \overset{3}{C}H_3-\overset{2}{C}H_2\overset{1}{C}HO+C_6H_5CHO$$

5.



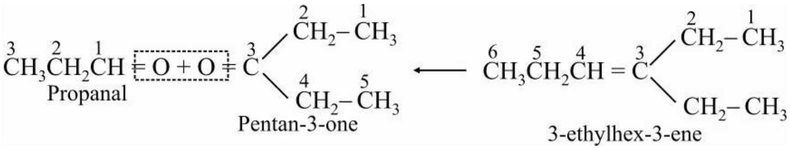
6. An aldehyde having molar mass 44 u is ethanal, CH_3CHO. Write the structures of two molecules of ethanal in such a way that their oxygen atoms pointing towards each other. Join the two ends through the double bond with the removal of both of the oxygen atoms to obtain alkene A.



$$CH_3CH=O+O=CHCH_3 \longleftarrow CH_3-CH=CH-CH_3$$

Hence, alkene (A), i.e., but-2-ene contains three C – C, eight C – H, $\sigma-$bonds and one $C-C$ $\pi-$bond (as given in the question).

7.



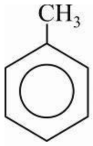
$$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H=O+O=\overset{3}{C}(\overset{2}{C}H_2-\overset{1}{C}H_3)(\overset{4}{C}H_2-\overset{5}{C}H_3) \longleftarrow \overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H=\overset{3}{C}(\overset{2}{C}H_2-\overset{1}{C}H_3)(CH_2-CH_3)$$

8. **(i)** $$\underset{\text{Butane}}{C_4H_{10}(g)}+\frac{13}{2}O_2(g)\xrightarrow{\Delta}4CO_2(g)+5H_2O(g)$$

(ii) $$\underset{\text{Pentene}}{C_5H_{10}(g)}+\frac{15}{2}O_2(g)\xrightarrow{\Delta}5CO_2(g)+5H_2O(g)$$

(iii) $$\underset{\text{Hexyne}}{C_6H_{10}(g)}+\frac{17}{2}O_2(g)\xrightarrow{\Delta}6CO_2(g)+5H_2O(g)$$

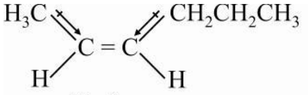
(iv)



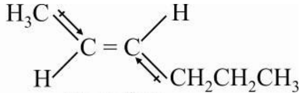
Toluene

$$(g)\text{ or }C_7H_8(g)+9O_2(g)\xrightarrow{\Delta}7CO_2(g)+4H_2O(g)$$

9. Hex-2-ene is $CH_3 - CH_2 - CH_2 - CH = CH - CH_3$. The structures of cis-and trans-isomers of hex-2-ene are shown :



Cis-form

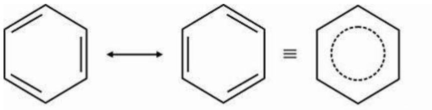


Trans-form

Cis-form is more polar than trans-form. Due to this cis-form has higher dipole moment than trans-form. Thus, the boiling point of cis-isomer is greater than that of trans-isomer because of the greater dipole-dipole interactions between the molecules in it. Further more trans-isomer of hex-2-ene is almost non-polar (weakly polar).

Note : *However the melting point of a trans-isomer is greater than that of cis-isomer ; melting point depends upon effectiveness of packing, which is better for a symmetric structure.*

10. Resonance and delocalization of electrons generally leads to the stability of benzene molecule.



Hybrid Structure

The dotted circle in the hybrid structure represents the six electrons which are delocalized between the six carbon atoms of the benzene ring. Therefore, presence of delocalized $\pi -$ electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

11. The necessary conditions for any system to be aromatic are

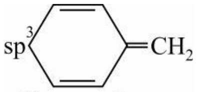
(i) The molecule should be planar.

(ii) The molecule should be cyclic and there should be complete delocalization of the π - electrons in the ring (i.e. complete conjugation)

(iii) The molecule should contain $(4n + 2)\pi$ - electrons, where, n = 0, 1, 2, 3, etc. (Huckel rule).

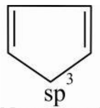
A molecule which does not satisfy any one or more of the above mentioned conditions is said to be non-aromatic.

12. **(i)** The molecule is not planar because of the presence of sp^3 hybridized carbon atom. It contains six $\pi -$ electrons but its $\pi -$ electrons cloud does not surround all the carbon atoms of the ring. Therefore, it is not an aromatic compound.



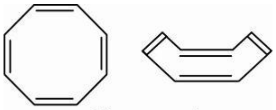
Non-aromatic

(ii) The molecule is not planar because of the presence of sp^3 hybridized carbon atom. Moreover, it contains only $4\pi -$ electrons. Thus, the molecule is not aromatic as it does not contain planar cyclic electron cloud, having $(4n + 2)\pi -$ electrons.



Non-aromatic

(iii) Cyclo octatetraene is non-planar with 8π - electrons and hence, it is non aromatic.



Non-aromatic

13. **(i)** Bromo is o/p-directing while NO_2 is m-directing, so to obtain p-nitrobromobenzene, first do bromination, followed by nitration.

(ii) Chloro is o/p-directing while NO_2 is m-directing, so to obtain m-nitrochlorobenzene, first do nitration followed by chlorination.

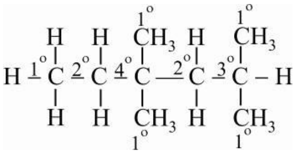
(iii) $-CH_3$ is o/p-directing while NO_2 is m-directing, so to obtain p-nitrotoluene, first do Friedel Craft's alkylation followed by nitration.

(iv) Friedel Craft's acylation introduces a–COR group.

14. 15 H-bonded to five $1^{\circ}C$ - atoms

4 H-bonded to two $2^{\circ}C$ - atoms

1 H-bonded to one $3^{\circ}C$ - atom



15. Van der Waal's force of attractions $\propto$ surface area. Surface area decreases with increase in branching. Hence, boiling point of an alkane decreases with increase in branching due to decrease in van der Waal's forces of attractions.

16. $$CH_3CH=CH_2 \xrightarrow{1.\,H^+} \underset{1^{\circ}\,C^+\text{(Less stable)}}{CH_3CH_2-\overset{+}{C}H_2} + \underset{2^{\circ}\,C^+\text{(More stable)}}{CH_3\overset{+}{C}H-CH_3} \xrightarrow{Br^-} \underset{\text{Major product}}{CH_3\overset{\overset{Br}{|}}{C}H-CH_3}$$

Note : Stability of carbocation follows : $\overset{+}{C}H_3 < 1^{\circ} < 2^{\circ} < 3^{\circ}$.

It depends upon $+I$ effect and hyperconjugation.

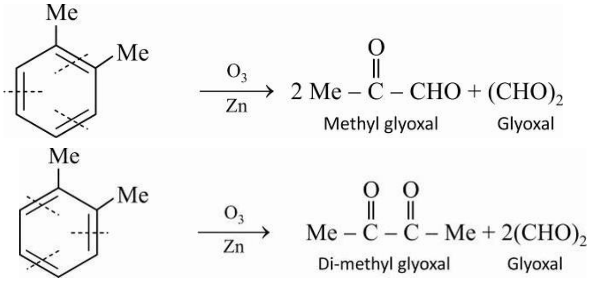
$$CH_3CH=CH_2 \xrightarrow{Br^{\circ}} \underset{2^{\circ}\text{ free radical (More stable)}}{CH_3\overset{\circ}{C}H-CH_2Br} + \underset{1^{\circ}\text{ free radical (Less stable)}}{CH_3CH(Br)-\overset{\circ}{C}H_2}$$

$$CH_3\overset{\circ}{C}H-CH_2Br \xrightarrow{HBr} \underset{\text{(Major)}}{CH_3CH_2CH_2Br} + \overset{\circ}{B}r \text{ (Will further propogate the reaction)}$$

Note : Benzoyl peroxide generates bromine free radical for the reaction as follows :

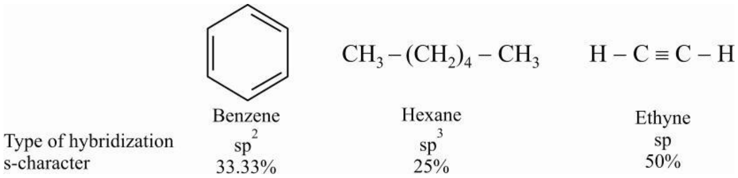
$$\left(Ph-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-Ph\right) \longrightarrow Ph-\overset{\overset{O}{\|}}{C}-\overset{\circ}{O} \xrightarrow{-CO_2} \overset{\circ}{Ph} \xrightarrow{HBr} PhH + \overset{\circ}{Br}$$

17.



Note : Due to two Kekule structures ; two resonating forms give different products, which justifies the concept of resonance in benzene and its derivatives.

18. The hybridization state of carbon in the given compounds is

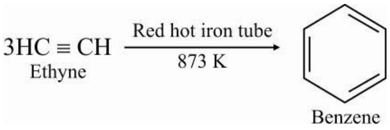


	Benzene	$CH_3-(CH_2)_4-CH_3$ Hexane	$H-C\equiv C-H$ Ethyne
Type of hybridization	sp^2	sp^3	sp
s-character	33.33%	25%	50%

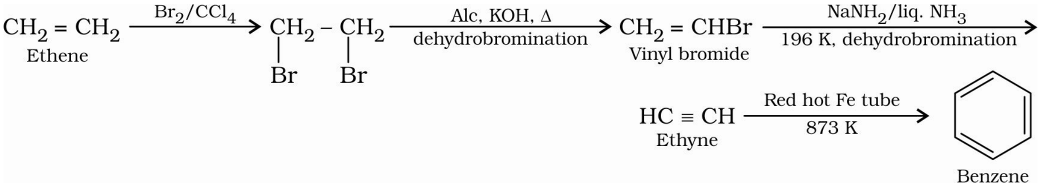
Acidic character increases with increase in s-character of the orbital. Hence decreasing order of acidic behaviour of benzene, n-hexane and ethyne is as follows : Ethyne > Benzene > Hexane

19. Due to the presence of delocalized $6\pi -$ electrons , benzene acts as a nucleophilic substrate. So, it attracts the electrophilic reagent (electron deficient species) towards itself but repels the nucleophilic reagents. That's why benzene gives electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty. Also when an electrophile (E^+) approaches benzene, a stable intermediate is formed (resonance).

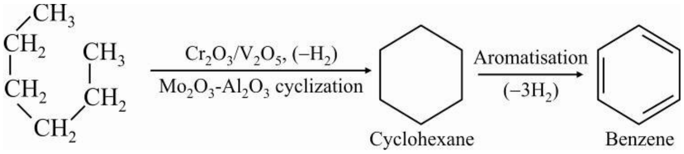
20. **(i)**



(ii)



(iii)



21. Presence of electron releasing group (or activating group) increases the electron density in benzene nucleus. Therefore, electrophile will attack benzene nucleus easily. But the presence of electron withdrawing group like $-NO_2$ decreases the electron density in benzene ring. Therefore, electrophile will attack benzene nucleus with difficulty.

The order of reactivity towards electrophile, E^+ in order of their decreasing relative reactivity is

(a) Chlorobenzene > p-nitrochlorobenzene > 2, 4-dinitrochlorobenzene

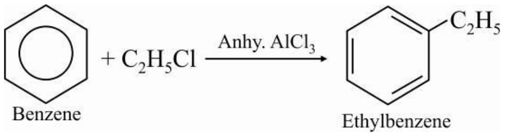
(b) $\text{Toluene} > p-CH_3-C_6H_4-NO_2 > p-O_2N-C_6H_4-NO_2$

22. Nitration of benzene is an electrophilic substitution reaction. Presence of electron releasing group such as $-CH_3$ activates the benzene nucleus towards electrophilic substitution while presence of electron withdrawing group such as $-NO_2$ deactivates the benzene nucleus towards electrophilic substitution.

Therefore, the ease of nitration decreases in the order toluene > benzene > m-dinitrobenzene

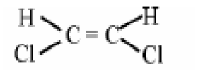
Thus, toluene will undergo nitration most easily.

23.

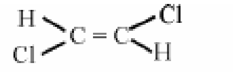


In ethylation of benzene, ethyl group is introduced in the benzene ring. This is carried out by Friedel Crafts alkylation reaction of benzene. Anhydrous $FeCl_3$ or $SnCl_4$ can also be used in place of anhydrous $AlCl_3$ as a catalyst. $FeCl_3$ and $SnCl_4$ are also Lewis acids.

24. **(i)**

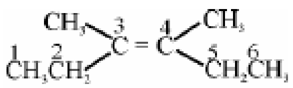


cis-1, 2-Dichloroethene

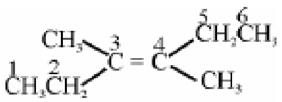


trans-1, 2-Dichloroethene

(ii)



cis-3,4-Dimethylhex-3-ene

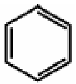


trans-3,4-Dimethylhex-3-ene

25. $$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[-H_2O]{NaOH(aq)} \underset{\text{Sod. ethanoate}}{CH_3COONa} \xrightarrow[630\ K]{\text{Soda-lime}} \underset{\text{Methane}}{CH_4} \xrightarrow[\text{(Chlorination)}]{Cl_2 / hv} \underset{\text{Chloromethane}}{CH_3Cl}$$

$$\xrightarrow[\text{(Wurtz reaction)}]{\text{Na, dry ether}} \underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[\text{(Chlorination)}]{Cl_2, hv} \underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow[\Delta]{KOH(alc.)} \underset{\text{Ethene}}{CH_2{=}CH_2} \xrightarrow{Br_2/CCl_4}$$

$$\underset{\text{1, 2- Dibromoethane}}{BrCH_2 - CH_2Br} \xrightarrow[\Delta]{KOH(alc.)} \underset{\text{Bromoethene}}{CH_2{=}CHBr} \xrightarrow[\text{in. liq.} NH_3]{NaNH_2} \underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[873\,K]{\text{Red hot Fe tube}}$$



Benzene

Alternatively, convert ethanoic acid to ethene as follows and then convert ethane to benzene as described above

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{LiAlH_4,\ \text{ether}} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\substack{433-443K \\ \text{(Dehydration)}}]{\text{conc.}\ H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2}$$