Date: 16/10/2021

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

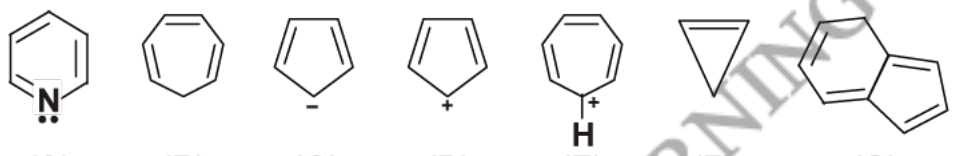
Q2. Suggest a method to separate a mixture of ethane, ethene and ethyne.

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?

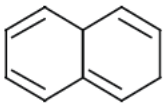
Q5. The ring systems having following characteristics are aromatic.
(a) Planar ring containing conjugated π-bonds.
(b) Complete delocalisation of the π-electrons in ring system *i.e.*, each atom in the ring has unhybridised *p*-orital, and
(c) Presence of $(4n + 2)$ π-electrons in the ring where n is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

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

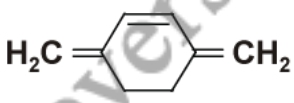


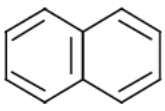
(A) (B) (C) (D) (E) (F) (G)

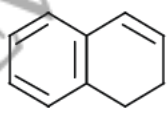
Q6. Classify the following compounds as aromatic/non-aromatic:

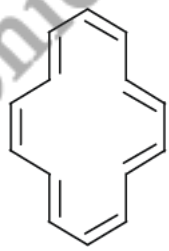
(A) 

(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.

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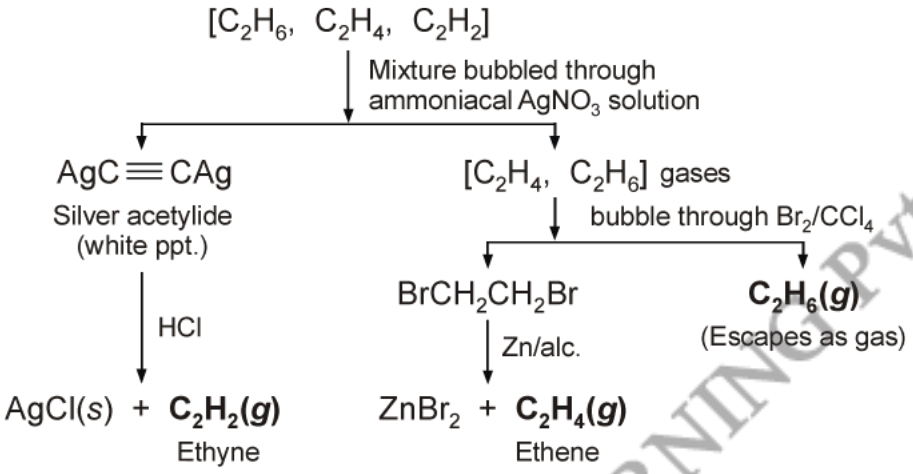
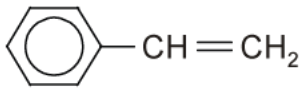
S1. (a) Upon treatment with amm. solution of $AgNO_3$, 1-butyne would give white ppt. whereas 2-butyne does not react.

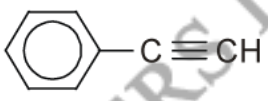
(b) Upon treatment with amm. solution of $AgNO_3$, propyne would give white ppt. whereas propene does not react.

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



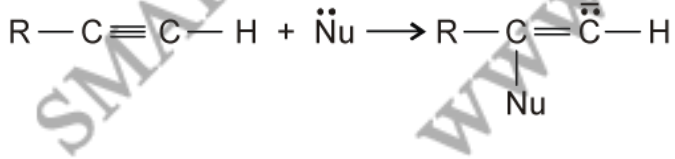
S3. (a) Upon treatment with alkaline solution of $KMnO_4$ (Bayer's reagent), the pink colour would be discharged in case of propene.

(b)  Styrene

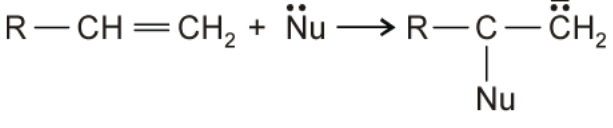
 Phenyl acetylene

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.



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



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.

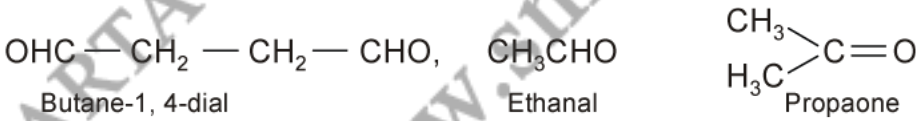
E = Has 8π-electrons, out of 8π-electrons it has delocalised 6π-electrons in one six membered planar ring, which follows Huckel's rule. Therefore, it is aromatic.

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

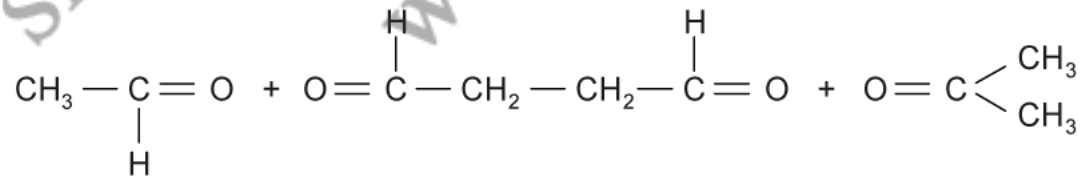
S7. Anti-Markovnikov rule or peroxide effect is followed only in cas of addition of HBr and not in case HCl and HI because HCl is more polar give 'H' which attack. of on C ═ C and gives carbocation while HI bond dissociation energy is very-very less and acts as reducing agent.

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

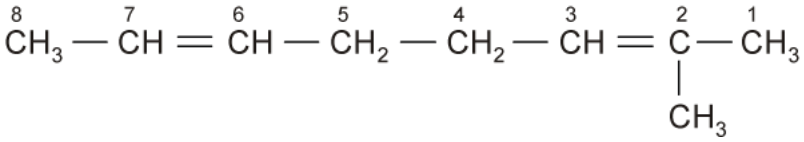
On reductive ozonolysis, 'A' gives three fragments and one of these is dialdehyde. Hence, the molecule has broken down at two sites. Therefore 'A' has two double bonds. The three fragments obtained on reductive ozonolysis are:



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

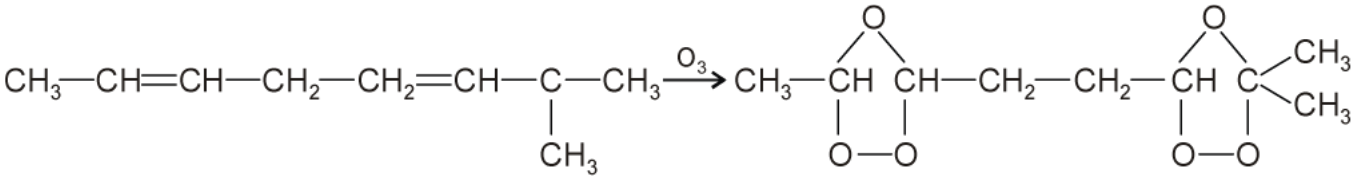


The hydrocarbon can be written by removing oxygen atoms and writing double bonds between the carbonyl carbon atoms.



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 = $\frac{3.28}{896} \times 22400 = 82 \text{ g mol}^{-1}$

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

Determination of empirical formula:

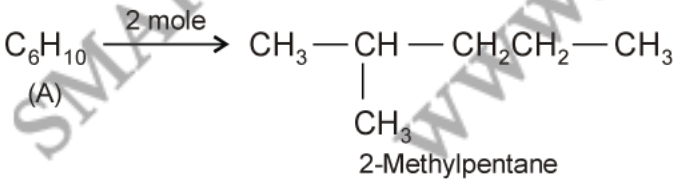
Element	%	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
C	87.9	12	87.80/12 = 7.31	7.32/7.31 = 1	3
H	12.19	1	12.19/1 = 12.19	12.19/7.31 = 1.66	4.98 = 5

Emirical formula of A = C_3H_5

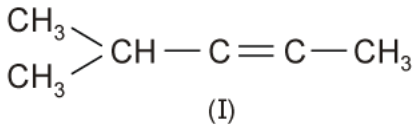
Empirical formula mass = $3 \times 12 + 5 \times 1 = 41$

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

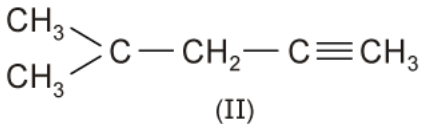
$\therefore$ Molecular formula = $(C_3H_6)_2 = C_6H_{10}$

Now, 

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:

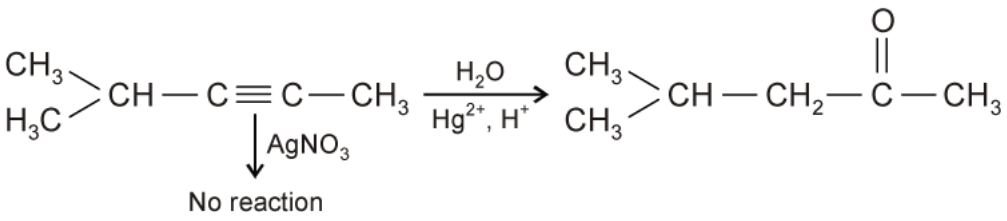


(I)

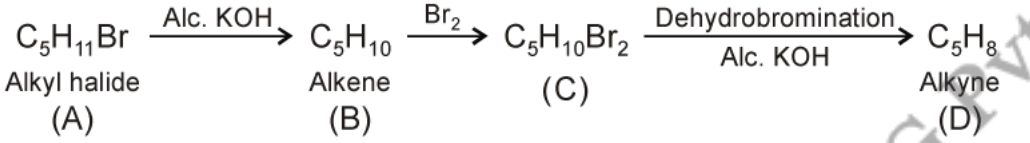


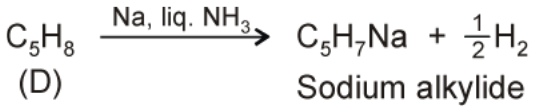
(II)

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.

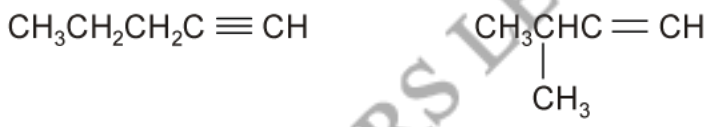


S10. The reactions are:



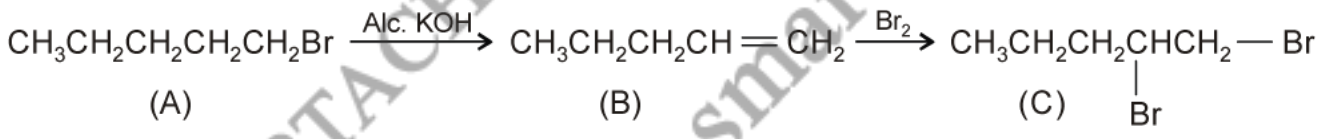


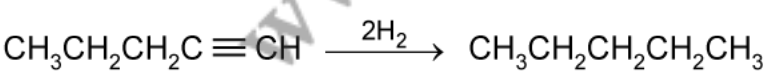
The reaction suggest that (D) is a terminal alkyne. The possible structures are:



(I) (II)

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



and 

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) $CH_3CH_2CH_2C\equiv CH$