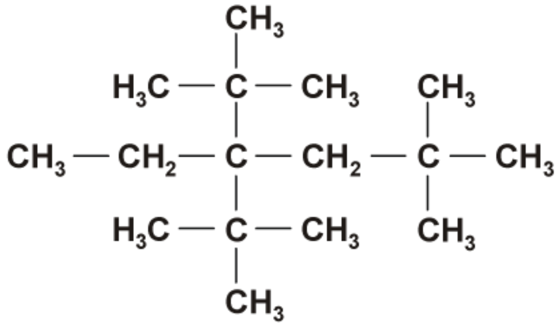
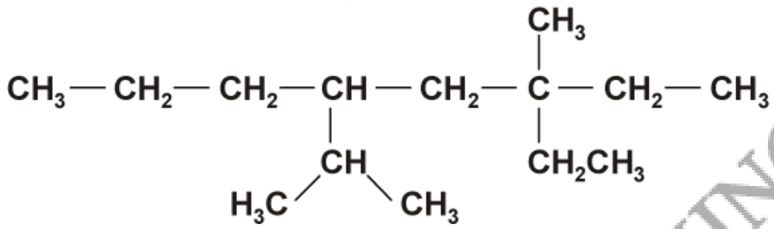
Date: 16/10/2021

Q1. Draw the structure of the (2-Methyl-3-isopropylheptane), showing all C and H atoms.

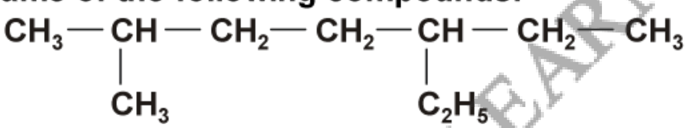
Q2. Give the IUPAC name of the following compounds:



Q3. Give the IUPAC name of the following compounds:

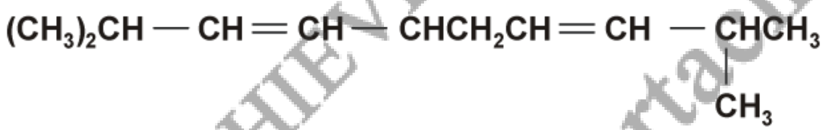


Q4. Give the IUPAC name of the following compounds:



Q5. Write IUPAC name of the following compounds:

Q6. Write IUPAC name of the following compounds:



Q7. Write IUPAC name of the following compounds: $C_2H_5C(CH_3)_2C_2H_5$.

Q8. Write IUPAC name of the following compounds: $(CH_3)_3CCH_2C(CH_3)_3$.

Q9. Draw the structure of the following compounds: 5-sec-Butyl-4-isopropyldecane.

Q10. Draw the structure of the following compounds: 4-Ethyl-2-methylhexane.

Q11. Write IUPAC name of the following compounds: $(CH_3)_3C — CH_2 — CH(C_2H_5)_2$.

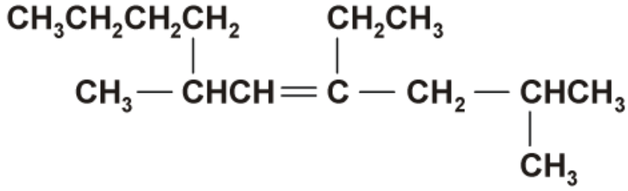
Q12. Write IUPAC name of the following compounds: $(C_2H_5)_4C$.

Q13. Draw the structure of the (Dicyclopropylmethane), showing all C and H atoms.

Q14. Write IUPAC name of the following compounds:

$$CH_2 = C(CH_2CH_2CH_3)_2$$

Q15. Write IUPAC name of the following compounds:



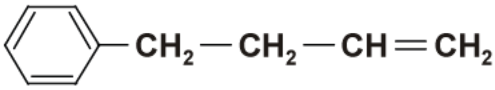
Q16. Write IUPAC name of the following compounds:

$$CH_2 = CH - C \equiv C - CH_3$$

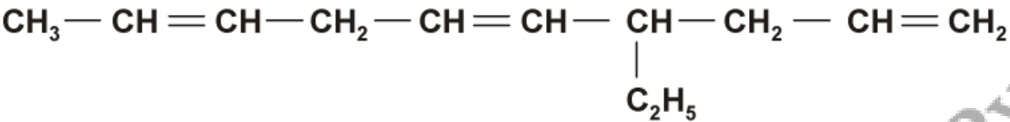
Q17. Write IUPAC name of the following compounds:

$$CH_3CH = C(CH_3)_2$$

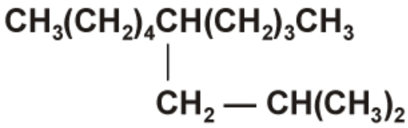
Q18. Write IUPAC name of the following compounds:



Q19. Write IUPAC name of the following compounds:

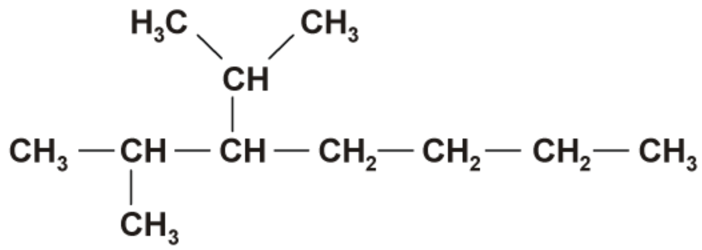


Q20. Write IUPAC name of the following compounds:



Date: 16/10/2021

S1.



S2. 4-*tert*-butyl-4-ethyl-2, 2, 5, 5-tetramethylhexane.

S3. 3-Ethyl-5-isopropyl-3-methyloctane.

S4. 5-Ethyl-2-methylheptane.

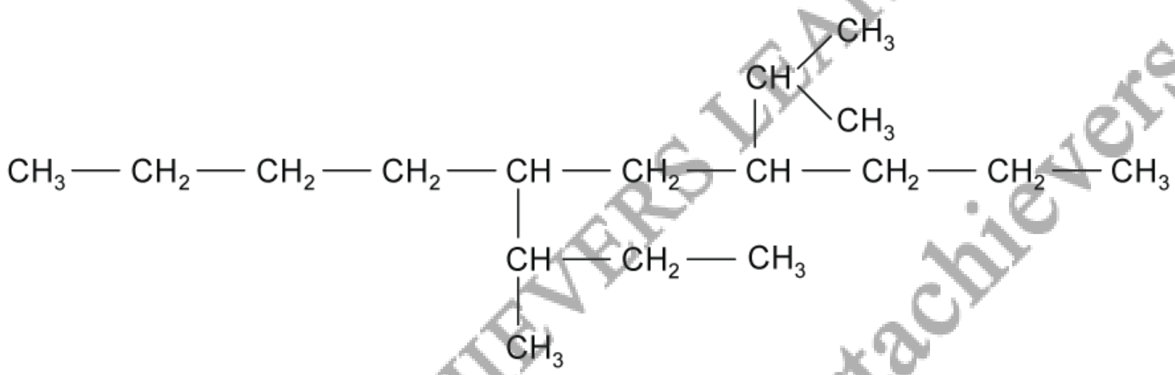
S5. Oct-1,3,5,7-tetraene.

S6. 2,9-dimethyldec-3,7-diene

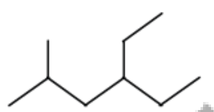
S7. 3,3-dimethylpentane

S8. 2,2,4,4-tetramethyl pentane.

S9.



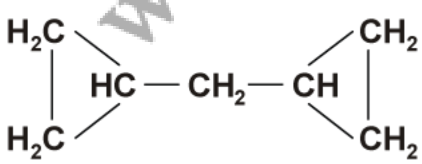
S10.



S11. 4-Ethyl-2, 2-dimethylhexane.

S12. 3, 3-diethylpentane.

S13.



S14. 2-propyl pentene.

S15. 4-ethyl-2,6-dimethyldec-4-ene.

S16.

$$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C} \equiv \overset{4}{C} - \overset{5}{C}H_3$$

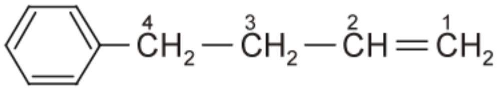
Pent-1-en-3-yne

S17.

$$\overset{4}{C}H_3\overset{3}{C}H = \overset{2}{C}(CH_3) - \overset{1}{C}H_3$$

2-Methylbut-2-ene

S18.



4-Phenylbut-1-ene

S19.

$$\overset{10}{C}H_3 - \overset{9}{C}H = \overset{8}{C}H - \overset{7}{C}H_2 - \overset{6}{C}H = \overset{5}{C}H - \overset{4}{C}H(C_2H_5) - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$$

4-Ethyldeca-1, 5, 8-triene

S20.

$$\overset{10}{C}H_3 - \overset{6-9}{(CH_2)_4} - \overset{5}{C}H[\overset{1}{C}H_2 - \overset{2}{C}H(CH_3) - \overset{3}{C}H_3] - \overset{2-4}{(CH_2)_3} - \overset{1}{C}H_3$$

5-(2-Methylpropyl)decane or 5-isobutyldecane

Date: 16/10/2021

Q1. How many isomers are possible for monosubstituted and disubstitued benzene?

Q2. What is the cause of geometrical isomerism in alkenes?

Q3. What is the difference between isomers and conformers?

Q4. Is it possible to isolate pure staggered ethane or pure eclipsed ethane at room temperature?

Q5. Why do alkynes not show geometrical isomerism?

Q6. Which of the two:
trans-but-2-ene or *trans*-pent-2-ene is nonpolar?

Q7. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

Q8. State the type of isomerism shown by following compounds:

(a) $CH_3-CH_2=CH-CH_3$ and $CH_3-CH2-CH=CH_2$

(b) $CH_3-C\equiv C-CH_3$ and $CH_2=CH-CH=CH_2$

Q9. State the type of isomerism shown by following compounds:

(a) CH_3-O-CH_3 and CH_3-CH_2-OH

(b) $CH_3-CO-CH_3$ and CH_3-CH_2-CHO

Q10. State the type of isomerism shown by following compounds:

(a) $CH_3.CO.C_3H_7$ and $C_2H_5.CO.C_2H_5$

(b) $CH_3.CO.CH_2.CH_2.CH_3$ and $CH_3.CO.CH(CH_3)_2$

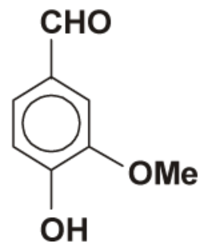
Q11. Write tautomeric forms for phenol.

Q12. Draw the *cis*- and *trans*-structures of hex-2-ene. Which isomer will have higher b.p. and why?

Q13. Mark the asymmetric carbon atoms and give the number of optical isomers in the following compounds:
$CH_3-(CHOH)_2-COOH$

Q14. Fill in the blank:
The structure of the enol form of $CH_3-CO-CH_2-CO-CH_3$ with intramolecular hydrogen bonding is ....

Q15. Identify the functional groups in the following:

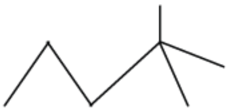
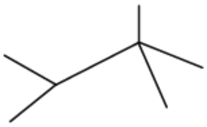


Q16. What type of structural isomerism is shown by

$$CH_3-S-CH_2CH_2CH_3 \quad \text{and} \quad CH_3-S-CH\begin{matrix}CH_3\\CH_3\end{matrix}$$

Q17. For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated: C_4H_8 (one double bond)

Q18. Arrance the following in increasing order of their release of energy on combustion:

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

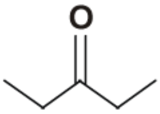
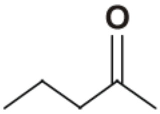
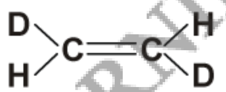
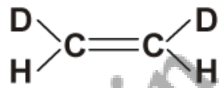
Q19. Draw the structures of three cycloalkane isomers weith molecular formula C_5H_{10} each with a different size ring.

Q20. Write the structural formulae of all the possible isomers of $C_2H_2Cl_2$ and indicate which of these is non-polar?

Q21. For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated:

(a) C_4H_8 (one double bond) (b) C_5H_8 (one triple bond)

Q22. What is the relation between the following pairs? Are they structural or geometrical isomers?

(a)  and  (b)  and 

Q23. Draw structures of all isomeric ethers corresponding to molecular formula $C_5H_{12}O$.

Q24. What is the relationship between the members of following pairs of structures? Are they structural, gemetrical isomers or resonance contributors?

Q25. Classify the following pairs as positioon, chain, functional isomers or metamers:

(a) Diethylamine and Methylpropylamine (b) Ethanol and Dimethylether

Q26. Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

Q27. Out of *cis* and *trans* 2,3-dichlorobut-2-ene:

(a) Which is more polar? (b) Which has higher boiling point?

(c) Which has higher melting point?

Q28. Write structures and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10}. Which of these can exhibit geometric isomerism?

Q29. Write structures and IUPAC names of different isomers corresponding to the 5th member of alkyne wires.

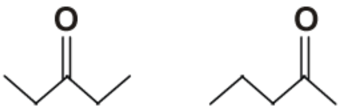
Q30. Answer of the following question is a single digit integer ranging from 0 to 9:
What is the total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_5H_6?

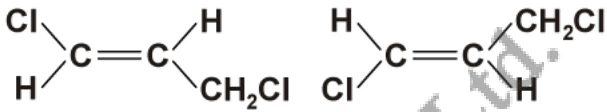
Hint: The possible cyclic isomers are:

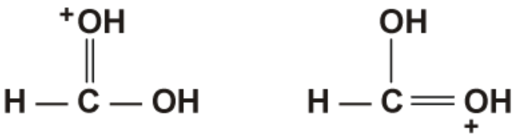
Q31. Draw polygon formulae for the molecular formula C_5H_{10}.

Q32. How many cyclic and acyclic isomers are possible for the molecular formula C_3H_6O? Draw these.

Q33. What is the relationship between the members of the following pairs of structures? Are they identical, structural, geometrical or resonance contributors?

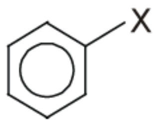
(a) 

(b) 

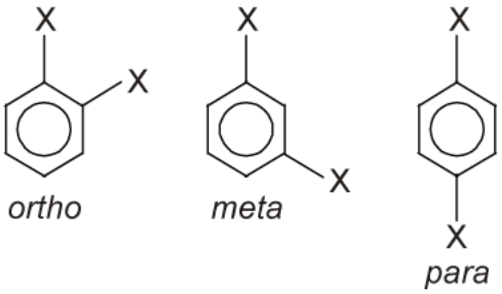
(c) 

(d) 

Date: 16/10/2021

S1. There is one monosubstituted benzene as 

There are three disubstituted benzenes.



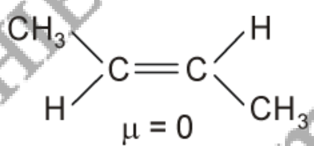
S2. Alkenes have a π-bond and the restricted rotation around the π-bond gives rise to geometrical isomerism.

S3. Isomers cannot be changed into one another and therefore, these are interconvertible. On the other hand, conformers are interconvertible.

S4. The energy difference is very small and can be easily overcome by the collisions of the molecules at room temperature. Therefore, it is not possible to isolate either pure eclipsed or pure staggered form at room temperature.

S5. Alkynes have linear shape and therefore, do no show geometrical isomerism

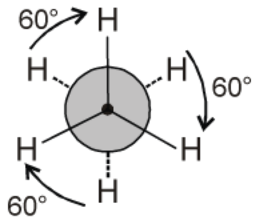
S6. In *trans*-but-2-ene, the dipole moments of the two C — CH_3 bonds are equal and opposite and therefore, they cancel out each other. Hence, *trans*-2-butene is not-polar.



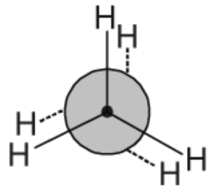
S7. Rotation around C — C single bond is not completely free and it is restricted due to repulsions between the electron clouds of C — H bonds in the adjacent carbon atoms. Therefore, ethane exists in infinite number of conformations. Out of these, two extreme conformations are staggered and eclipsed.

(a) **Staggered conformation:** In this arrangement, the hydrogens of the two carbon atoms are staggered with respect to one another. As a result, they are at maximum distance apart and have minimum repulsion between them.

(b) **Eclipsed conformation:** In this conformation, the hydrogens of one carbon atom are directly behind those of the other. Consequently, the repulsion in these atoms is maximum. The sawhorse projections of these conformations are represented in figure (a). The newman projections for staggered and eclipsed conformations of ethane are shown in figure (b). It is clear that when the staggered conformation is rotated through an angle of 60°, it changes to eclipsed conformation and similarly, when eclipsed conformation is rotated through the same angle, it gives back the staggered conformation.



(a)
Staggered conformation



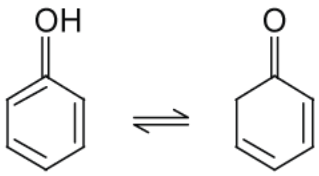
(b)
Eclipsed conformation

S8. (a) Position isomerism (b) Functional isomerism

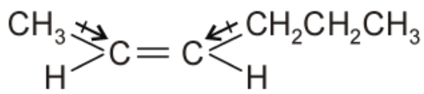
S9. (a) Functional isomerism (b) Functional isomerism

S10. (a) Position isomerism (b) Chain isomerism

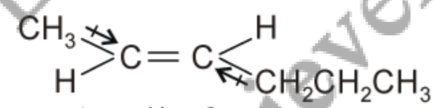
S11.



S12. The structure of *cis*- and *trans*-Hex-2-ene are:



cis-Hex-2-ene



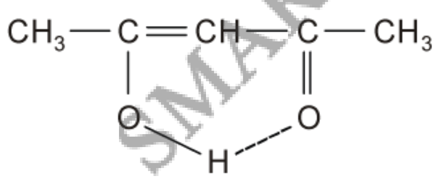
trans-Hex-2-ene

cis-Hex-2-ene has large dipole moment and therefore will have stronger dipole-dipole interactions and hence higher boiling point.

S13. $CH_3 — \overset{*}{C}H(OH) — \overset{*}{C}H(OH) — COOH$

The starred carbon atoms are asymmetric and the number of optical isomers is 4.

S14.



S15. — CHO is the principal functional group.

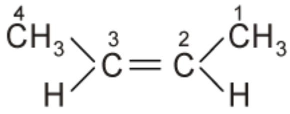
— OH and — OMe are secondary functional groups.

S16. Metamerism.

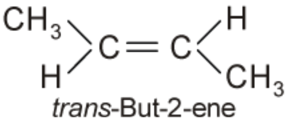
S17. Isomers of C_4H_8 having one double bond are:

(a) $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H = \overset{1}{C}H_2$

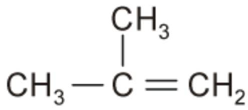
But-1-ene

(b) 

cis-But-2-ene

(c) 

trans-But-2-ene

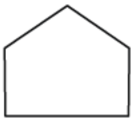
(d) 

2-Methylprop-1-ene

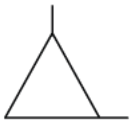
S18. Largest the number of carbon atoms having maximum hydrogens (*i.e.*, CH_3 groups), greater is the heat of combustion. Thus, the increasing order of heat of combustion:

(iii) < (iv) < (i) < (ii).

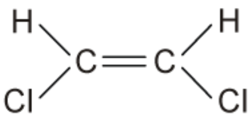
S19.

(a)  Cyclopentane

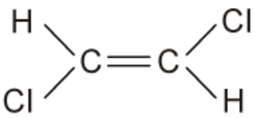
(b)  Methyl cyclobutane

(c)  1, 1-Dimethyl cyclopropane or  1, 2-Dimethyl cyclopropane

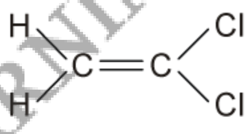
S20.



(i) *cis*-1, 2-dichloroethene



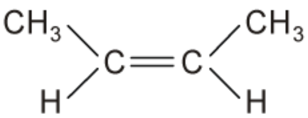
(ii) *trans*-1, 2-dichloroethene

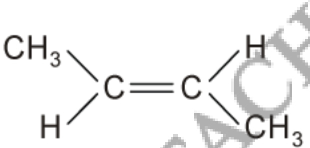


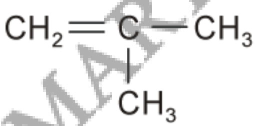
(iii) 1, 2-dichloroethene

Out of these (ii) is non-polar.

S21. (a) (i) $CH_2 = CH - CH_2 - CH_3$ But-1-ene

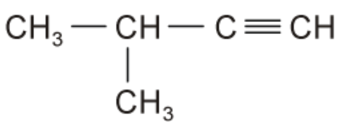
(ii)  *cis*-But-2-ene

(iii)  *trans*-But-2-ene

(iv)  2-Methylpropene

(b) (i) $HC \equiv C - CH_2 - CH_2 - CH_3$ Pent-1-yne

(ii) $CH_3 - C \equiv CH - CH_2 - CH_3$ Pent-2-yne

(iii)  3-Methylbut-1-yne

S22. (a) Metamer (structural isomers) (b) *cis* and *trans* (geometrical isomers)

S23. The isomeric ethers for $C_5H_{12}O$ are:

(a) $CH_3CH_2CH_2CH_2OCH_3$

(b) $CH_3CH_2CH_2OCH_2CH_3$

(c) $\underset{\displaystyle CH_3}{\underset{|}{CH_3CH}} — OCH_2CH_3$

(d) $CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} — OCH_3$

S24. These are resonance hybrid structure.

Resonance contributors.

S25. (a) Metamers

(b) Functional isomer

S26. (a) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

n-Hexane

(b) $CH_3 — \underset{\displaystyle CH_3}{\underset{|}{CH}} — CH_2— CH_2— CH_3$

2-Methylpentane

(c) $CH_3— CH_2 — \underset{\displaystyle CH_3}{\underset{|}{CH}} — CH_2— CH_3$

3-Methylpentane

(d) $CH_3— \underset{\displaystyle CH_3}{\underset{|}{CH}} — \underset{\displaystyle CH_3}{\underset{|}{CH}} — CH_3$

2,3-Dimethylbutane

(e) $CH_3— \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} — CH_2— CH_3$

2, 2-Dimethylbutane

S27. (a) Out of *cis* and *trans* 2, 3-dichlorobut-2-ene, *cis* isomer is more polar because in *trans* isomer dipole moment of one C — Cl bond cancels the dipole moment of the other C — Cl bond whereas in *cis* isomer they do not cancel each other.

(b) The boiling point *cis* isomer is higher than that of *trans* isomer because the interparticle forces in the *cis* isomer are stronger due to greater polarity.

(c) The melting point of *trans* isomer is higher than that of *cis* isomer because molecules of *trans* isomer due to close to each other. So, forces of attraction between them are quite strong.

S28. (a) $CH_2 = CH — CH_2 — CH_2 — CH_3$

Pent-1-ene

(b) $CH_3 — CH = CH — CH_2 — CH_3$

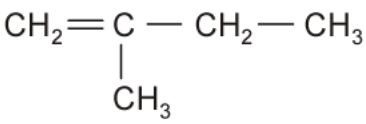
Pent-2-ene

(c) $CH_3— \underset{\displaystyle CH_3}{\underset{|}{C}} = CH — CH_3$

2-Methylbut-2-ene

(d) $CH_3— \underset{\displaystyle CH_3}{\underset{|}{CH}} — CH = CH_2$

3-Methylbut-1-ene

(e) 

2-Methylbut-1-ene

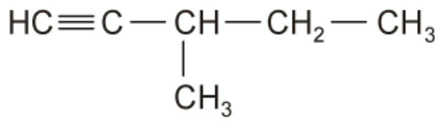
The compound (b), pent-2-ene can exhibit geometric isomerism because it has two different atoms or groups attached to both double bonded carbon atoms.

S29. 5th member of alkyne has the molecular formula C_6H_{10}. The possible isomers are:

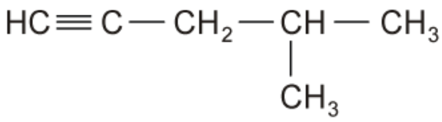
(a) $HC \equiv C - CH_2 - CH_2 - CH_2 - CH_3$
Hex-1-yne

(b) $CH_3 - C \equiv C - CH_2 - CH_2 - CH_3$
Hex-2-yne

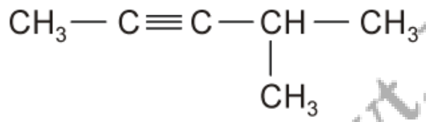
(c) $CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$
Hex-3-yne

(d) 

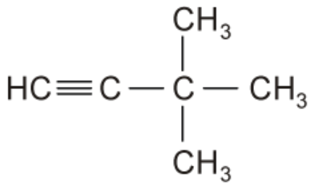
3-Methylpent-1-yne

(e) 

4-Methylpent-1-yne

(f) 

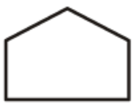
4-Methylpent-2-yne

(g) 

3,3-Dimethylbut-1-yne

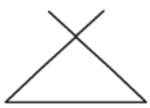
S30. 5.

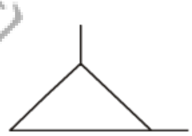
S31.

(a) 

(b) 

(c) 

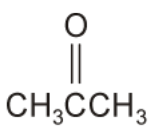
(d) 

(e) 

S32. Seven isomers are possible. These are:

(a) Acyclic isomers:

(i) CH_3CH_2CHO
Propanal

(ii) 
Propanone

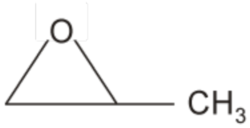
(iii) $CH_2 = CHCH_2OH$
Prop-2-en-1-ol

(iv) $CH_2 = CHOCH_3$
Methoxyethene

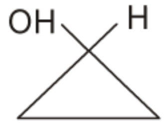
(b) Cyclic isomers:

(i) 

Oxetane

(ii) 

Propylidene oxide

(iii) 

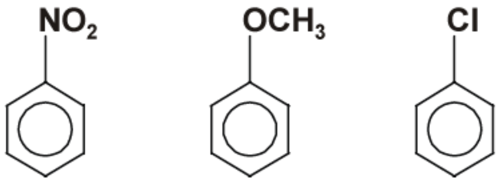
Cyclopropanol

S33. (a) Structural isomers (b) Identical

(c) Resonance contributors (d) Geometrical isomers.

Date: 16/10/2021

Q1. Arrange the following set of compounds in the order of decreasing reactivity with an electrophile. Give reason.



Q2. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids?

Q3. Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?

Q4. What effect does branching of an alkane chain has on its boiling point?

Q5. What are the necessary conditions for any system to be aromatic?

Q6. Why is benzene extra ordinarily stable though it contains three double bonds?

Q7. Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour.

Q8. Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?

Q9. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+.

Toluene, *p*-$H_3C — C_6H_4 — NO_2$, *p*-$O_2N — C_6H_4 — NO_2$.

Q10. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+.

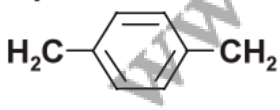
Chlorobenzene, 2, 4-dinitrochlorobenzene, *p*-nitrochlorobenzene

Q11. In the alkane, $H_3CCH_2C(CH_3)_2CH_2CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the total number of H atoms bonded to each one of these.

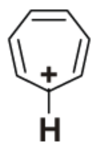
Q12. Why do alkenes prefer to undergo electrophilic additon reactions while arenes prefer electrophilic substitution reaction? Explain.

Q13. Which of the following compounds are aromatic according to Huckel rule?

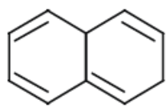
(a) 

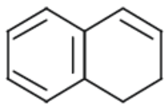
(b) 

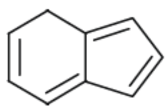
(c) 

(d) 

(e) 

(f) 

(g) 

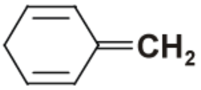
(h) 

Q14. Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

Q15. What effect does branching of an alkane chain has on its melting point?

Q16. Why do alkynes undergo nucleophilic addition reactions while simple alkenes do not?

Q17. Explain why the following systems are not aromatic?

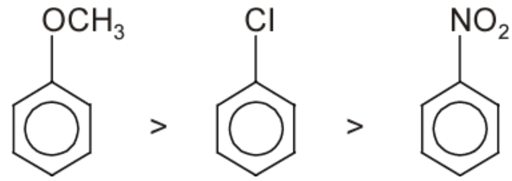
(a) 

(b) 

(c) 

Date: 16/10/2021

S1. The + R effect of — OCH_3 group is more than that of — Cl, whereas — NO_2 group has – R effect. Therefore, reactivity of the substituted benzene rings is



S2. The bond dissociation enthalpy decreases in the order, HCl > HBr > HI, therefore, the order of reactivity is in the reverse order *i.e.*, HI > HBr > HCl.

S3. CH_3 group is electron releasing group while — NO_2 group is electron withdrawing group. Therefore, the electron density will be more in toluene than in benzene and the electron density in *m*-dinitrobenzene will be less than in benzene. Therefore, the case of nitration decreases in the order:

tolune > benzene > *m*-dinitrobenzene.

S4. The boiling point of the alkanes decreases with branching. This is because with the increase in branching, the surface area of an alkane approaches that of a sphere. Since sphere has minimum surface are, therefore, van der Waals forces of attraction are minimum and hence boiling point decreases with branching.

S5. The necessary conditions for a molecule to be aromatic are:

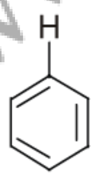
(a) The molecule should contain a cyclic cloud of delocalized π-electrons above and below the plane of the molecule.

(b) For the delocalisation of π-electrons the ring must be planar to allow cyclic overlap of *p*-orbitals.

(c) It should contain $(4n + 2)$ π-electrons where $n = 0, 1, 2, 3, \ldots$. This is known as Huckel rule.

S6. The extra ordianrily stability of benzene is due to resonance. In benzene, all the six π-electrons of three double bonds get delocalised resulting stability of the molecule.

S7. Ethyne > Benzene > *n*-hexane

$HC \equiv CH$ >  > $CH_3(CH_2)CH_3$

Ethyne | Benzene | *n*-hexane

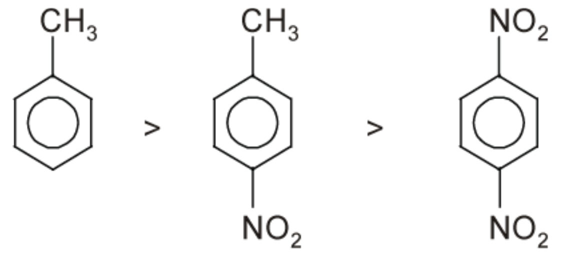
sp carbon (50% *s*-character) sp^2 carbon (33% *s*-character) sp^3 carbon (25% *s*-character)

This is because of maximum *s*-character in ethyne (50%) as compared to benzene (33%) and *n*-hexane (25%).

S8. Out benzene, *m*-dinitrobenzene and toluene, toluene would undergo nitration most easily because methyl group in toluene is electron releasing group and hence, it activates the benzene ring towards electrophilic reactions such as nitration. On the other hand, nitro groups in dinitrobenzene are electron withdrawing in nature. They deactivate the benzene towards electrophilic substitution reactions. Thus, ease of nitration in these compounds is in the order:

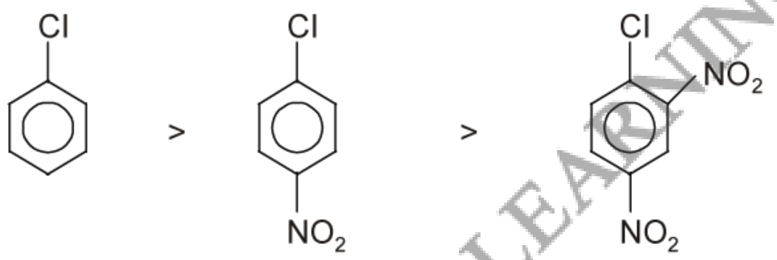
Toluene > Benzene > *m*-Dinitrobenzene.

S9. Methyl group is an elecrtron releasing group. It increases the reactivity of benazene ring with an electrophile. On the other hand, nitro group is an electron withdrawing group. It deactivates the benzene ring towards reaction with an electrophile. Therefore, the decreasing order of reactivity with an electrophile E^+ is



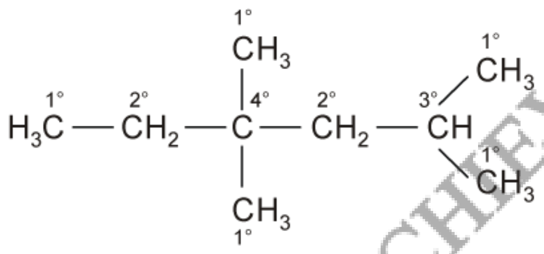
Toluene 4-Nitrotoluene 1, 4-Dnitrobenzene

S10. Nitro group is electron withdrawing group. It deactivates the benzene ring towards reaction with electrophile. Thus, greater the number of nitrogroups attached to the benzene ring, smaler is its reactivity with an electrophile E^+.



Chlorobenzene *p*-Nitrochlorobenzene 2, 4-Dnitrochlorobenzene

S11.



1° Carbon atoms = 5

Hydrogen atoms attached to 1° carbon atoms = 15

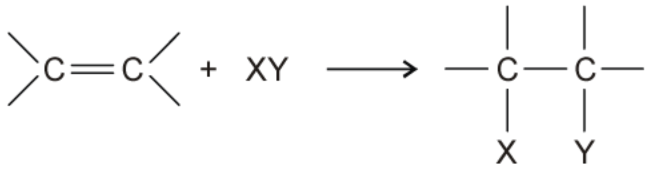
2° Carbon atoms = 2

Hydrogen atoms attached to 2° carbon atoms = 4

3° Carbon atom = 1

Hydrogen atoms attached to 3° carbon atom = 1.

S12. Due to the presence of π-electron cloud above and below the plane of alkenes and arenes, these are electron rich molecules and therefore, provide sites for the attack of electrophiles. Hence, they undergo electrophilic reactions. The alkenes undergo electrophilic additon reactions because alkenes are unsaturated molecules, For example,



Addition product

Arenes, on the other hand cannot undergo electrophilic addition reactions. This is because benzene has a large reasoance energy of 150.4 kJ mol^{-1}. During electrophilic addition reaction two new σ-bonds are formed but the aromatic character of benzene gets destroyed and therefore, reasonnce energy of benzene ring is lost. Hence, electrophilic addition reactions of arenes are not energetically favourable. Arenes, in contrast undergo electrophilic substitution reactions in which σC — H bond is broken and new σC — X bond is formed. The aromatic character of benzene ring is not destroyed and benzene retains its resoanace energy. Hence, arenes undergo electrophilic substitution reactions.

S13. (d), (e), (g) are aromatic. (g) is aromatic because out of 8π electrons, it has 6π delocalised electrons in one six membered planar ring, which obey Huckel rule and therefore, it is aromatic.

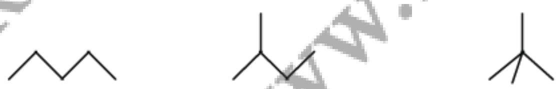
S14. For preparing alkanes containing odd number of carbon atoms, a mixture of two alkyl halides has to be used. These two alkyl halides may react in three different ways producing a mixture of three alkane of odd number of C — atoms.

$$\underset{\text{Bromoethane}}{CH_3CH_2}\boxed{Br + 2Na + Br}CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

$$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2}\boxed{Br + 2Na + Br}CH_2CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{n\text{-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

$$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2}\boxed{Br + 2Na + Br}\underset{\text{Bromoethane}}{CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{n\text{-Pentane (desire)}}{CH_3CH_2CH_2CH_2CH_3}$$

S15. Melting point of a compound depends not only upon size of the molecule but also upon the packing of the molecules in the crystal lattice. Generally, the branching in alkane results in less efficient packing and hence more the branching in the alkane lower is the melting point. However, if the branching leads to a more compact structure, which can pack more closely in solid state, the melting point increases. For example, among isomeric pentanes neo-pentane has the highest melting point (because its molecules being almost spherical pack more closely in crystal lattice) while 2-methylbutane has the lowest (because its molecules pack least efficiently due to side chain). Thus, branching may increase or decrease the melting point.



Pentane m.p. = 143.3 K | 2-Methylbutane m.p. = 113.1 K | 2, 2-Dimethylbutane m.p. = 256.4 K

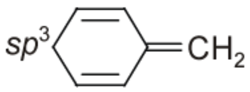
S16. Nucleophilic addition proceeds via carbanion as intermediate. The intermediate carbanion formed rom nucleophilic attack on alkyne is more stable than formed from alkene. This is due to greater electronegativity of the sp^2-hybridized carbon than the sp^3-hybridized carbon. therefore, alkenes undergo nucleophilic addition reactions while simple alkenes do not.

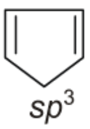
$$R-C\equiv C-H + \ddot{N}u \longrightarrow R-\underset{\displaystyle Nu}{\underset{|}{C}}=\overset{\bar{..}}{C}-H$$

More stable
(Carbon atom carrying negative charge is sp^2-hybridized)

$$R-CH=CH_2 + \ddot{N}u \longrightarrow R-\underset{\displaystyle Nu}{\underset{|}{C}}-\overset{\bar{..}}{C}H_2$$

Less stable
(Carbon atom carrying negative charge is sp^3-hybridized)

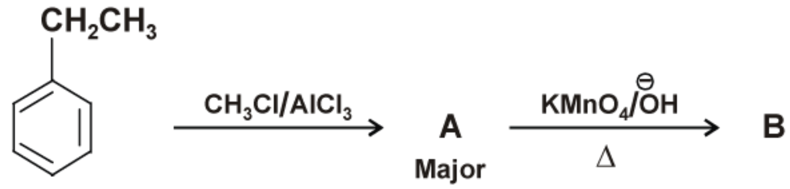
S17. (a)  contain one sp^3 hyridised carbon atom and therefore, the system is not planar. Though it contains 6π-electrons but the system is not fully conjugated because all the 6π-electros donot form a cyclic electron cloud which surrounds all the atoms of the ring. Therefore, the compound is not aromatic.

(b)  is not aromatic because it contains one sp^3 hybridised carbon atom and the molecule is not planar. Moreover, it contains only 4π-electrons and does not obey Huckel rule *i.e.*, $(4n + 2)$-π-electrons.

(c)  is not aromatic because it is a non-planar system having 8π-electrons. Therefore, it does not obey Hxckel rule *i.e.*, $(4n + 2)$-π-electrons rule.

Date: 16/10/2021

Q1. **Complete the following reaction**



Q2. **Give the product of ozonolysis of *p*-xylene.**

Q3. **Give the product of ozonolysis of isoprene.**

Q4. **Give the product of ozonolysis of mesitylene.**

Q5. **Complete the following:**

$$C_6H_5CH{=}CH_2 \xrightarrow{Br_2} [A] \xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3 equi)}} [B]$$

Q6. **Predict the major product in the following reaction:**

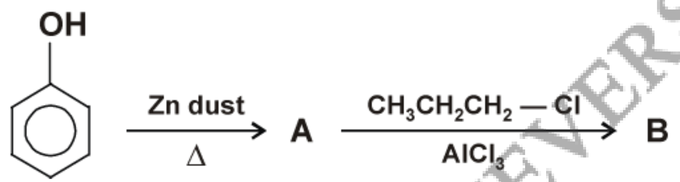
$$R-C{\equiv}C-R + H_2 \xrightarrow{\text{Lindlar's Catalyst}}$$

Q7. **Predict the major product in the following reaction:**

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

Q8. **Sodium salt of which acid will be needed for preparation of propane? Write chemical equation for the reaction.**

Q9.



Q10. $CH_3-C{\equiv}CH \xrightarrow{\text{HOCl excess}} A$

Q11. $CH_3CH{=}CH_2 \xrightarrow{HOCl} A \xrightarrow{\text{aq. KOH}} B$

Q12. **Propyne** $\xrightarrow[\text{873 K}]{\text{Iron tube}}$ **P.**

Q13. **How would you obtain butane by:**
(a) **Wurtz reaction** (b) **Kolbe's electrolysis**

Q14. **Alkeynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on reduction of 2-butyne show the geometrical isomerism?**

Q15. **Write structures of all the alkenes which on hydrogenation give 2-methylbutane.**

Q16. **Propanal and pentan-3-one are the oxonolysis products of an alkene? What is the structural formula of the alkene?**

Q17. An alkene 'A' contains three C — C, eight C — H σ-bonds and one C — C π-bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44u. Write IUPAC name of 'A'.

Q18. An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.

Q19. How do you account for formation of ethane during chlorination of methane?

Q20. A hydrocarbon containing two double bonds gave on reductive ozonolysis, glyoxal, ethanal and propanone. Predict the structure of the hydrocarbon and also give its IUPAC name.

Q21. Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene
(a) in the absence of peroxide (b) in the presence of peroxide.

Q22. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classsify the following species as electrophiles and nucleophiles.

(a) H_3CO^- (b) $H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - O^-$ (c) $\dot{C}l$ (d) $Cl_2C:$
(e) $(H_3C)_3C^+$ (f) Br^- (g) H_3COH (h) $R - NH - R$

Q23. Predict the major product(s) of the following reactions and explain their formation.

(a) $H_3C - CH = CH_2 \xrightarrow[HBr]{(Ph-CO-O)_2}$ (b) $H_3C - CH = CH_2 \xrightarrow{HBr}$

Q24. An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

Q25. Write hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane? Which of them is more stable? Give reasons.

Q26. What will be product obtained as a result of following reaction and why?

 $+ \; CH_3CH_2CH_2Cl \xrightarrow{AlCl_3}$

Q27. Write the mechanisum of Sulphonation of benzene.

Q28. Write the mechanisum of alkylation of benzene.

Q29. Write the mechanisum of nitration of benzene.

Q30. Write the mechanisum of chlorination of benzene.

Q31. A compound *A* with molecular formula $C_6H_{13}Cl$ gave two isomeric alkenes *B* and *C* with formula C_6H_{12}. The mixture of *B* and *C* on reductive ozonolysis furnished four compounds

(i) CH_3CHO (ii) C_2H_5CHO (iii) CH_3COCH_3 (iv) $CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCHO$

Give the structural formulae of *A*, *B*, *C*.

Q32. Describe the mechanism of addition of bromine to alkenes.

Q33. Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.

Q34. Explain the ozonolysis structure of *o*-xylene resonance hybidrized.

Q35. Addition of HBr to propene ields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

Q36. Write IUPAC names of the products obtaind by the ozonolysis of the following compounds:

(a) 3,4 Dimethylept-3-ene (b) 2-Ethylbut-1-ene (c) 1-Phenylbut-1-ene

Q37. Two cyclic dienes *A* and *B* have molecular formula C_6H_8. The mixture of the two on reductive ozonolysis gave the following products succinaldehyde, propan-1, 3-dial and glyoxal. Mixture of *A* and *B* on hydrogenation produces only cyclohexane. Suggest the structures of *A* and *B*.

Q38. In alkyl halide X of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes *Y* and *Z* (C_6H_{12}). Both alkenes on hydrogenation, give 2, 3-dimethylbutane. Predict the structures of *X*, *Y*, *Z*.

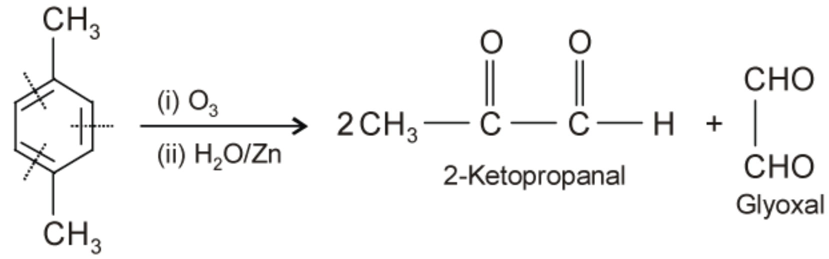
Q39. Give the structures of the major products from 3-ethylpent-2-ene under each of the following reaction conditions.

(a) HBr in the presence of peroxide (b) Br_2/H_2O

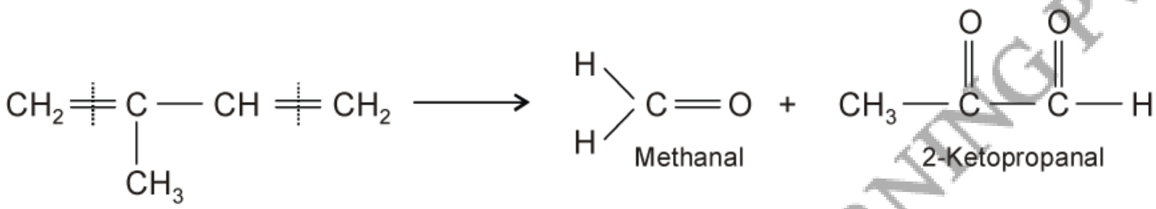
Date: 16/10/2021

S1.

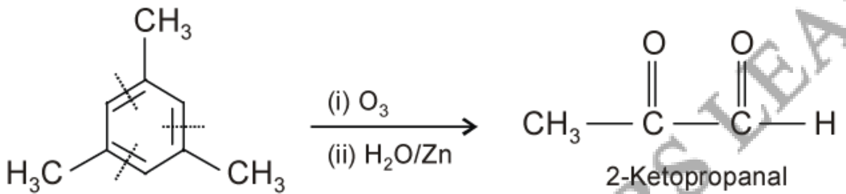
S2.



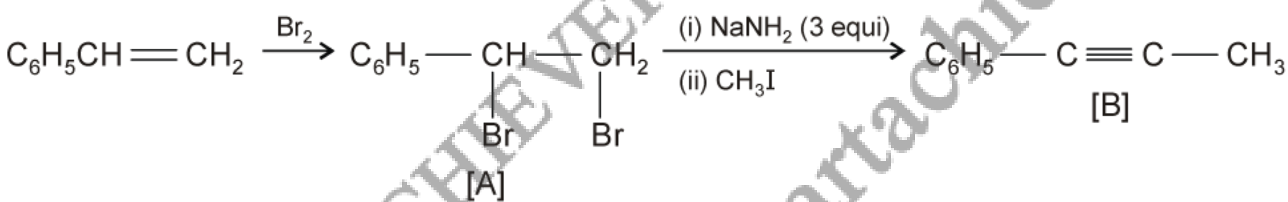
S3.



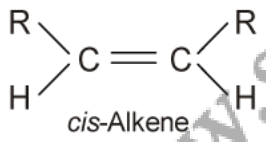
S4.



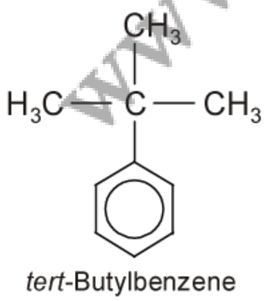
S5.



S6.



S7.

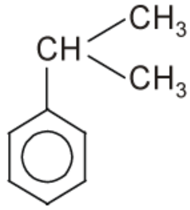


S8. Sodium salt of butanoic acid will be needed for preparation of propane.

$$\underset{\text{Sodium butanoate}}{CH_3CH_2CH_2COO^-Na} + NaOH \xrightarrow{CaO} CH_3CH_2CH_3 + Na_2CO_3$$

S9.

(A) 

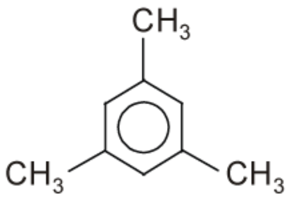
(B) 

S10.

(A) $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CHCl_2$

S11. (A) $CH_3 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_2 - Cl$ (B) $CH_3 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_2 - OH$

S12.



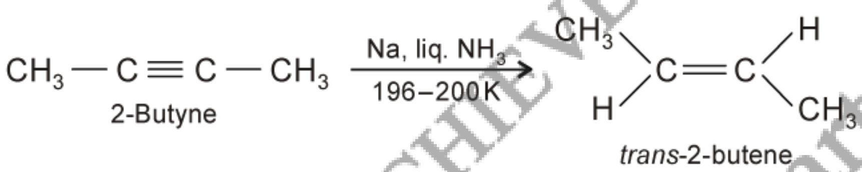
S13. (a) Ethyl bromide on reaction with sodium in the presence of dry ether yields buane

$$2C_2H_5Br + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_3 + 2NaBr$$

(b) An aqueous concentrated solution of sodium propanoate on electrolysis yields butane at anode.

$$2CH_3CH_2COONa(aq) + 2H_2O(l) \xrightarrow{\text{Electrolysis}} CH_3CH_2CH_2CH_3 + 2CO_2 + H_2 + 2NaOH$$

S14.



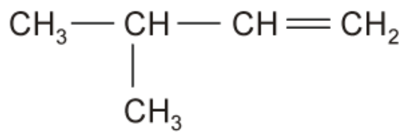
2-butene is capable of showing geometrical isomerism.

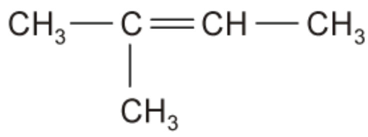
S15. The product is:

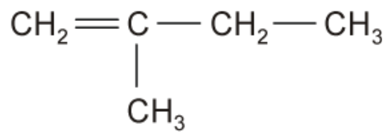
$$\overset{1}{CH_3} - \underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{CH}} - \overset{3}{CH_2} - \overset{4}{CH_3}$$

2-Methylbutane

The different alkenes which give the product on hydrogenation are given ahead:

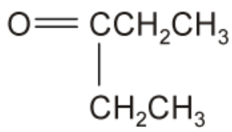

3-Methylbut-1-ene

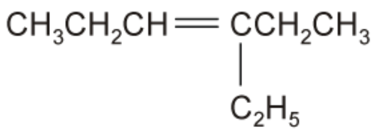

2-Methylbut-2-ene


2-Methylbut-1-ene

S16. The products are:

$CH_3CH_2CH{=}O$
Propanal

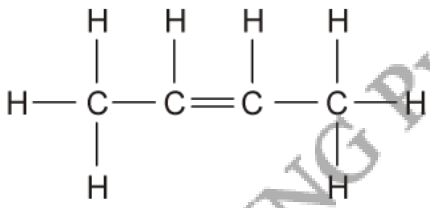

Pentan-3-one

Alkene is 
3-Ethylhex-3-ene

S17. An aldehyde having molecular mass of 44 a.m.u. is ethanal, CH_3CHO.

It gives two moles of ethanal

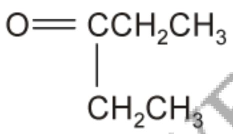
$CH_3CH{=}O$ $\qquad$ $O{=}CHCH_3$

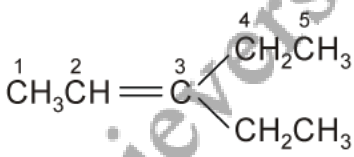
Alkene is $CH_3CH{=}CH-CH_3$ or 

But-2-ene has two C — C, one C ═ C and eight C — H bonds.

S18. The products are:

CH_3CHO
Ethanal


Pentan-3-one

Alkene is 
3-Ethylpent-2-ene

S19. Chlorination of methane takes place through a free radical chain mechanism as given below:

(a) **Chain initiation:**

$$Cl - Cl \xrightarrow{\text{Homolytic Cleavage}} 2\dot{C}l$$

Chlorine free radical

(b) **Chain propagation:**

$$H_3C-H + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \dot{C}l$$

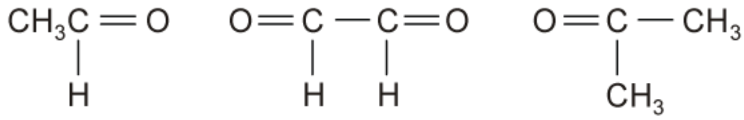
(c) **Chain termination:**

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3-Cl$$

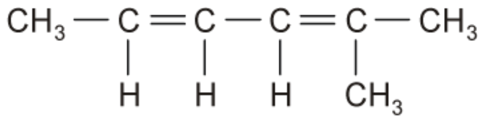
From the above mechanism, it is evident that during chain propagation step, $\dot{C}H_3$ free radicals are produced. In the chain termination step, the two $\dot{C}H_3$ free radicals may combine together to form ethane (CH_3-CH_3) molecule.

S20. **Step 1:**



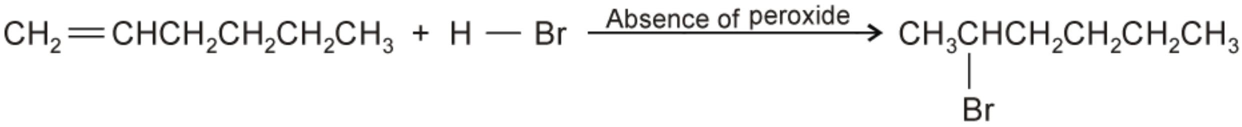
Ethanal Glyxal Propanone

Step 2:



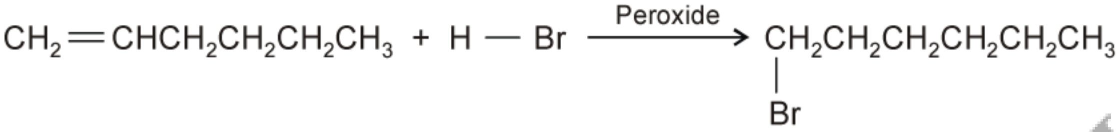
Thus, the compound is **2-Methyl-2, 4-hexadiene**.

S21. (a)



2-Bromohexane

(b)



1-Bromohexane

S22.

Nucleophiles: (a) H_3CO^- (b) $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$ (g) $CH_3-\ddot{\underset{\cdot\cdot}{O}}-H$ (h) $R-NH-R$

Electrophiles: (c) $\dot{C}l$ (d) $Cl_2C:$ (e) $(H_3C)_3C^+$

S23. (a) $H_3C-CH=CH_2 \xrightarrow[HBr]{(PhCOO)_2} H_3C-CH_2-CH_2Br$ (Anti Markovnikov rule)

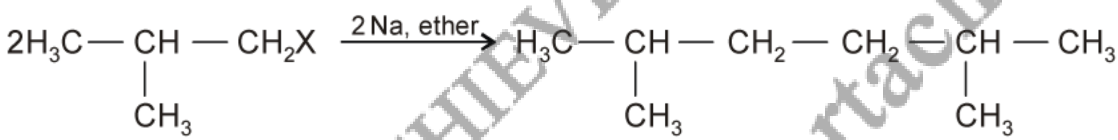
1-Broopropane

(b)

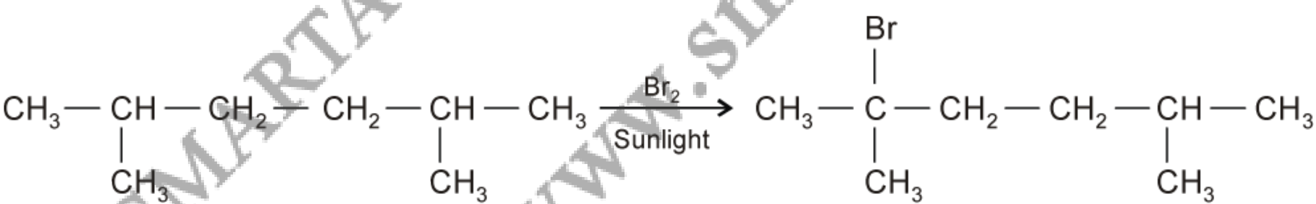
(Markovnikov rule)

2-Bromopropane

S24.

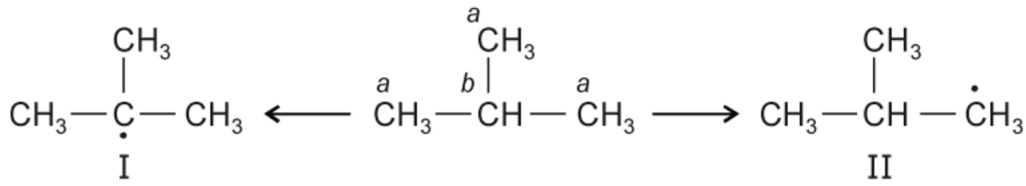


2, 5-Dimethylhexane



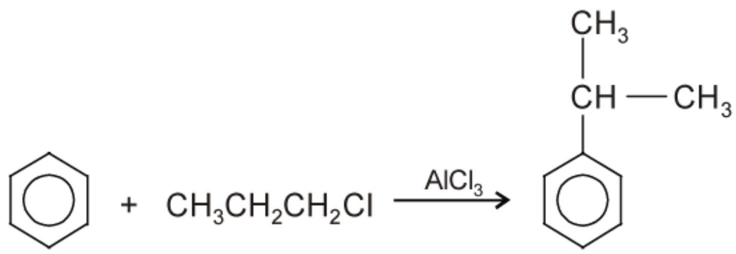
2-Bromo-2, 5-Dimethylhexane (3°)

S25. 2-Methylpropane has two sets of equivalent hydrogens marked as *a* and *b* and therefore, gives two radicals I and II



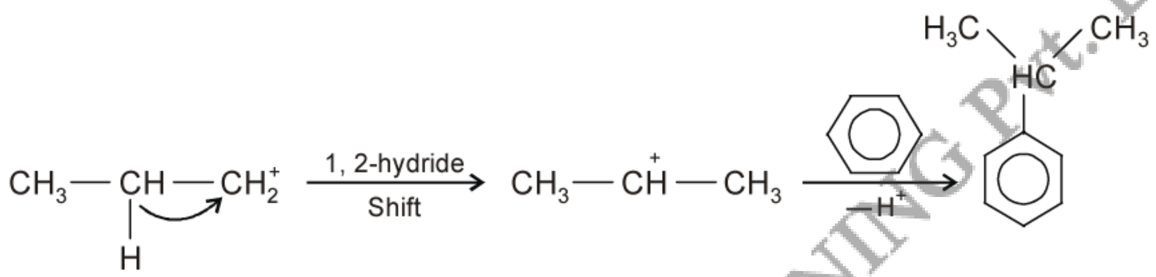
Radical I is more stable than radicalII because it is tertiary while radical II is primary. It is also stabilized due to hyperconjugation (nine structures).

S26.



Isopropyl benene

Propyl chloride forms carbocation, $CH_3-CH_2-CH_2^+$ with anhydrous $AlCl_3$ which is less stable. This rearranges to a more stable carbocation as:



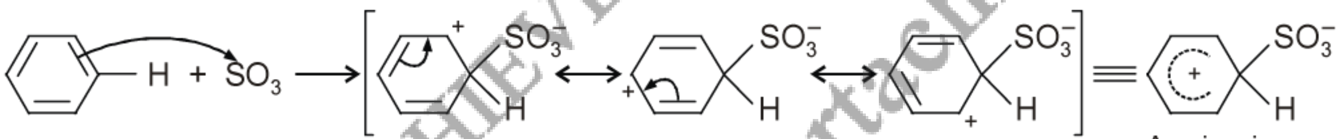
Therefore, it forms isopropyl benzene.

S27. Mechanisum of Sulphonation of benzene:

Step - I: Generation of Electrophile:

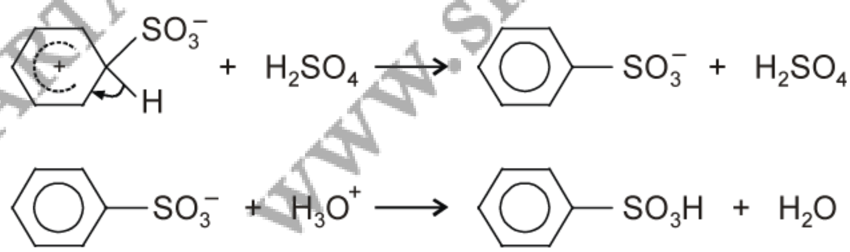
$$2H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO_4^-$$

Step - II: Attack of Electrophile:



Arenium ion

Step - III: Abstraction of Proton:



Benzene sulphonic acid

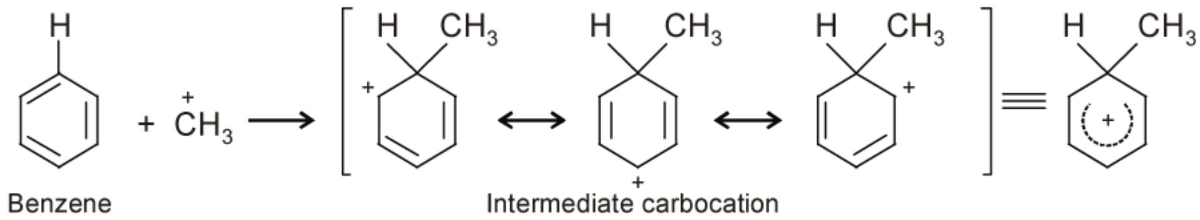
S28. Mechanisum of Alkylation of benzene:

Step - I: Generation of Electrophile:

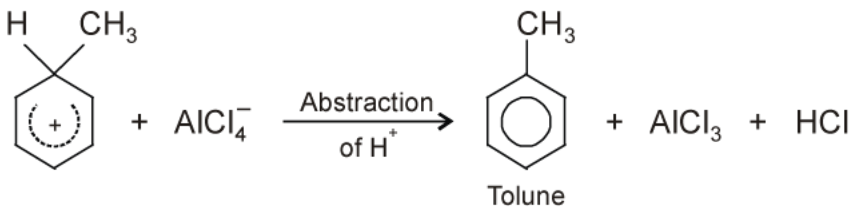
$$CH_3Cl + AlCl_3 \longrightarrow AlCl_4^- + \overset{+}{C}H_3$$

Carbocation

Step - II: Attack of Electrophile:



Step - III: Abstraction of Proton:



S29. Mechanisum of Nitration of benzene:

Step - I: Generation of Electrophile:

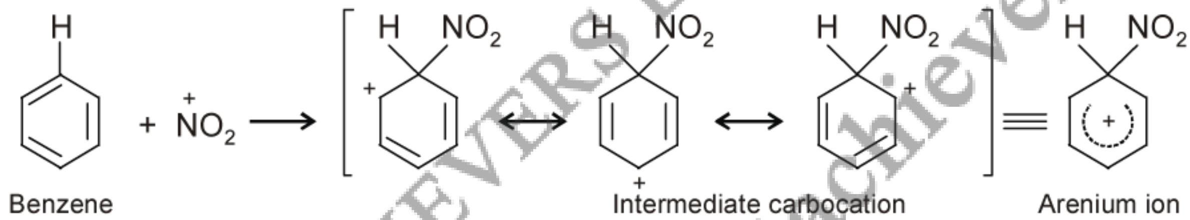
$$H_2SO_4 + HO-NO_2 \rightleftharpoons HSO_4^- + H-\overset{+}{\underset{\underset{H}{|}}{O}}-NO_2$$

$$H-\overset{+}{\underset{\underset{H}{|}}{O}}-NO_2 \rightleftharpoons H_2O + \overset{+}{N}O_2$$

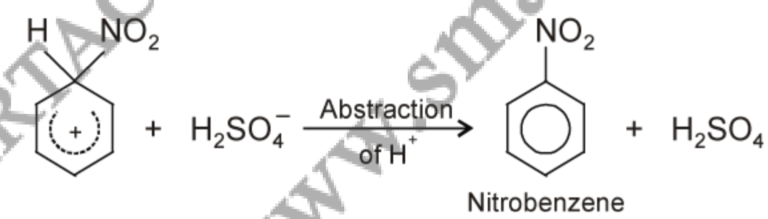
Nitronium ion

It may be noted that in the process of generation of NO_2^+ ion, sulphuric acid behaves as an acid while nitric acid behaves as a base.

Step - II: Attack of Electrophile:



Step - III: Abstraction of Proton:

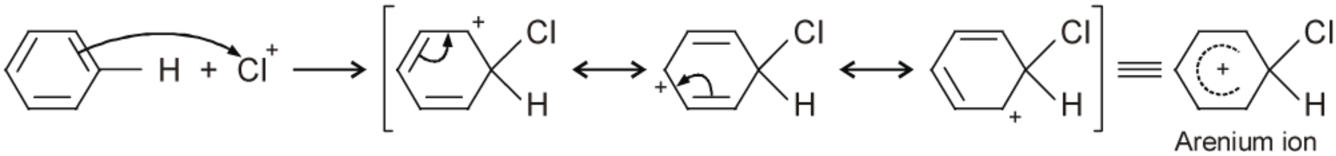


S30. Mechanisum of chlorination of benzene:

Step - I: Generation of Electrophile:

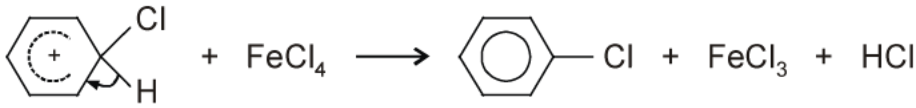
$$Cl_2 + FeCl_2 \longrightarrow FeCl_2^- + Cl^+$$

Step - II: Attack of Electrophile:



Arenium ion

Step - III: Abstraction of Proton:



S31. Alkenes *B* and *C* have 6 carbon atoms each. Therefore, the ozonolysis products of *B* and *C* are respectively.

B: $CH_3C(CH_3){=}O$ and $O{=}C(H){-}CH(CH_3)CH_3$ C: $CH_3{-}C(CH_3){=}O$ and $O{=}C(H){-}C_2H_5$

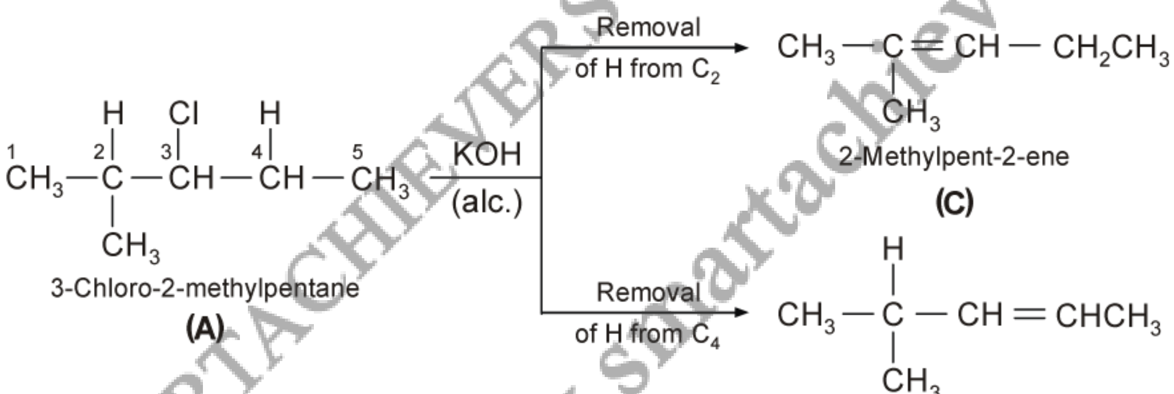
(Sum of the number of carbon atoms in each pair should be equal to six.)

Thus, alkene *B* is $CH_3{-}CH{=}CH{-}CH(CH_3){-}CH_3$ and alkene *C* is $CH_3{-}C(CH_3){=}CH{-}CH_2CH_3$

The above alkenes can be produced from the dehydrohalogenation of halide '*A*' with formula:

$$CH_3{-}CH(CH_3){-}CH(Cl){-}CH_2CH_3$$

The chemical reactions are as under:



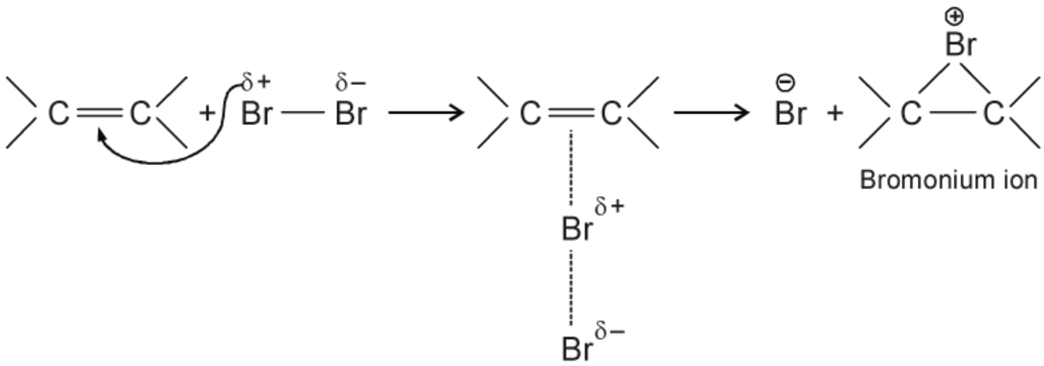
3-Chloro-2-methylpentane
(A)

2-Methylpent-2-ene
(C)

4-Methylpent-2-ene
(B)

S32. Addition of bromine to alkenes takes place through the following steps:

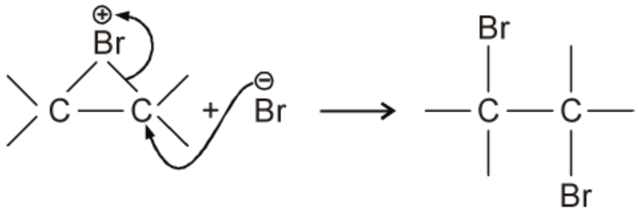
Step - I: The first step involves the electropilic attack of bromine molecule on the double bond resulting in the formation of cyclic bromonium ion.



Bromonium ion

π-complex

Step - II: The second step involves the attack of Br^- ion on bromonium ion to form the 1, 2-dibromo compound.



1, 2-Dibromo compound

S33. The following three products are formed:

(a) $$CH_3\underset{\substack{|\\CH_3}}{CH}-CH_2\boxed{I + 2Na + I}CH_2\underset{\substack{|\\CH_3}}{CH}-CH_3 \xrightarrow[\text{reaction}]{\text{Wurtz}} CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3 + 2NaI$$

1-Iodo-2-methylpropane (2 molecules) → 2, 5-Dimethylhexane

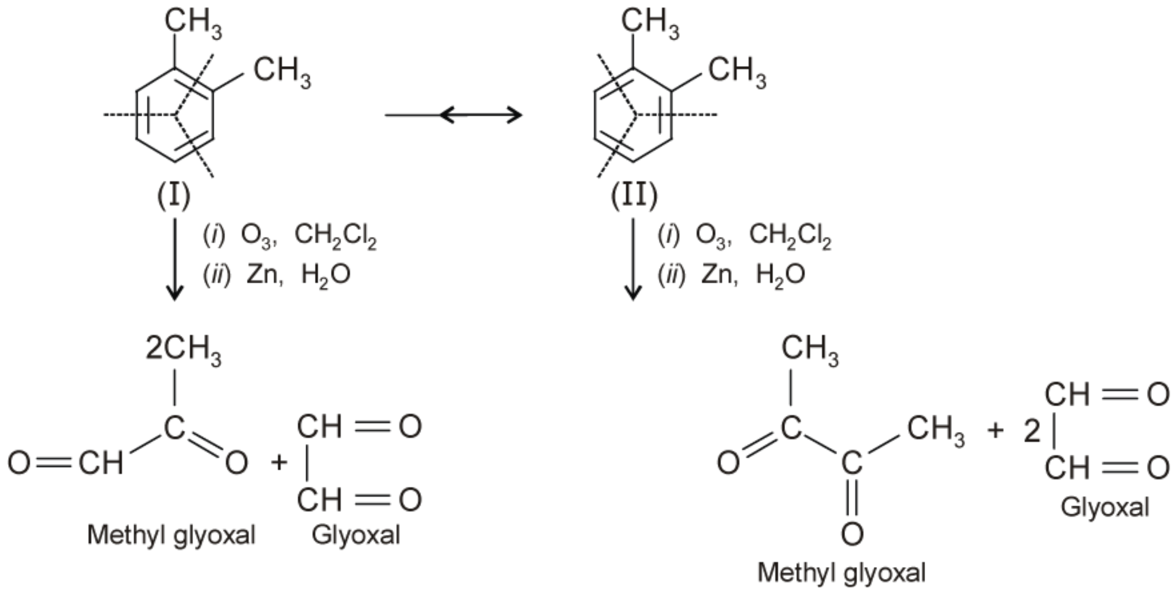
(b) $$(CH_3)_2CH-\boxed{I + 2Na + I}-CH(CH_3)_2 \xrightarrow[\text{reaction}]{\text{Wurtz}} (CH_3)_2CH-CH(CH_3)_2 + 2NaI$$

2-Iodopropane (2 molecules) → 2, 3-Dimethylbutane

(c) $$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2\boxed{I + 2Na + I}-\underset{\substack{|\\CH_3}}{CH}-CH_3 \xrightarrow[\text{reaction}]{\text{Wurtz}} CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3 + 2NaI$$

1-Iodo-2-methylpropane (2 molecules) → 2, 5-Dimethylhexane

S34. *o*-xylene may be regarded as a resonance hybrid of the following structures. Ozonolysis of each one o these gives two products as shown below:



Therefore, only three products are formed. Since all the three products cannot be obtained from any one of the two Kekule structures, this shows that *o*-xyles is a resonance hybrid of two Kekule structures (I) and K(II).

S35. Addition of HBr to propene is an ionic electrophilic addition reaction which follows Markonikov rule. In this case H^+ adds to alkene to give a more stable 2° carbocation. This is rapidly attacked by nucleophile Br^- ion to give 2-bromopropane.

$$H-Br \rightleftharpoons H^+ + Br^-$$

$$CH_3-CH=CH_2 + H^+ \xrightarrow{\text{Slow}} \underset{\substack{\text{2°-Carbocation} \\ \text{(more stable)}}}{CH_3-\overset{+}{C}H-CH_3}$$

$$CH_3-\overset{+}{C}H-CH_3 + Br^- \xrightarrow{\text{Fast}} \underset{\text{2-Bromopropane}}{CH_3-\underset{\substack{| \\ Br}}{CH}-CH_3}$$

In the presence of benzoyl peroxide, the reaction follows free radical addition. In this case $\dot{Br}$ free radical acts as electrophile which is obtained from the action of benzoyl peroxide on HBr.

$$C_6H_5CO-O-O-COC_6H_5 \xrightarrow[\text{Heat}]{\text{Homolytic fission}} 2C_6H_5CO\dot{O} \longrightarrow \underset{\text{Phenyl free radical}}{2C_6\dot{H}_5} + 2CO_2$$

$$C_6\dot{H}_5 + HBr \longrightarrow \underset{\text{Benzene}}{C_6H_5} + \dot{Br}$$

$\dot{Br}$ free radical attacks propene in such a way to generate a more stable 2° free radical. This free radical obtained rapidly abstracts a hydrogen atom of HBr to give 1-Bromopropane.

$$CH_3-CH=CH_2 + \dot{Br} \xrightarrow{\text{Slow}} \underset{\text{2°-Free radical (stable)}}{CH_3-\dot{C}H-CH_2Br}$$

$$CH_3-\dot{C}H-CH_2Br + H-Br \xrightarrow{\text{Fast}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} + \dot{Br}$$

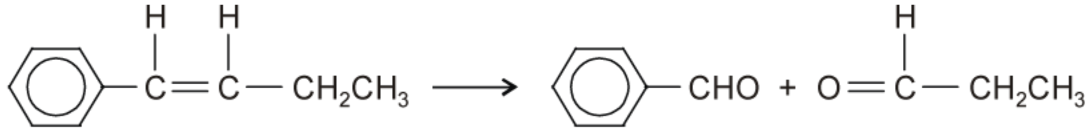
S36.

(a)
$$CH_3CH_2\overset{CH_3}{C}=\overset{CH_3}{C}CH_2CH_2CH_3 \longrightarrow CH_3CH_2\overset{CH_3}{C}=O + O=\overset{CH_3}{C}-CH_2CH_2CH_3$$

3, 4-Dimethylept-3-ene   Butan-2-one   Pentan-2-one

(b)
$$CH_3CH_2-\overset{C_2H_5}{C}=CH_2 \longrightarrow CH_3CH_2-\overset{C_2H_5}{C}=O + O=C\begin{matrix}H\\H\end{matrix}$$

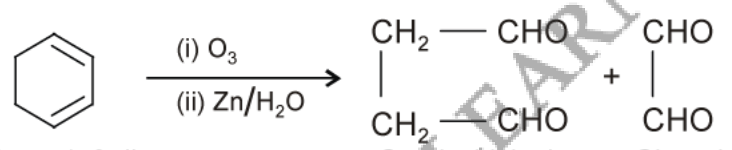
2-Ethylbut-1-ene   Pentan-3-one   Methanal

(c)


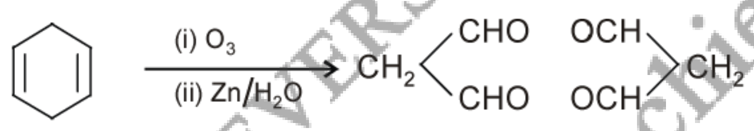
1-Phenylbut-1-ene   Benzaldehyde   Propanal

S37. Since ***A*** and ***B*** give cyclohexane. This implies that both ***A*** and ***B*** should be cyclohexadienes. The ozonolysis products suggest the presence of double bonds in 1 and 3-positions in one while at 1 and 4-positions in the other. Hence, ***A*** and ***B*** should be

(Cyclohexa-1, 3-diene)   (Cyclohexa-1, 4-diene)



Cyclohexa-1, 3-diene   Succinaldehyde   Glyoxal



Cyclohexa-1, 4-diene   Propan-1, 3-dial

S38.
$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{— HCl}]{(CH_3)_3COK} CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_3 + CH_3=\overset{CH_3}{C}-\overset{CH_3}{C}-CH_3$$

(Elimination occurs)

2-Chloro-2, 3-dimethylbutane (**X**)   2, 3-Dimethylbut-2-ene (**Y**)   2, 3-Dimethylbut-1-ene (**Z**)

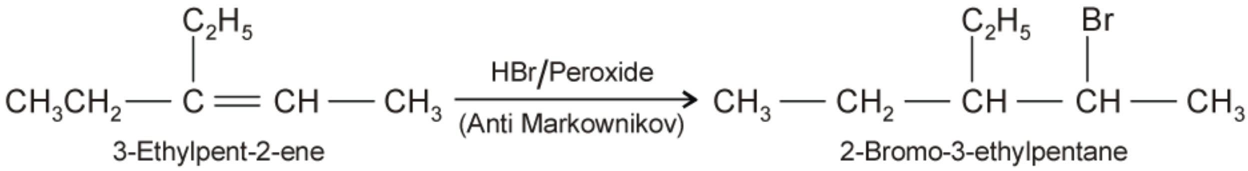
$$\downarrow H_2/Pt$$

$$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$$

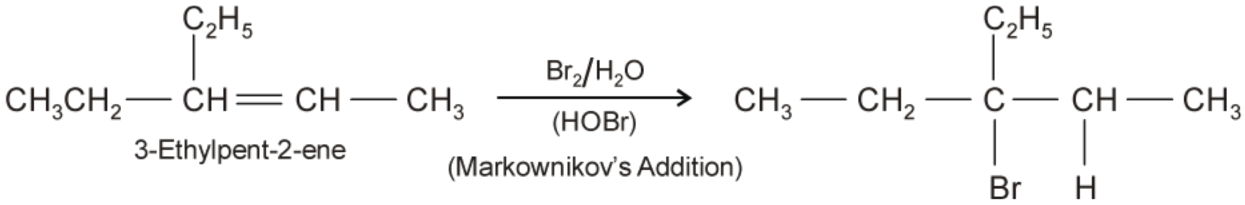
2, 3-Dimethylbutane

S39.

(a)


HBr/Peroxide
(Anti Markownikov)
3-Ethylpent-2-ene
2-Bromo-3-ethylpentane

(b)


Br_2/H_2O
(HOBr)
(Markownikov's Addition)
3-Ethylpent-2-ene

Date: 16/10/2021

Q1. Bring out the folowing conversion: Methane to ethane.

Q2. Bring out the folowing conversion: Ethane to Ethene.

Q3. Bring out the folowing conversion: Ethane to Butane.

Q4. Bring out the folowing conversion: Propene to 2, 3-Dimethylbutane.

Q5. Bring out the folowing conversion: Ethene to Ethyne.

Q6. Bring out the folowing conversion: Carbon and hydrogen to toluene.

Q7. Bring out the folowing conversion: Calcium carbide to oxalic acid.

Q8. Bring out the folowing conversion: Isopropyl bromide to *n*-propyl bromide.

Q9. Bring out the folowing conversion: Ethyne to *m*-nitrotoluene.

Q10. Bring out the folowing conversion: Benzene to *m*-nitrobenzoic acid.

Q11. Bring out the folowing conversion: Ethyne to dichloro acetaldehyde.

Q12. Bring out the folowing conversion: Acetylene to dichloroacetylene.

Q13. Bring out the folowing conversion: Ethylbenzene to benzene.

Q14. Outline all the steps in the synthesis of following compounds: *m*-Bromobenzenesulphonic acid from benzene

Q15. Bring out the folowing conversion: Ethyne to methane

Q16. How would you carry out the folloing conversions?

(a) $Br_2CH-CHBr_2 \longrightarrow HC\equiv CH$ (b) $H_3CC\equiv CH \longrightarrow H_3CCOCH_3$

Q17. How would you carry out the folloing conversionsl?

(a) $H_3C-CH_2-CH=CH_2 \longrightarrow H_3C-CH_2-CH_2-CH_2OH$

(b) $H_3C-CH_2-CH=CH_2 \longrightarrow H_3C-CH_2-CH(OH)-CH_2OH$

Q18. Outline all the steps in the synthesis of following compounds: Butane from methane

Q19. Outline all the steps in the synthesis of following compounds: *p*-Chlorostyrene from ethylbenzene.

Q20. Outline all the steps in the synthesis of following compounds: Styrene from benzene.

Q21. Outline all the steps in the synthesis of following compounds: 3, 4-Dibromonitrobenzene from benzene.

Q22. How will you prepare deuteriopropane?

Q23. Suggest a route for the preparation of nitrobenzene starting from acetylene?

Q24. Suggest a route to prepare ethyl hydrogen sulphate ($CH_3 — CH_2 — OSO_2 — OH$) starting from ethanol (C_2H_5OH).

Q25. How will you convert benzene into:

(a) *p*-nitrobromobenzene (b) *m*-nitrochlorobenzene (c) acetophenone

Q26. How would you convert the following compounds into benzene?

(a) Ethyne (b) Ethene (c) Hexane

Q27. How would you convert:

(a) Ethane to ethyne
(b) Ethane to 1, 2-ethanediol
(c) Ethane to 1, 2-dibromoethane
(d) Ethynl to glyoxal
(e) Ethyne to oxalic acid
(f) 1, 1-Dibromopropane to 2, 2-dibromopropane

Date: 16/10/2021

S1. Methane to ethane:

$$\underset{\text{Methane}}{CH_4} \xrightarrow[HIO_3]{I_2} CH_3I \xrightarrow[\text{Wurtz reaction}]{\text{2Na/Ether}} \underset{\text{Ethane}}{CH_3-CH_3}$$

S2. Ethane to Ethene:

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[-HI]{I_2/HNO_3} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow{\text{KOH (alc.)}} \underset{\text{Ethene}}{CH_2=CH_2}$$

S3. Ethane to Butane:

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[-HI]{I_2/HIO_3} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[\text{Wurtz reaction}]{\text{2Na/Ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

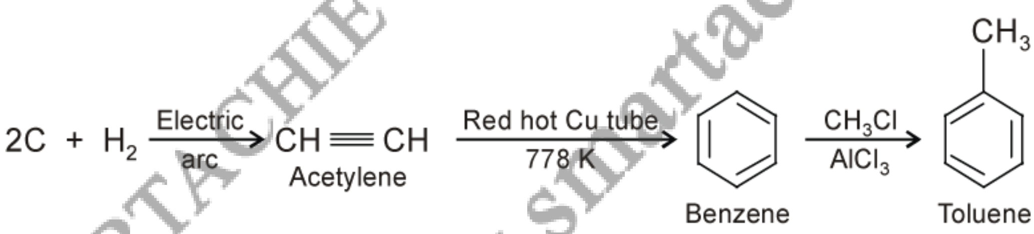
S4. Propene to 2, 3-Dimethylbutane:

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \longrightarrow CH_3\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow[\text{Wurtz reaction}]{\text{2Na/Ether}} \underset{\text{2, 3-Dimethylbutane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3}$$

S5. Ethene to Ethyne:

$$CH_2=CH_2 \xrightarrow{Br_2/CCl_4} \underset{\underset{Br}{|}}{CH_2}-\underset{\underset{Br}{|}}{CH_2} \xrightarrow[\text{Heat}]{\text{KOH (alc.)}} \underset{\text{Ethyne}}{CH\equiv CH}$$

S6. Carbon and hydrogen to toluene:



S7. Calcium carbide to oxalic acid:

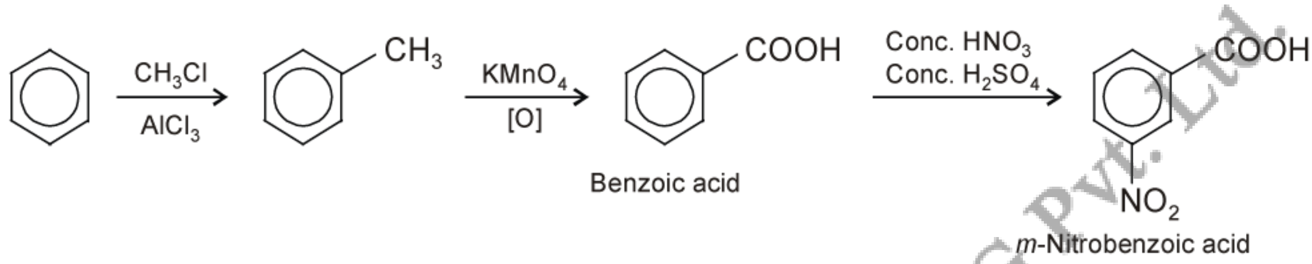
$$CaC_2 + H_2O \xrightarrow[-Ca(OH)_2]{} \underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[KMnO_4\ 4(O)]{\text{Hot alkaline}} \underset{\text{Oxalic acid}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}}$$

S8. Isopropyl bromide to *n*-propyl bromide:

$$\underset{CH_3}{\overset{CH_3}{>}}CH-Br \xrightarrow[443\ K]{Conc.\ H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{Organic peroxide}]{HBr} \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br}$$

S9. Ethyne to *m*-nitrotoluene:

S10. Benzene to *m*-nitrobenzoic acid:



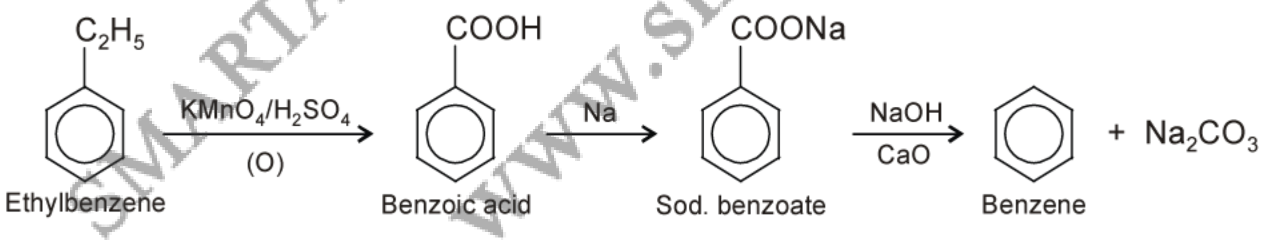
S11. Ethyne to dichloro acetaldehyde:

$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + HOCl \xrightarrow{Cl_2/H_2O} \begin{matrix}CHOH\\ \|\\ CHCl\end{matrix} \xrightarrow{HOCl} \begin{matrix}HO\diagdown\ \diagup OH\\ CH\\ |\\ CHCl_2\end{matrix} \xrightarrow{-H_2O} \underset{\text{Dichloroacetaldehyde}}{\begin{matrix}CHO\\ |\\ CHCl_2\end{matrix}}$$

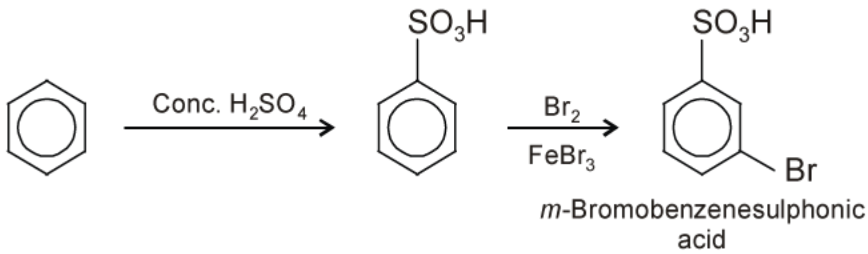
S12. Acetylene to dichloroacetylene:

$$\begin{matrix}CH\\ |||\\ CH\end{matrix} \xrightarrow{2Cl_2} \underset{\text{Tetrachloroethane}}{\begin{matrix}Cl-CH-Cl\\ |\\ Cl-CH-Cl\end{matrix}} \xrightarrow[-2HCl]{2KOH(alc.)} \underset{\text{Dichloroacetylene}}{\begin{matrix}CCl\\ |||\\ CCl\end{matrix}}$$

S13. Ethylbenzene to benzene:



S14. ***m*-Bromobenzenesulphonic acid from benzene:**



Note: — SO_3H is *meta* directing group.

S15. Ethyne to methane:

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[Hg^{2+}/H_2SO_4]{H_2O} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[K_2Cr_2O_7/H^+]{(O)} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sodium ethanoate}}{CH_3COONa} \xrightarrow[CaO]{NaOH} \underset{\text{Methane}}{CH_4}$$

S16. (a) $Br_2CH - CHBr_2 + 2Zn \xrightarrow{Heat} HC\equiv CH + ZnBr_2$

(b) $H_3C - C\equiv CH + H_2O \xrightarrow{Hg^{2+}/H^+} H_3C - \underset{\displaystyle OH}{\underset{|}{C}} = CH_2 \xrightleftharpoons{\text{Tautomerization}} H_3C - \underset{\displaystyle O}{\underset{\|}{C}} - CH_3$

S17. (a) $H_3C - CH_2 - CH = CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } (BH_3)_3} H_3C - CH_2 - CH_2 - CH_2OH$

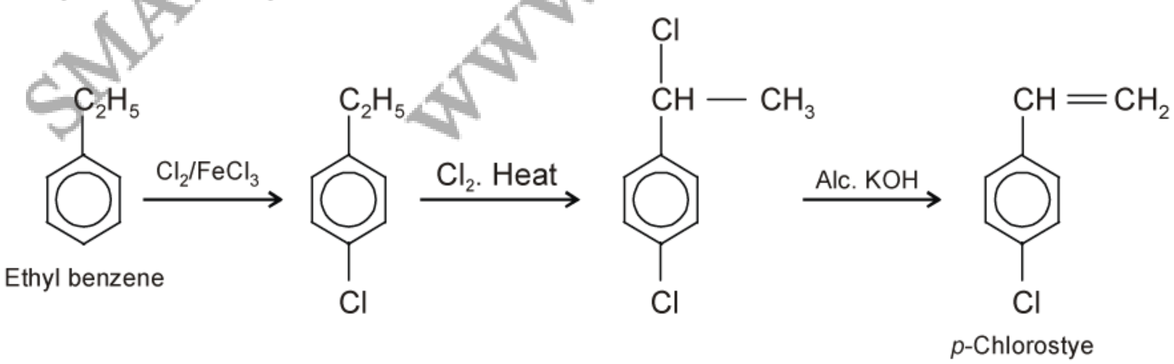
(b) $H_3C - CH_2 - CH = CH_2 + H_2O + O \xrightarrow{KMnO_4/OH^-} H_3C - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle OH}{\underset{|}{CH_2}}$

S18. Butane from methane:

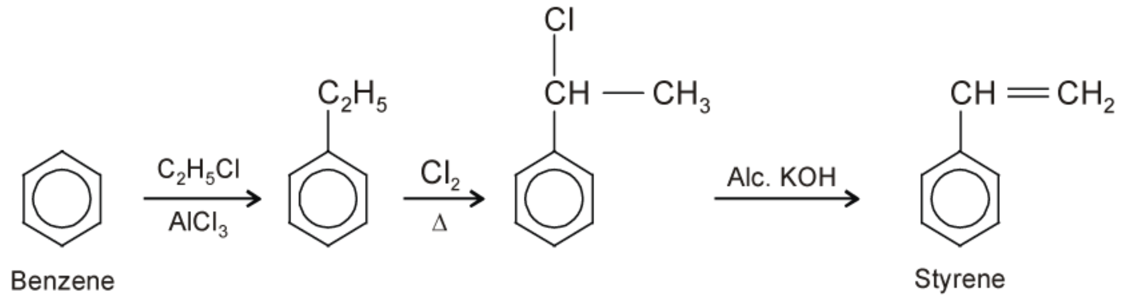
$$2CH_4 \xrightarrow[Heat]{Cl_2} 2CH_3Cl \xrightarrow[\text{Wurtz reaction}]{2Na/ether} CH_3 - CH_3 \xrightarrow{Cl_2,\ Heat} CH_3CH_2Cl$$

$$2CH_3CH_2Cl \xrightarrow{2Na/ether} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

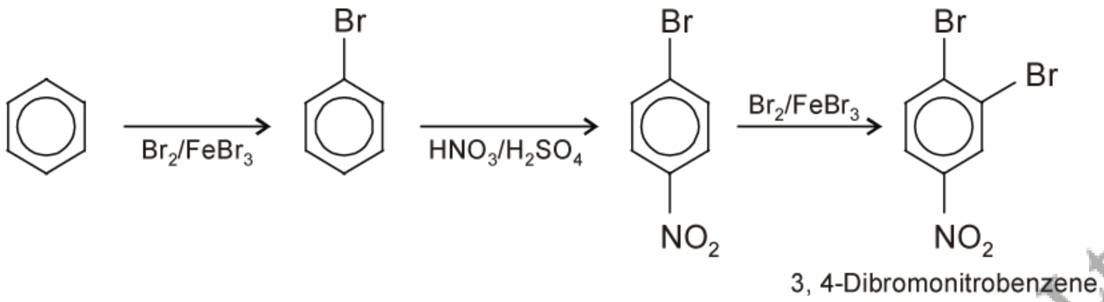
S19. *p*-Chlorostyrene from ethylbenzene:



S20. **Styrene from benzene:**



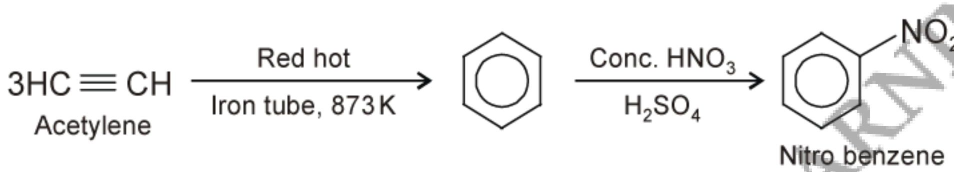
S21. **3, 4-Dibromonitrobenzene from benzene:**



S22.

$$\underset{\text{Isopropyl iodide}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-I} \xrightarrow{\text{Mg. ether}} CH_3-\underset{\underset{CH_3}{|}}{CHMgI} \xrightarrow{D_2O} \underset{\text{Deuteriopropane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-D} + Mg(OD)I$$

S23.



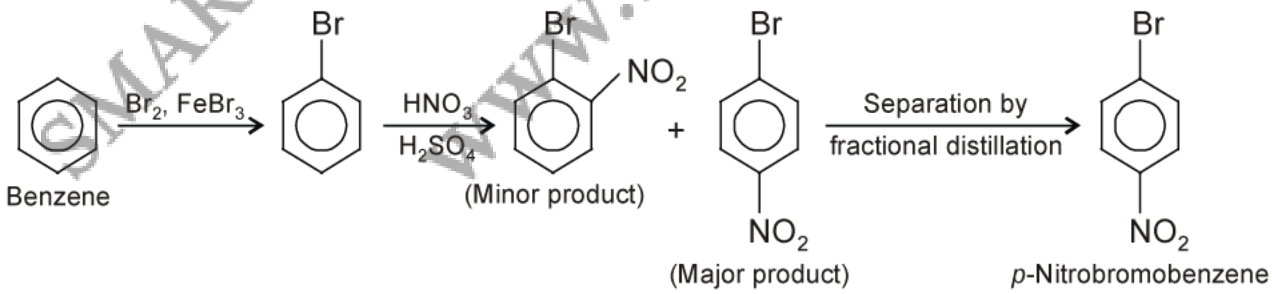
S24. When ethanol is heated with conc. H_2SO_4 at 383 K, ethyl hydrogen sulphate is formed.

$$H_2SO_4 \longrightarrow H^+ + \bar{O}SO_2OH$$

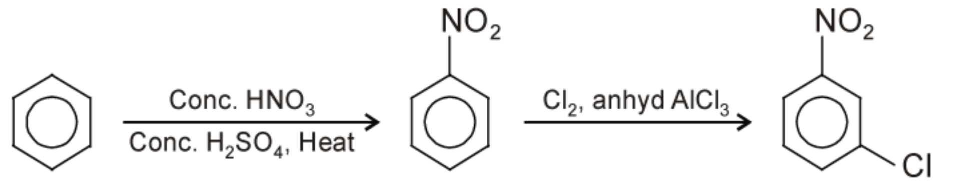
$$CH_3CH_2OH + H^+ \longrightarrow \underset{\text{Protonated alcohol}}{CH_3-CH_2-\underset{\underset{H}{|}}{O^+}-H}$$

$$\underset{\text{Hydrogen sulphate ion}}{HO-SO_2-O^-} + CH_3-CH_2-\underset{\underset{H}{|}}{O^+}-H \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_2OH} + H_2O$$

S25. (a) ***p*-nitrobromobenzene:**

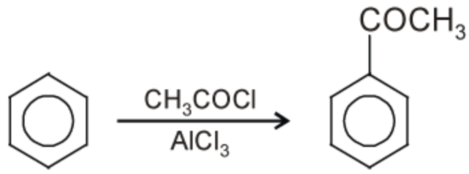


(b) ***m*-nitrochlorobenzene;**



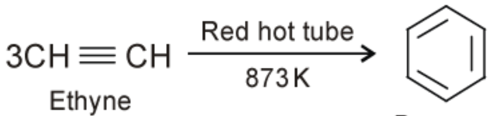
m-Nitrochlorobenzene

(c) **Acetophenone:**



Acetophenone

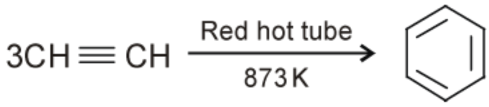
S26. (a) Ethyne is converted into benzene by passing its vapours through red hot tube at 873 K.



Benzene

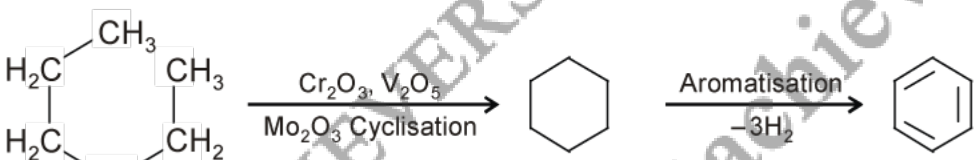
(b) Ethene is first converted into ethyne and then to benzene as:

$$\underset{\text{Ethene}}{CH_2 - CH_2} \xrightarrow{Br_2/CCl_4} \underset{Br\qquad\; Br}{CH_2 - CH_2} \xrightarrow[\text{Heat}]{\text{Alc. KOH}} \underset{\text{Ethyne}}{HC \equiv CH}$$



Benzene

(c) *n*-hexane is converted to benzene as:



n-Hexane Cyclohexane Benzene

S27. (a) $\underset{\text{Ethane}}{CH_3 - CH_3} \xrightarrow[\text{Heat}]{Cl_2} CH_3 - CH_2Cl \xrightarrow[\text{Heat}]{\text{alc. KOH}} CH_2 = CH_2 \xrightarrow{Br_2,\ CCl_4} \underset{Br\qquad\; Br}{CH_2 - CH_2} \xrightarrow{\text{alc. KOH}} \underset{\text{Ethyne}}{HC \equiv CH}$

(b) $\underset{\text{Ethane}}{CH_3 - CH_3} \xrightarrow[\text{Heat}]{Cl_2} CH_3 - CH_2Cl \xrightarrow[\text{Heat}]{\text{alc. KOH}} CH_2 = CH_2 \xrightarrow{\text{alk. } KMnO_4} \underset{\text{1, 2-Ethanediol}}{\underset{OH\qquad OH}{CH_2 - CH_2}}$

(c) $$\underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[CCl_4]{Br_2} \underset{Br\quad\ \ Br}{CH_2 - CH_2} \xrightarrow{\text{alc. KOH}} HC \equiv CH \xrightarrow{HCl} \underset{\text{1, 1-Dichloroethane}}{CH_3 - CHCl_2}$$

(d) First convert ethene to ethyne as in (c) and then convert ethyne to glyoxal

$$H - C \equiv C - H \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3} \underset{\text{Glyoxal}}{H - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - H}$$

(e) First convert ethane to ethyne as in (a) and then oxidise ethyne with $KMnO_4$.

$$H - C \equiv C - H \xrightarrow{KMnO_4} \underset{\text{Oxalic acid}}{HO - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - OH}$$

(f) $$\underset{\text{1, 1-Dibromopropane}}{CH_3 - CH_2 - CHBr_2} \xrightarrow{\text{alc. KOH}} CH_3 - C \equiv CH \xrightarrow{HBr} \underset{\text{2, 2-Dibromopropane}}{CH_3 - \overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}} - CH_3}$$

Date: 16/10/2021

Q1. How would you distinguish between:
(a) 1-Butyne and 2-Butyne (b) Propene and Propyne

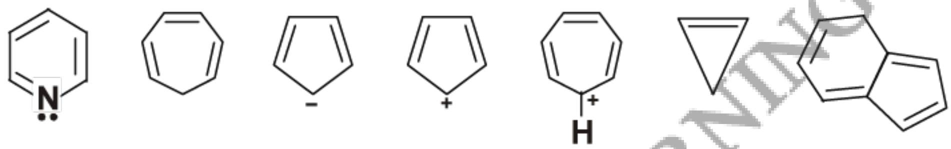
Q2. Suggest a method to separate a mixture of ethane, ethene and ethyne.

Q3. How would you distinguish between:
(a) Propane and Propene (b) Styrene and Phenyl acetylene

Q4. Why do alkynes undergo nucleopilic addition reactions while simple alkenes do not?

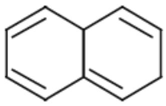
Q5. The ring systems having following characteristics are aromatic.
(a) Planar ring containing conjugated π-bonds.
(b) Complete delocalisation of the π-electrons in ring system *i.e.*, each atom in the ring has unhybridised *p*-orital, and
(c) Presence of $(4n + 2)$ π-electrons in the ring where *n* is an integer ($n = 0, 1, 2, ...$) [Huckel rule].

Using this information classify the following compounds as aromatic/non-aromatic.

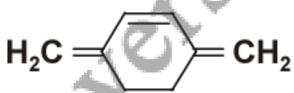


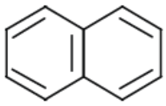
(A) (B) (C) (D) (E) (F) (G)

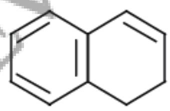
Q6. Classify the following compounds as aromatic/non-aromatic:

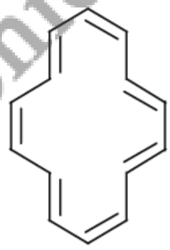
(A) 

(B) 

(C) 

(E) 

(F) 

(G) 

Q7. In the presence of peroxide addition of HBr to propene takes place according to anti Markovnikon's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

Q8. An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane-1, 4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.

Q9. 896 mL of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone 'B' having molecular formula $C_6H_{12}O$. The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.

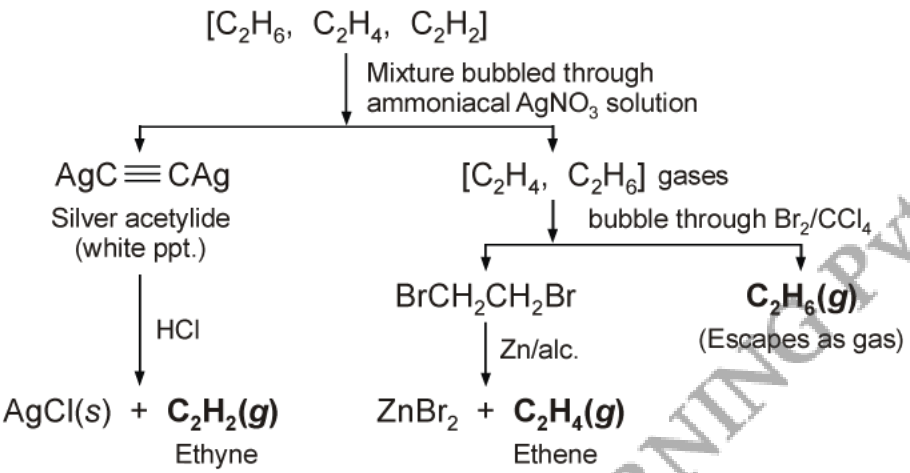
Q10. An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehyrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A, B, C and D. Give the reactions involved.

Date: 16/10/2021

S1. (a) Upon treatment with amm. solution of $AgNO_3$, 1-butyne would give white ppt. whereas 2-butyne does not react.

(b) Upon treatment with amm. solution of $AgNO_3$, propyne would give white ppt. whereas propene does not react.

S2. The flow sheet for the separation is as follows:



S3. (a) Upon treatment with alkaline solution of $KMnO_4$ (Bayer's reagent), the pink colour would be discharged in case of propene.

(b)

Styrene Phenyl acetylene

Phenyl acetylene, being a terminal alkyne would give white ppt. with ammonical solution of $AgNO_3$.

S4. Nucleophilic addition proceeds via carbanion as intermediate. The intermediate carbanion formed from nucleophilic attack on alkyne is more stable than formed from alkene. This is due to greater electronegativity of the sp^2-hybridized carbon than the sp^3-hybridized carbon. Therefore, alkynes undergo nucleophilic addition reactions while simple alkenes do not.

$$R-C\equiv C-H + \ddot{N}u \longrightarrow R-\underset{\displaystyle |\atop Nu}{C}=\overset{\bullet\bullet}{C}-H$$

More stable
(Carbon atom carrying negative charge is sp^2-hybridized)

$$R-CH=CH_2 + \ddot{N}u \longrightarrow R-\underset{\displaystyle |\atop Nu}{C}-\overset{\bullet\bullet}{C}H_2$$

Less stable
(Carbon atom carrying negative charge is sp^3-hybridized)

S5. A = Planar ring, all atoms (C and N) of the ring are sp^2 hybridised. It has 6 delocalised π-electrons and follows Huckel rule. Therefore, it is aromatic.

B = Has 6π-electrons, but the delocalisation stops at sp^3 hybridised CH_2-carbon. Therefore, it is not aromatic.

C = 6 delocalised π-electrons (4π-electrons of the two double bonds and 2 unshared electrons on negatively charged carbon) in a planar ring, follows Huckel's rule. It is aromatic.

D = Has only 4 delocalised π-electrons. It is non-aromatic.

E = 6 delocalised π-electrons follows Huckel's rule. π-electrons are in sp^2 hybridised orbitals, conjugation all over the ring because of positively charged caron. The ring is planar. Therefore, it is aromatic.

F = Follows Huckel's rule, has 2π-electrons *i.e.*, $(4n + 2)$ π-electrons where $(n = 0)$, delocalised π-electrons. Therefore, it is aromatic.

G = 8π-electrons, does not follow Huckel's rule *i.e.*, $(4n + 2)$ π-electrons rule. It is not aromatic.

S6. A = Has 8π-electrons, does not follow Huckel's rule. The orbitals of one carbon atom are not in conjugation. Therefore, it is not aromatic.

B = Has 6π delocalised electrons. Therefore, it is aromatic.

C = Has 6π-electrons in conjugation but not in the ring. Therefore, it is not aromatic.

D = Has 10π-electrons, all the C-atoms are sp^2 hybridised, the ring is planar. Therefore, it is aromatic.

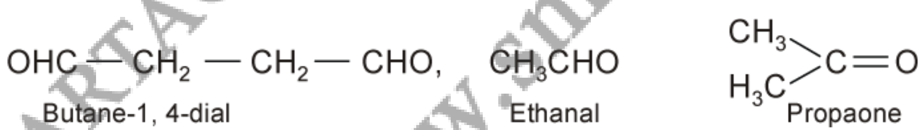
E = Has 8π-electrons, out of 8π-electrons it has delocalised 6π-electrons in one six membered planar ring, which follows Huckel's rule. Therefore, it is aromatic.

F = Has 14π-electrons which are in conjugation and are present in a ring. Therefore, it is aromatic if ring is planar.

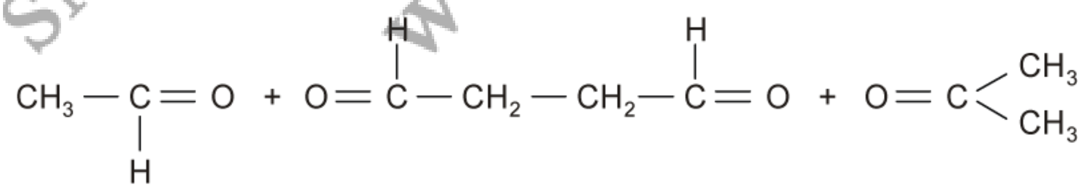
S7. Anti-Markovnikov rule or peroxide effect is followed only in cas of addition of HBr and not in case HCl and HI because HCl is more polar give 'H' which attack. of on C ═ C and gives carbocation while HI bond dissociation energy is very-very less and acts as reducing agent.

S8. Two molecules of hydrogen add on A and this means that 'A' is either an alkadiene or alkyne.

On reductive ozonolysis, 'A' gives three fragments and one of these is dialdehyde. Hence, the molecule has broken down at two sites. Therefore 'A' has two double bonds. The three fragments obtained on reductive ozonolysis are:



The structure of 'A' as deduced from three fragments is

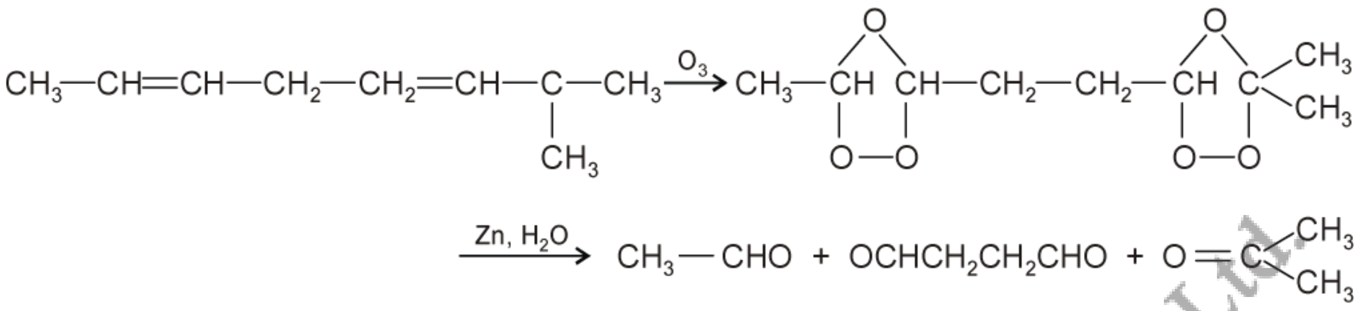


The hydrocarbon can be written by removing oxygen atoms and writing double bonds between the carbonyl carbon atoms.

$$\overset{8}{C}H_3 - \overset{7}{C}H = \overset{6}{C}H - \overset{5}{C}H_2 - \overset{4}{C}H_2 - \overset{3}{C}H = \underset{\displaystyle | \atop \displaystyle CH_3}{\overset{2}{C}} - \overset{1}{C}H_3$$

IUPAC name: 2-Methylocta-2, 6-diene

Reactions are:



S9. 896 mL of C_xH_y(A) weigh = 3.28 g

22400 mL of C_xH_y(A) weigh = $\dfrac{3.28}{896} \times 22400$ = 82 g mol^{-1}

$\therefore$ Molecular mass of C_xH_y = 82 g mol^{-1}.

Determination of empirical formula:

Element	%	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
C	87.9	12	87.80/12 = 7.31	7.32/7.31 = 1	3
H	12.19	1	12.19/1 = 12.19	12.19/7.31 = 1.66	4.98 = 5

Emirical formula of A = C_3H_5

Empirical formula mass = $3 \times 12 + 5 \times 1 = 41$

$$n = \frac{\text{Molecular formula mass}}{\text{Empirical formuls mass}} = \frac{82}{41} = 2$$

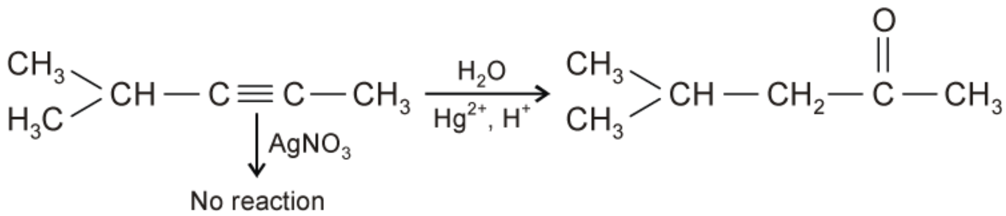
$\therefore$ Molecular formula = $(C_3H_6)_2 = C_6H_{10}$

Now, $\underset{(A)}{C_6H_{10}} \xrightarrow{\text{2 mole}} CH_3 - \underset{\displaystyle | \atop \displaystyle CH_3}{CH} - CH_2CH_2 - CH_3$

2-Methylpentane

The molecule has a chain of 5 carbon atoms with a methyl group at the second carbon atom. Since A adds a molecule of H_2O in the presence of Hg^{2+} and H^+ to give a ketone (B), it should be an alkyne, Two possible structures of 'A' are:

Since the compound B does not react with $AgNO_3$ solution, the triple bond is not terminal and therefore, structure (I) is he correct structure.



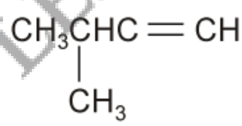
S10. The reactions are:

$$\underset{\text{(A)}}{\underset{\text{Alkyl halide}}{C_5H_{11}Br}} \xrightarrow{\text{Alc. KOH}} \underset{\text{(B)}}{\underset{\text{Alkene}}{C_5H_{10}}} \xrightarrow{Br_2} \underset{\text{(C)}}{C_5H_{10}Br_2} \xrightarrow[\text{Alc. KOH}]{\text{Dehydrobromination}} \underset{\text{(D)}}{\underset{\text{Alkyne}}{C_5H_8}}$$

$$\underset{\text{(D)}}{C_5H_8} \xrightarrow{\text{Na, liq. } NH_3} \underset{\text{Sodium alkylide}}{C_5H_7Na} + \tfrac{1}{2}H_2$$

The reaction suggest that (D) is a terminal alkyne. The possible structures are:

$$\underset{\text{(I)}}{CH_3CH_2CH_2C\equiv CH}$$



(II)

Since alkyne (D) gives straight chain on complete hydrogenation, therefore, only structure (I) is possible. Hence the reactions may be written as:

$$\underset{\text{(A)}}{CH_3CH_2CH_2CH_2CH_2Br} \xrightarrow{\text{Alc. KOH}} \underset{\text{(B)}}{CH_3CH_2CH_2CH=CH_2} \xrightarrow{Br_2} \underset{\text{(C)}}{CH_3CH_2CH_2\underset{\underset{Br}{|}}{CH}CH_2-Br}$$

$$\xrightarrow{\text{Alc. KOH}} \underset{\text{(D)}}{CH_3CH_2CH_2C\equiv CH} \xrightarrow{\text{Na, liq. } NH_3} CH_3CH_2CH_2C\equiv \bar{C}Na^+$$

and $$CH_3CH_2CH_2C\equiv CH \xrightarrow{2H_2} CH_3CH_2CH_2CH_2CH_3$$

Hence the structures of A, B, C and D are:

(A) $CH_3CH_2CH_2CH_2CH_2Br$ (B) $CH_3CH_2CH_2CH=CH_2$

(C) $CH_3CH_2CH_2CH(Br)CH_2Br$ (D) $CH_3CH_2CH_2C\equiv CH$