Hydrocarbons

Solution NCERT FOCUS

ANSWERS

Topic 1

1. The chlorination of methane follows a free radical mechanism. **Initiation :** Initially, by the action of heat or sunlight on Cl_2 , the Cl - Cl bond breaks. Chlorine free radical generate.

Propagation : This produces two Cl free radicals which abstract a hydrogen free radical from the methane molecule thereby generating a methyl free radical.

$$\dot{C}I + \dot{H} \xrightarrow{C} CH_3 \longrightarrow H - CI + \dot{C}H_3$$

Methyl radical

Termination : Now this methyl free radical may either combine with a chlorine free radical to form the desired product – chloromethane or may combine with another methyl radical to form an ethane molecule.

$$\dot{C}H_3 + \dot{C}I \longrightarrow CH_3CI$$

Methyl chloride
or $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 \longrightarrow CH_3$
Ethane

This is how ethane is generated during the chlorination of methane.

2.
$$H_{3}C - CH_{2} - CH_{3} - CH_{2} - CH_{2} - CH_{2} - CH_{2} - CH_{2} - CH_{3} - CH_{3$$

15 H attached to 1° carbon atoms. 4 H attached to two 2° carbon atom 1 H attached to one 3° carbon atom.

3. As the branching in an alkane increases, the shape of the molecule approaches a sphere and size of the branched chain alkane becomes less than that of its straight chain counterpart. The reduced surface area results in decreased van der Waals' interaction and finally leads to lower boiling point as compared to straight chain alkanes of comparable molar mass.

4. Wurtz reaction is used for preparation of alkanes. During this reaction, an alkyl halide with half the number of carbon atoms than the desired alkane is made to react with sodium metal in dry ether. This leads to the formation of the desired alkane.

e.g., If the desired alkane is ethane, methyl iodide is taken.

$$H_3C \xrightarrow{+} I + 2Na + I \xrightarrow{+} CH_3 \xrightarrow{Dry ether} H_3C \longrightarrow CH_3 + 2NaI$$

Ethane

While this method is highly successful for producing alkanes with even number of carbon atoms but it gives a mixture of alkanes when odd numbered alkanes are to be formed. This happens because two different alkyl halides not only react with each other but also with themselves.

This can be better illustrated with an example - propane is prepared by taking methyl iodide and ethyl iodide.

$$H_3C - I + 2Na + I - C_2H_5 \xrightarrow{Dry \text{ ether}}$$

 $CH_3 - CH_2 - CH_3 + 2NaI$
Propane

The side reactions that take place in the reaction mixture are : $H_2C - I + 2Na + I - CH_2 - \frac{Dry \text{ ether}}{Dry \text{ ether}}$

$$H_{3}C - CH_{3} + 2NaI$$

$$H_{3}C - CH_{3} + 2NaI$$

$$E thane$$

$$C_{2}H_{5} - I + 2Na + I - C_{2}H_{5} - C_{2}H_{5} + 2NaI$$

$$C_{2}H_{5} - C_{2}H_{5} + 2NaI$$
But ane

Thus, one gets a mixture of propane, ethane and butane which need to be separated in order to get the desired product.

That is why Wurtz reaction is not preferred for preparation of alkanes containing odd number of carbon atoms.

1. (i)
$$CH_3 - CH_2 - HC = CH - CH_3 \xrightarrow{ozonolysis} CH_2 - CHO + CH_3CHO \xrightarrow{Propanal} Ethanal CH_3 + CH_2 - CHO + CH_3CHO \xrightarrow{Propanal} Ethanal CH_3 + CH_2 - CH_2 - CH_3 \xrightarrow{ozonolysis} CH_3 + CH_2 - CH_2 - CH_3 \xrightarrow{Ozonolysis} CH_3 + CH_3 - CH_2 - C = O \xrightarrow{CH_3} CH_3 - CH_2 - C = O \xrightarrow{CH_3} Butan-2-one + CH_3 - CH_2 - C = O \xrightarrow{CH_3} CH_2 = O + CH_3 - CH_2 - C = O \xrightarrow{CH_3} CH_2 = O + CH_3 - CH_2 - C = O \xrightarrow{Methanal} Pentan-3-one + CH_3 - CH_2 - C = O \xrightarrow{Methanal} Pentan-3-one + CH_3 - CH_2 - CH = O + CH_3 - CH_$$

Benzaldehyde

2

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2. (A)
$$\xrightarrow{\text{ozonolysis}} CH_3 - CHO + O = C < CH_2 - CH_3$$

Alkene Ethanal Pentan-3-one

An alkene when subjected to ozonolysis, cleaves at the double bond and gives rise to carbonyl compounds.

Since, the given compounds here are ethanal and pentan-3-one, the alkene can be predicted to be:



3. *A* is an alkene. *A* contains (i) $3 \subset - \subset \sigma$ bonds, (ii) $8 \subset - H \sigma$ - bonds and (iii) $1 \subset - \subset \pi$ -bond.

 $(A) \xrightarrow{O_3} 2BCHO$

Molar mass of RCHO = 44u

(i) The clue to finding the structure and therefore the IUPAC name of *A* lies in the aldehyde *R*CHO.

The mass of —CHO group is 29 u. This implies that the alkyl group attached has a mass of 44 - 29 = 15. This can be the mass of $-CH_3$ group only.

 \therefore RCHO is CH₃CHO.

(ii) Since only 2 moles of CH_3CHO is obtained.

Therefore, the alkene is

$$H_{3}C - C = 0 + 0 = C - CH_{3} \rightarrow H_{3}C - HC = CH - CH_{3}$$

$$H H H$$

But-2-ene

Thus, (A) is $CH_3 - HC = CH - CH_3$ and its IUPAC name is But-2-ene.

This structure also confirms the given number of σ and π bonds.

4. Alkene
$$\xrightarrow{\text{ozonolysis}}$$
 Pentan-3-one + Propanal

$$CH_{3} - CH_{2} - C = 0 + 0 = C - CH_{2} - CH_{3} \longrightarrow$$

$$(H_{3} - CH_{2} + H)$$

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

$$CH_{3} - CH_{2} - C = CH - CH_{2} - CH_{3}$$

$$(H_{3} - CH_{2} - C = CH - CH_{2} - CH_{3}$$

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



Of the given isomers, the *cis*-isomer has a higher boiling point. This difference arises due to higher dipole moment of the *cis*-isomer which introduces a somewhat ionic character in the compound. In the *trans*-isomer, the dipoles cancel each other resulting in a small dipole moment as the case may be.

6. Addition of HBr to propene takes place as per the Markovnikov's rule via the formation of most stable carbocation as follows :

Step 1 :
$$\overset{+}{HBr}$$
 + CH₃ - CH = CH₂ \longrightarrow CH₃ - $\overset{+}{CH}$ - CH₃
2° carbocation
Step 2 : Br + CH₃ - CH - CH₃ \longrightarrow CH₃ - CH - CH₃
Br

Thus, it is an example of electrophilic addition reaction. But, when the same reaction is carried out in the presence of peroxide, which is a free-radical generator, the mechanism follows free radical mechanism where the intermediate is a carbon free radical.

2-Bromopropane

Step-1:
$$C_6H_5 - \dot{C} - \dot{O} - \dot{O} - \dot{C} - C_6H_5 \rightarrow 2C_6H_5 - \dot{C} - \dot{O}$$

Benzoyl peroxide
 $2C_6H_5 - \dot{C} - \dot{O} - \dot{O} - \dot{C} - C_6H_5 + 2CO_2$
Step-2: Generation of Br[•]: $\dot{C}_6H_5 + \dot{H} - Br \rightarrow C_6H_5 + Br'$
Step-3: $CH_3 - C\dot{H} - CH_2 + B\dot{r} \rightarrow CH_3 - \dot{C}H - CH_2 - Br$
more stable

Here, the free radical is the 2° free radical and therefore it is the one which finally forms 1-bromopropane.

Step 4:
$$CH_3 \longrightarrow CH_2Br + H \longrightarrow Br \longrightarrow CH_3CH_2CH_2Br + Br$$

Step 5: $Br + Br \longrightarrow Br_2$

This explains why different products are formed under different reaction conditions.

7. 2-Methylbutane is
$$H_3C - H_2C - HC - CH_3$$

The structure of the compounds which on hydrogenation produce 2-methylbutane are:

$$\begin{array}{c} CH_{3} \\ H_{3}C - CH_{2} - C = CH_{2} \\ CH_{3} \\ CH_{3} - CH = C - CH_{3} \\ CH_{3} \\ 2 - Methylbut - 2 - ene \end{array}$$

$$CH_3$$

|
 $CH_2 = CH - CH - CH_3$ 3-Methylbut-1-ene

Topic 3

1. (a) C_4H_8 can have the following structures with one double bond :

(i)
$$H_3C - H_2C - HC = CH_2$$
 (ii) $H_3C - C = CH_2$
But-1-ene
(iii) $H_3C - HC = CH - CH_3$
But-2-ene
 $CH_3 - C = C - CH_3 - CH_3 - C = C - CH_3$
(b) C_5H_8 can have the following structures with one triple bond :
(i) $H_3C - H_2C - H_2C - C \equiv CH$
Pent-1-yne
(ii) $H_3C - H_2C - C \equiv C - CH_3$
Pent-2-yne

(iii) $H_3C - HC - C \equiv CH$ CH_3 3-Methylbut-1-yne

Topic 4

1. (a) $CH_3 - CH_3 = C - CH_3$

2-Methylbut-2-ene $CH_2 = CH - C = C - CH_3$

(c) 4Buta-1, 3-diene

(b)

(f)
$${}^{10}_{\text{CH}_3}$$
 $-{}^{9}_{\text{CH}_2}$ $-{}^{8}_{\text{CH}_2}$ $-{}^{7}_{\text{CH}_2}$ $-{}^{6}_{\text{CH}_2}$ $-{}^{5}_{\text{CH}_2}$ $-{}^{4}_{\text{CH}_2}$ $-{}^{3}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{1}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_3}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_3}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_3}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_3}$ $-{}^{2}_{\text{CH}_2}$ $-{}^{2}_{\text{CH}_3}$ $-{}^{2}_{\text{CH}_3}$

(g)
$${}^{10}_{CH_3} - {}^{9}_{CH} = {}^{8}_{CH} - {}^{7}_{CH_2} - {}^{6}_{CH} = {}^{5}_{CH} - {}^{4}_{CH} - {}^{3}_{CH_2} - {}^{2}_{CH} = {}^{1}_{CH_2}$$

 $| {}^{C_2H_5}_{4-Ethyldeca-1,5,8-triene}$

2. Upon combustion, any hydrocarbon produces CO_2 and H_2O . For the given hydrocarbons the reactions may be represented as :

(i) Butane : $C_4H_{10} + \frac{13}{2}O_2 \xrightarrow{\Delta} 4CO_2 + 5H_2O$ (ii) Pentene : $C_5H_{10} + \frac{15}{2}O_2 \xrightarrow{\Delta} 5CO_2 + 5H_2O$ (iii) Hexyne : $C_6H_{10} + \frac{17}{2}O_2 \xrightarrow{\Delta} 6CO_2 + 5H_2O$ (iv) Toluene : $C_7H_8 + 9O_2 \xrightarrow{\Delta} 7CO_2 + 4H_2O$

3. (i) The extra ordinary stability of benzene molecule may be attributed to resonance in the molecule. In benzene, each of the 6 C atoms is sp^2 hybridised with one *p*-orbital on each carbon atom left unhybridised. While two of the sp^2 orbitals form bonds with 2 C-atoms, the third one is involved in bonding with the hydrogen atom. Thus, 3 of the valencies of C are satisfied.

(ii) This leaves the unhybridised p-orbital containing 1 electron each for bonding. Each of these p-orbitals can overlap with the adjacent C atom and thus, results in bonding.

(iii) Since the probability for each *p*-orbital to overlap with either of the two immediate neighbours is equal. Therefore, it alternately does so.

(iv) Thus, the π electrons (in unhybridised *p*-orbitals) are no more localised between just 2 carbon atoms but these 6π electrons are shared or attracted by all the 6 carbon atoms.

(v) This increased attraction is the reason for the extra ordinary stability of the benzene molecule with 3 double bonds.

(vi) These 3 $\pi\text{-}\text{bonds}$ are not localised but are spread over the entire molecule.



4. The necessary and sufficient condition for any system to be aromatic is given by Huckel's rule. As per Huckel's rule, any system is said to be aromatic if it satisfies the following 3 conditions:

(i) Contains $(4n + 2) \pi$ electrons, where *n* is any positive integer or 0,

(ii) Shows complete delocalisation of π electrons and

(iii) The molecule must be planar.

5. One of the conditions stated by the Huckel's rule for any system to be aromatic is that of planarity *i.e.*, all atoms of the molecule must be present on the same plane. This rule is violated in structure (i) and (ii). The carbon atom indicated below are sp^3 hybridised which disallow planarity (sp^3 hybridised carbon is tetrahedral in geometry).

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In (iii) the number of π electrons is 8. (2 per double bond). The Huckel's rule allows 2, 6, 10, 14, ... etc. π electrons for any aromatic system. Since (iii) does not have $(4n + 2) \pi$ electrons, therefore, it is not aromatic.



These three products cannot be obtained if we assume a triene structure of benzene. They can be obtained only if it is assumed that the double bonds in benzene are delocalised.

If the double bonds are assumed to be between C1 — C2, C3 — C4 and C5 — C6 then

$$\begin{array}{c} CH_{3} \\ H_{3}C \\ C = 0 \\ H_{3}C$$

If the double bonds are assumed to be localized between $C_2 - C_3$, $C_4 - C_5$, $C_6 - C_1$, then

But since all the above products are obtained, it indicates that only one structure is not possible and the resonance structures proposed by Kekule are the only possibilities.

8. The decreasing order of acidity is:

$$HC \equiv CH \\ Ethyne > \left\langle \bigcirc \right\rangle > n - Hexane \\ Benzene > Renzene > n - Hexane$$

Acidic strength of any compound is defined as its ability to release H atom as $\overset{+}{H}$. This atom to which H is attached is highly electronegative. Such atoms tend to pull the bond pair of electrons towards themselves, thereby polarising the bond and creating δ^+ charge on H.

$$A \xleftarrow{+} H$$

Electronegative atom

In the compounds given in question, the H is attached to carbon atom which does not has a very high electronegativity value. Moreover, the electronegativity of carbon is somewhat increased if the *s*-character of its hybridised orbitals is high. Greater is the *s*-character of carbon, greater is its electronegativity. As a result of which, the bond pair of electrons of the C — H bond moves towards carbon atom, creating a partial positive charge on H and facilitating its release as H⁺.

Based on this the order of acidic strength may be predicted as

$$HC \equiv CH > \bigotimes > C_6H_{14}$$

Hybridisation of C sp sp² sp³
% s-character 50% 33% 25%

9. Electrophiles are species that are electron deficient and hence, seek electron rich molecules. Benzene is one such molecule which is rich in electrons. It is so because benzene has 6π electrons delocalised over the entire molecule which act as a good host for electrophiles.

Hydrocarbons

Another point working in favour of electrophilic substitution reactions is the retention of aromaticity. A benzene molecule is highly stable owing to its aromatic character. Therefore, it would not want to lose its aromaticity. Upon undergoing electrophilic substitution reaction, this aromaticity is not lost, it is retained and hence, benzene undergoes electrophilic substitution.



Contrast this with a nucleophilic substitution reaction where the nucleophile attacks. A nucleophile (Nu⁻) is a species that seeks a positive centre or an electron deficient species. Obviously, benzene is not electron deficient and therefore, will not be a welcome site for a Nu⁻. This is the major reason why benzene does not undergo a nucleophilic substitution reaction.

Another reason working against these reactions is the difficulty with which the transition state is formed. The transition state benzyne involved here is formed with great difficulty and hence, these reactions are difficult to bring about.



(iii)
$$C_6H_{14} \xrightarrow{Cr_2O_3/V_2O_5/MO_2O_3} \longrightarrow O_8$$

Hexane Benzene

11. Any substituted benzene compound is said to be more reactive towards an electrophile if the substituent on benzene increases electron density on it by electron donation.

Based on this, the given compounds may be arranged as :



12. During nitration, the electrophile NO_2^+ attacks the benzene ring. Nitration will be easier if the benzene ring shows increased electron density. This happens when electron releasing groups such as -R, $-NH_2$, $-NHCOCH_3$, -OH, -OMe etc. are attached to the ring whereas, the attachment of electron withdrawing groups such as $-NO_2$, -CHO, -COR, -COOH reduces the electron availability for NO_2^+ and nitration becomes difficult.

Therefore, relative ease of nitration of given molecules may be arranged as:



13. Other Lewis acids besides anhyd. $AICI_3$ that may be used during ethylation of benzene is anhy. $FeCI_3$.

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