Chemistry 2025 Paper II

Q2 (a)

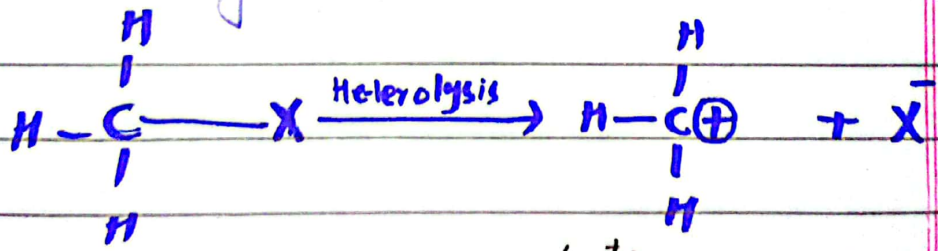
Elaborate with examples that how resonance, hyperconjugation and inductive effect, can contribute towards the stability of carbocations. (10)

(Ans)

Definition and formation of carbocations:

Carbocation is a type of reaction intermediates which has very short life of 10^{-6} seconds or a few seconds. They decide the final products of reaction.

Carbocation is formed by heterolysis.



(CH_3^+) Methyl Carbocation

$CH_3-\overset{+}{C}H_2$, $CH_3-CH_2-\overset{+}{C}H_2$ and $CH_3-\overset{+}{C}H-CH_3$ are some examples of carbocations.

In a carbocation, carbon has 6 electrons in valence shell so this electron

deficient specie is also called as an electrophile. Carbon is sp^2 hybridised here and carbocation has trigonal planar shape. They form in E_1 reactions, electrophilic addition and in S_N1 reactions.

Stability of a carbocation:

Stability of a carbocation is affected by resonance or mesomeric effect, hyperconjugation and inductive effect.

1- Contribution of resonance in stability of Carbocation:

Resonance stabilizes carbocations by delocalizing positive charge over multiple atoms or by π bonds or lone pairs. This dispersal of charge lowers energy of system.

Example:

$CH_2 = CH - CH_2^+$ (Allyl carbocation) can be written as $CH_2 - {}^+CH = CH_2$. Here charge is delocalized over three carbon atoms, making

it more stable than a non-resonating structure. ($Ph_3C^+ > Ph_2CH^+ > (PH)CH_2^+$)

More R.S ↑ → stability ↑

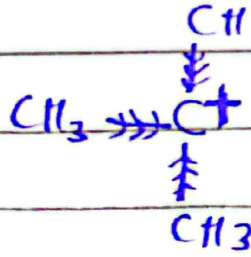
2- Contribution of Hyperconjugation in Stability of Carbocation:

Hyperconjugation involves interaction of sigma electrons in C-H or C-C bonds adjacent to positively charged C-atoms with empty p-orbital of carbocation. This helps in stabilizing the carbocation.

Example:

Tertiary butyl carbocation ($(CH_3)_3C^+$):

Here adjacent C-H sigma bonds donate electrons density into empty p-orbital of carbocation, stabilizing it. More will be alkyl groups greater will be α-Hydrogens and hyperconjugation and stability



9α-H

Hyperconjugation

Stability ↑

3. Inductive Effect and stability of Carbocation:

Inductive effect involves polarization of sigma bonds by adjacent electron donating or electron withdrawing groups. In carbocations, alkyl groups donate electron density through the σ-framework, stabilizing positive charge.

Example:

Comparison of methyl carbocation (CH_3^+) with ethyl carbocation ($CH_3CH_2^+$):

CH_2 group donates electron by inductive effect in $CH_3-CH_2^+$ thus stabilize positive charge on adjacent carbon.

More alkyl groups attached to carbocation, greater will be inductive effect and stability. Stability order will be

$$CH_3^+ < CH_3CH_2^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$$

→ stability increases by +I effect.

-I effect can destablize carbocation.

The effect of resonance, hyperconjugation and inductive effect on carbocation in order will be:

Resonance Effect > Hyperconjugation > Inductive Effect

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Q No 2 (b)

How dipole moment can be measured? Indicate; among following molecules which does not have dipole moment and why? (i) CCl_4 ii) BF_3 iii) CH_2Cl_2 iv) NH_3

(Ans) (10)

Dipole Moment:

Dipole moment is a measure of separation of positive and negative charges in a molecule, resulting in a molecular polarity. It arises when atoms with different electronegativites are bonded together. Dipole moment (μ) is calculated as;

$$\mu = q \times d$$

- q = magnitude of Charge (in Coulombs)
- d = distance between the Charges (in meters)

SI unit of μ is Cm or Debye.

Examples:

1- HCl: $H^{\delta+} - Cl^{\delta-}$ Polar covalent bond where $\mu = 1.08$ D (Debye units)

2- H_2O: Bent structure with $\mu = 1.85$ D

3- CO_2: Linear structure O=C=O net dipole moment will be zero.

Measurement of dipole Moment:

1-Dielectric Constant Method:

This method measures dielectric constant of a substance, which is related to dipole moment (μ). The substance is placed between the plates of a capacitor, and the change in capacitance is measured.

2. Microwave Spectroscopy Method:

This involves measuring rotational spectra of molecules in microwave region. Dipole moment is determined from interaction of molecule's rotation with electric field of microwave radiation.

3. Stark Effect Method:

This measures splitting of spectral lines when a molecule is exposed to an external electrical field. The amount of splitting is proportional to the dipole moment

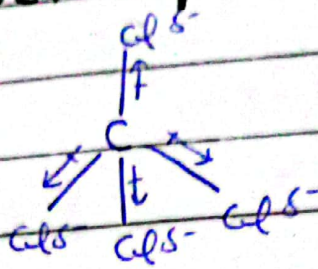
4. Electro-optical Methods (e.g. Kerr Effect):

This measures the birefringence (change in refractive index) induced in a substance by an electric field. The dipole moment is related to the Kerr constant.

1- CCl_4 (Carbon tetrachloride):

CCl_4 has tetrahedral geometry with four C-Cl bonds. Dipole moments of individual C-Cl bonds cancel each other out due to symmetrical arrangement.

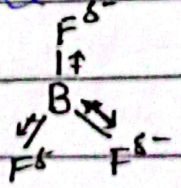
$\mu = 0$ D (no net dipole moment)



2- BF_3 (

2. BF_3 (Boron Trifluoride):

It has Trigonal planar geometry with three B-F bonds. Dipole moments of B-F bonds cancel each other due to symmetrical arrangement. $\mu = 0$ D



3- $CHCl_3$ (Chloroform):

Tetrahedral geometry with three C-Cl bonds and one C-H bond. Dipole moments of C-Cl bonds do not cancel out

completely, resulting in a net dipole moment. $\mu \neq 0$ D

4- NH_3 (Ammonia):

Trigonal pyramidal geometry with three N-H bonds and one lone pair on nitrogen. Dipole moments of N-H bonds do not cancel out, resulting in a net dipole moment.

$\mu \neq 0$ D

Based on above analysis, molecules do not having dipole moment are **CCl_4 and BF_3**. Both of these molecules have symmetrical structures that result in cancellation of individual bond dipoles, leading to a net dipole moment of zero.

Q. 3(a)

How does the reaction mechanism work for the electrophilic addition of bromine to ethene? Explain the intermediate (s)? (10)

(Ans)

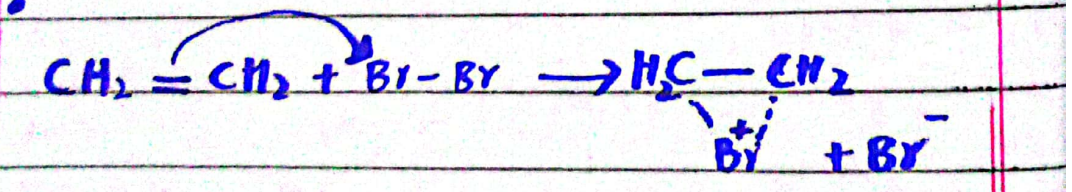
Electrophilic addition of Bromine to ethene:

Electrophilic addition of bromin to ethene is a two-step process involving an intermedia and resulting in a final product 1,2-dibromoethane.

Mechanism of Reaction:

Two steps are involved in this.

Step 1: Formation of the bromonium ion and bromide ion:



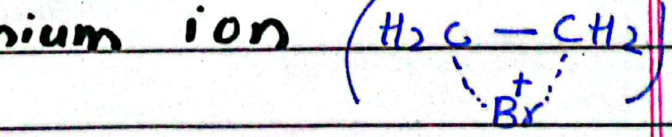
The non-polar Br_2 molecule becomes polarized as it approaches the electron-rich double bond of ethene.

The pi-electrons of ethene's double bond push electrons in Br-Br bond away from closest bromine atom, inducing a partial positive charge (δ^+) on that bromine atom and a partial negative charge (δ^-) on the other.

δ^+ bromine atom is then attacked by ethene's pi-bond electrons, causing Br-Br bond to break heterolytically.

This forms 3-membered ring intermediate called a **cyclic bromonium ion**, wher positively charged bromine atom is bonded to both carbon atoms of original double bond.

A free bromide ion (Br^-) is also produced.

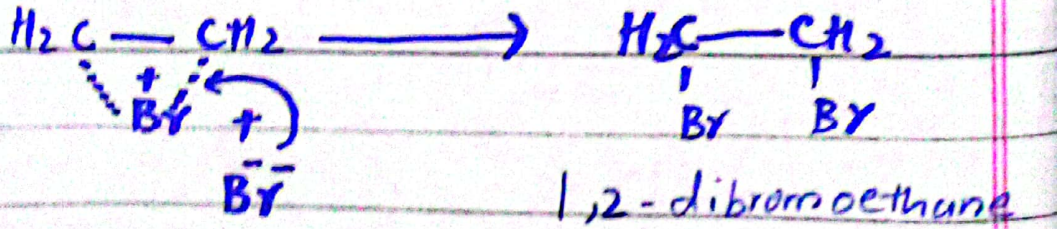
In Bromonium ion 

Bromine atom forms a 3-membered ring with 2-carbon atoms of the double bond. This intermediate is highly strained and reactive, ~~but~~ positive charge is being shared between

two carbon atoms
The bromonium ion is a key intermediate that explains the stereospecificity of the reaction.

Step 2: Nucleophilic attack by the bromide ion: (Br^-)

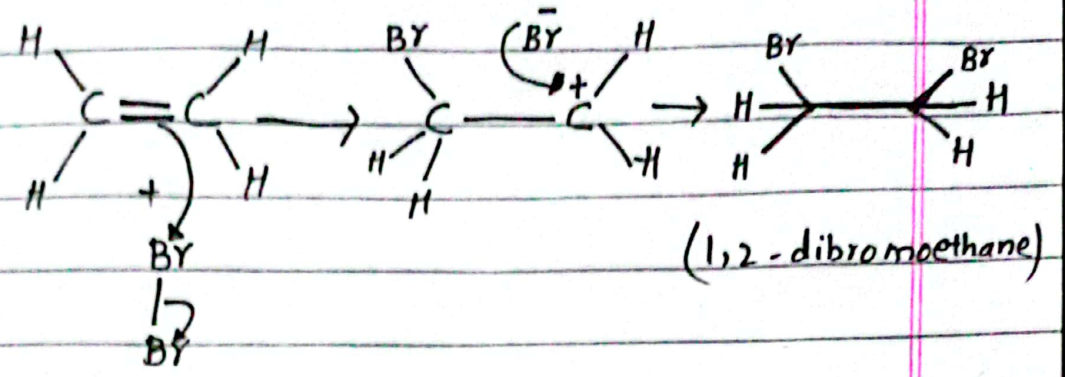
Br^- acts as a nucleophile and attacks one of the carbon atoms of the bromonium.
Attack occurs from back side, opposite to already attached bromine atom.
This backside attack causes 3-membered ring to open, forming final product of **1,2-dibromoethane**, with 2 bromine atoms now on opposite carbons.



1,2-dibromoethane

The reaction proceeds via anti-addition.

Overall Reaction:



(1,2-dibromoethane)

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Q3 (b)

Describe IUPAC rules for naming alkenes and alkyne with appropriate examples.

(Ans)

Alkenes:

Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond (C=C). They are also known as olefins and have the general formula C_nH_{2n} for a single double bond.

Examples: $CH_2=CH_2$ ethylene

$CH_2=CH-CH_3$ propylene

Alkyne:

Alkynes are a class of organic compounds known as

hydrocarbons that contain at least one carbon- carbon triple bond (C≡C). They are unsaturated hydrocarbons because triple bond means they have fewer H-atoms than alkanes with same number of C-atoms. Simplest alkyne is ethyne (C_2H_2) also known as acetylene.

IUPAC Rules for Naming alkenes and Alkynes:

1-Identify the parent Chain:

Identify and name longest continuous chain of C-atoms which contains double or triple bonds. If molecule contains more than one double or triple bond, use prexises di, tri etc before 'ene' or 'yne' e.g diene, triyne etc.

2- Number the parent Chain:

- Number the longest chain so that C's joined by double or

triple bond has lowest number possible. If multiple bond has same position starting from either end, use position of substituents to determine beginning of chain.

- The position of that double or triple bond must be located by lower membered carbon atom joined by multiple bond. for example for double/triple bond betwee 2nd and 3rd. carbons, number 2 is used.

3- Name the parent Chain:

- Use the Greek prefix that corresponds to number of carbons in parent chain (meth-, eth-, prop- etc).
- Add appropriate suffix: "ene" for a double bond or "-yne" for a triple bond.
- Place the number indicating position of multiple bond before suffix, separated by a dash e.g hex-1-ene. For simple

molecules like ethene or ethyne, number is often omitted as there is only one possible position for the bond.

4- Add and position Substituents:

- For any other groups attached to parent Chain (substituents), determine their position number based on the numbering from step 2.
- List substituents alphabetically before the parent name, with their position numbers e.g 3-Chloro-4-methylhex-1-ene)
- Use prefixes like di, tri or tetra to indicate multiple identical substituents.

Examples: of IUPAC Nomenclature of Alkenes:

1- $CH_3-CH_2-CH_2-CH=CH_2$

Pent-1-ene

2- $CH_3CH_2CH=CHCH_3$

Pent-2-ene

3- $CH_3C(CH_3) = CHCH_3$

3-methylbut-2-ene

Examples : IUPAC Numenclature of Alkynes:

1- $CH_3 - C \equiv C - CH_3$

But-2-Yne

2- $HC \equiv C - CH_2 - CH_2 - CH_3$

Pent-1-Yne

3- $CH_2 - CH_2 - C \equiv CH$

But-1-yne

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