II.M.Sc.,CHEMISTRY

ORGANIC CHEMISTRY -III

SEMESTER-III

UNITS – 3

PHYSICAL METHODS OF STRUCTURAL DETERMINATION

PART - 3

By,

Dr.B.SHARMILA INDIRANI,

ASSOCIATE PROFESER OF CHEMISTRY ,

PERIYAR ARTS COLLEGE,

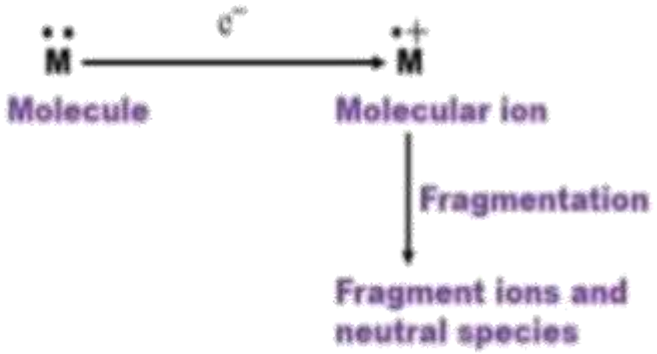
CUDDALORE – 1.

MASS SPECTROSCOPY FRAGMENTATION PROBLEMS

PROBLEMS

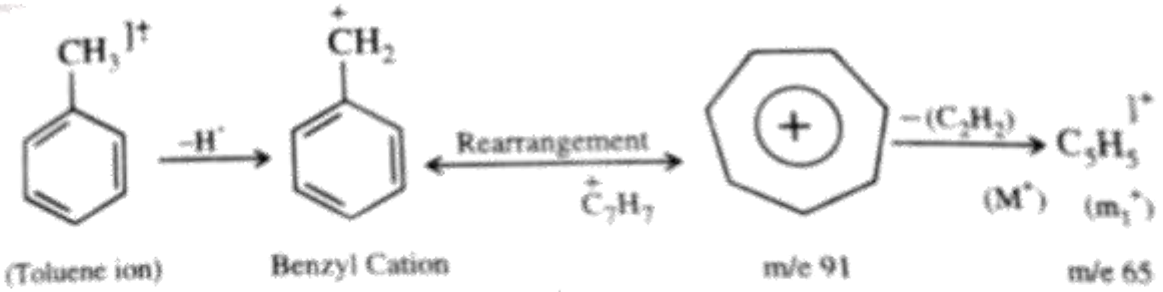
- Benzyl radical ion
- Phenyl acetic acid
- Bytyraldehyde
- Pentanal

Fragmentation patterns



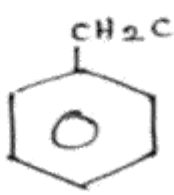
- α-Cleavage
- β-Cleavage
- Inductive cleavage
- Elimination
- Retro-Diels Alder reaction
- McLafferty rearrangement

BENZYL RADICAL ION



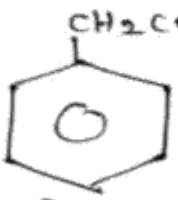
PHENYL ACEDIC ACID

Structure :-



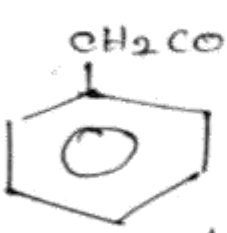
→ phenyl audic acid

Molecular ion peak

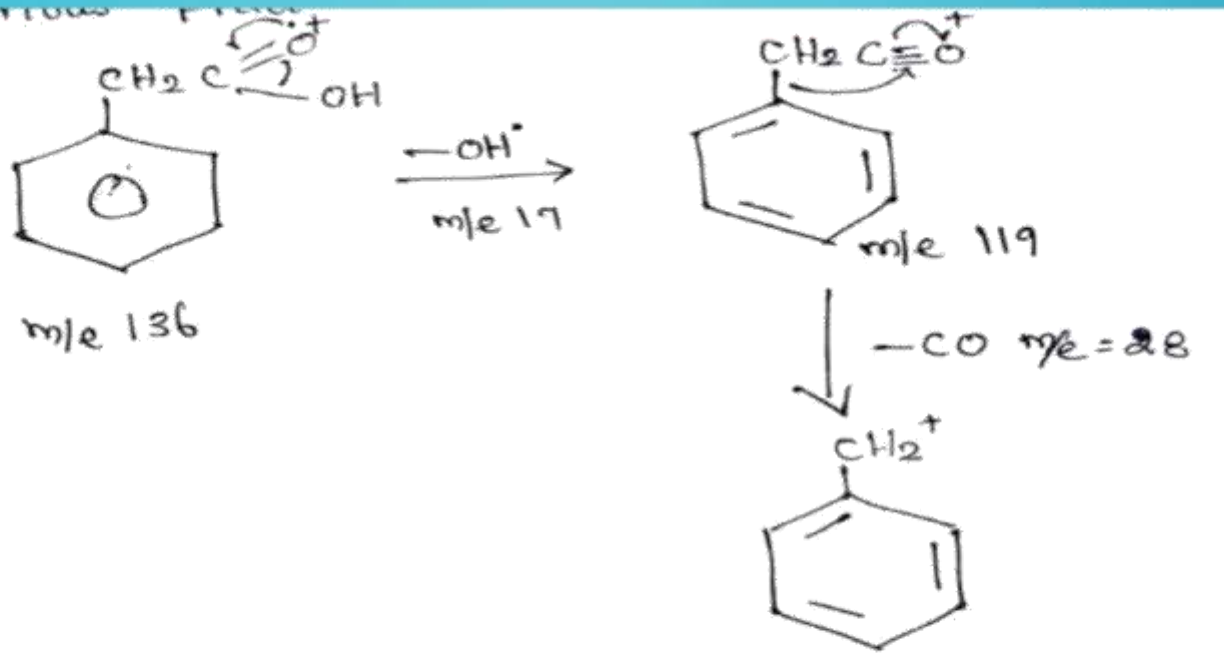


$C_8H_8O_2$

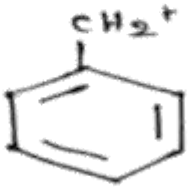
e



m/e 136


CH2 C
OH
m/e 136
−OH•
m/e 17
CH2 C
m/e 119
−CO m/e = 28
CH2+
Benzyl radicalion
m/e 91

Formation of tropylium radical ion

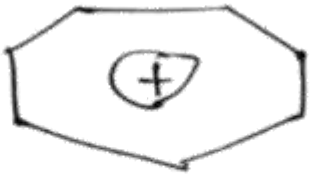


m/e 91

Rearrangement

$C_7H_7^+$

Tropylium radical ion m/e = 91



m/e 91

$C_7H_7^+$

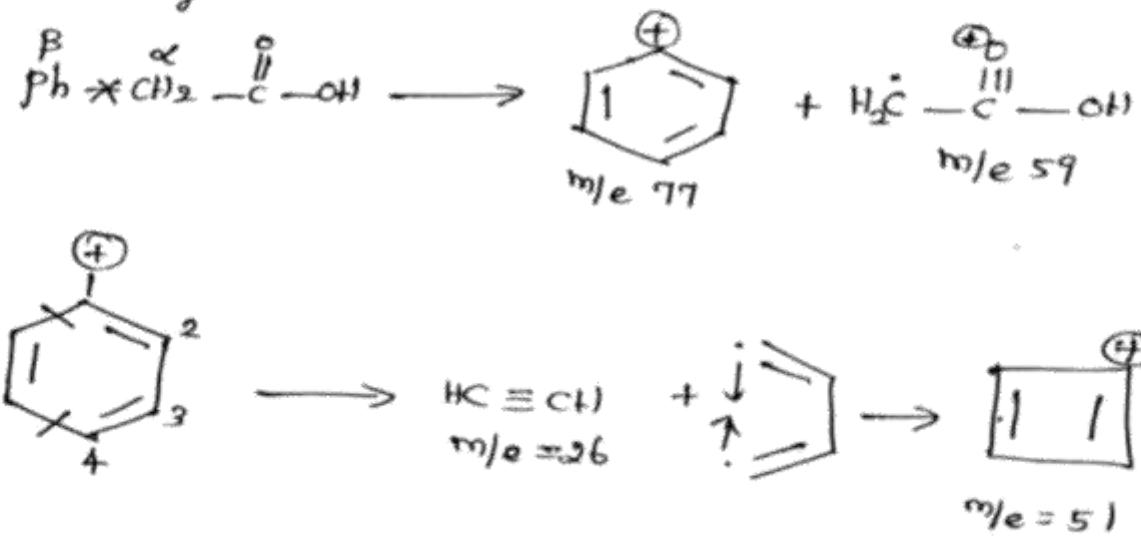
$-CH \equiv CH$

$C_5H_5^+$

m/e 65

BETA CLEVAGE

β -cleavage



BUTYRALDEHYDE

(i) Structure

$CH_3-CH_2-CH_2-CHO$ - Butyraldehyde

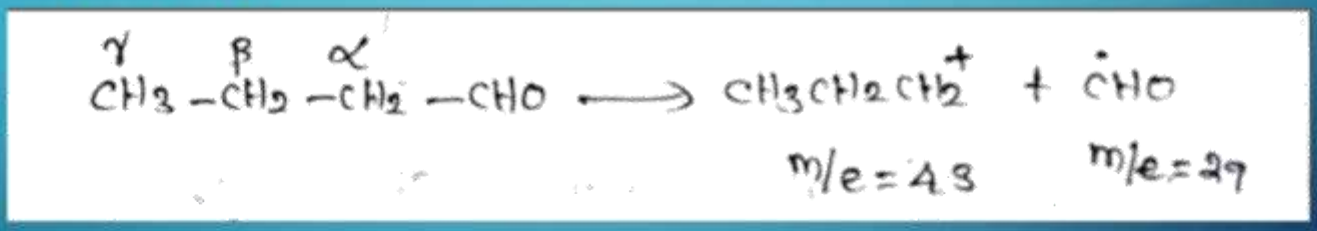
(ii) Molecular ion peak

$$CH_3-CH_2-CH_2-CHO \xrightarrow{e^-} CH_3-CH_2-CH_2-\dot{C}HO]^{+\cdot} + 2e^-$$

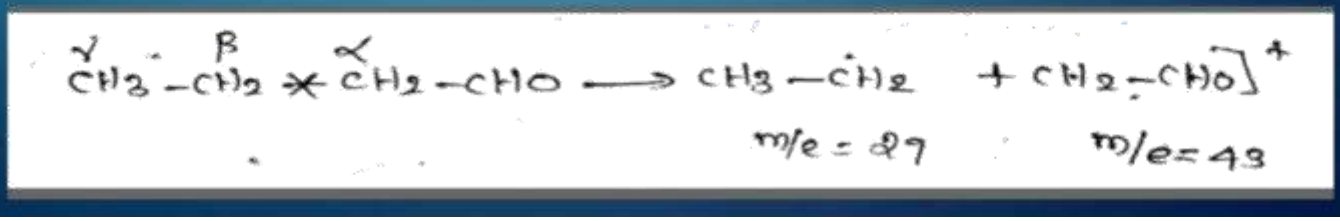
m/e = 72

VARIOUS FRAGMENTS ARE

- Alpha clevage



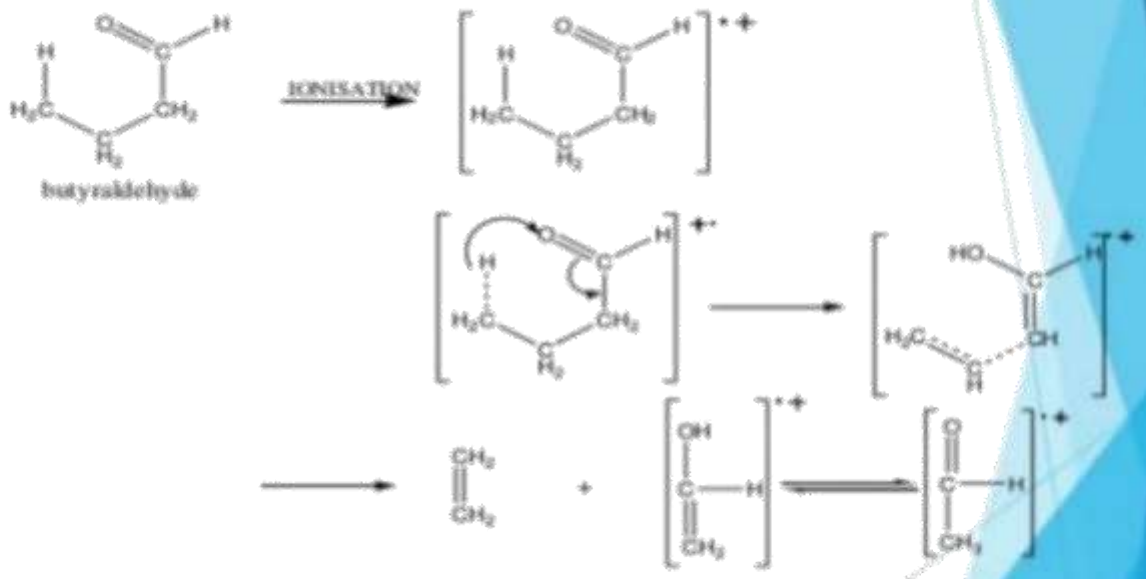
- Beta clevage



MCLAFFERTY REARRANGEMENT

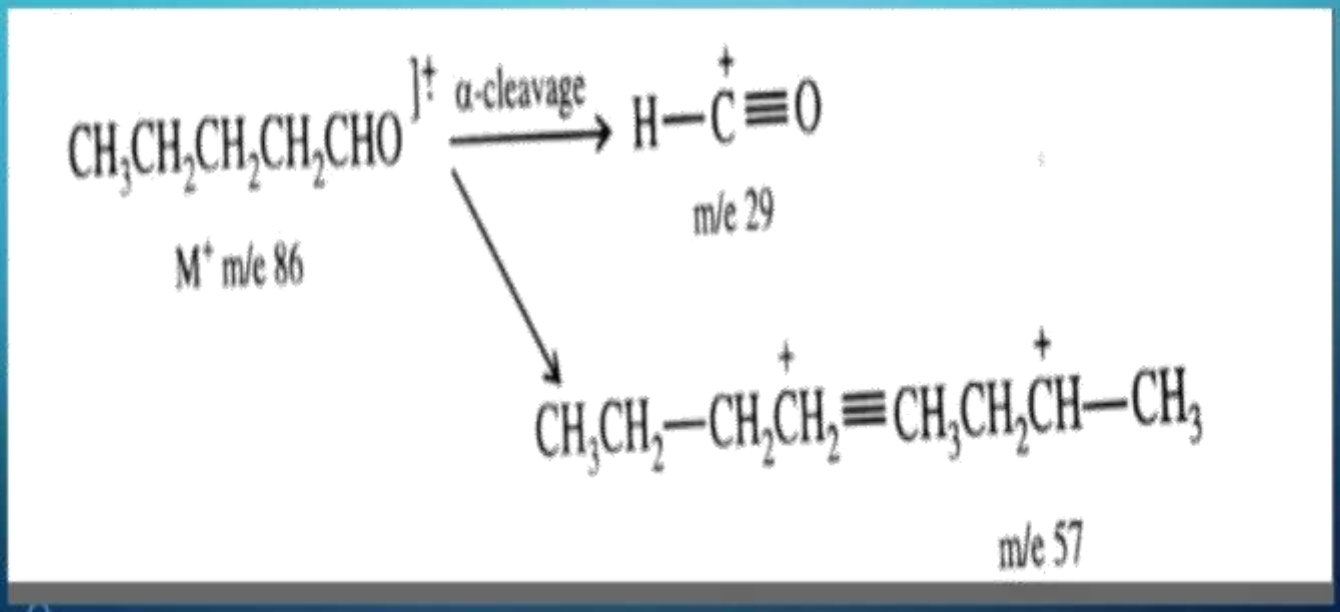
- Long enough to form a six membered transition state
- Atleast one gamma hydrogen
- Beta Cleavage
- Product another alkene
- Example

Carbonyl compound, Alkene, Ester(both aromatic or aliphatic)

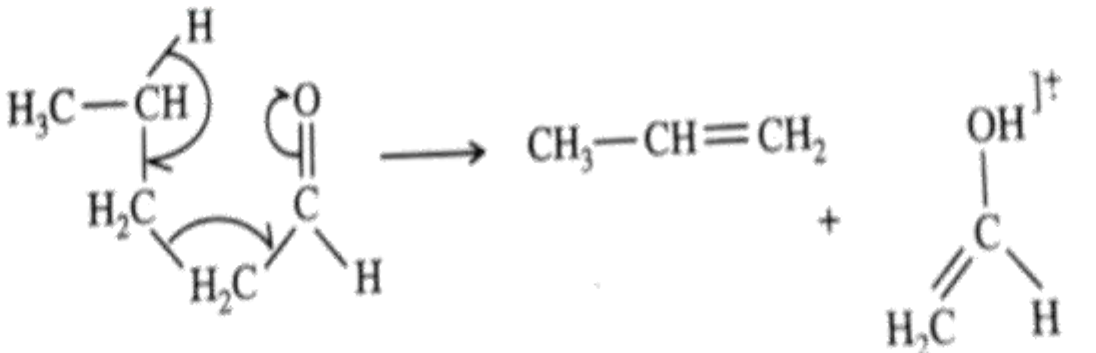


If m/z value is 44(24+4+16) that indicates aldehyde is present and connected to C_3 chain.

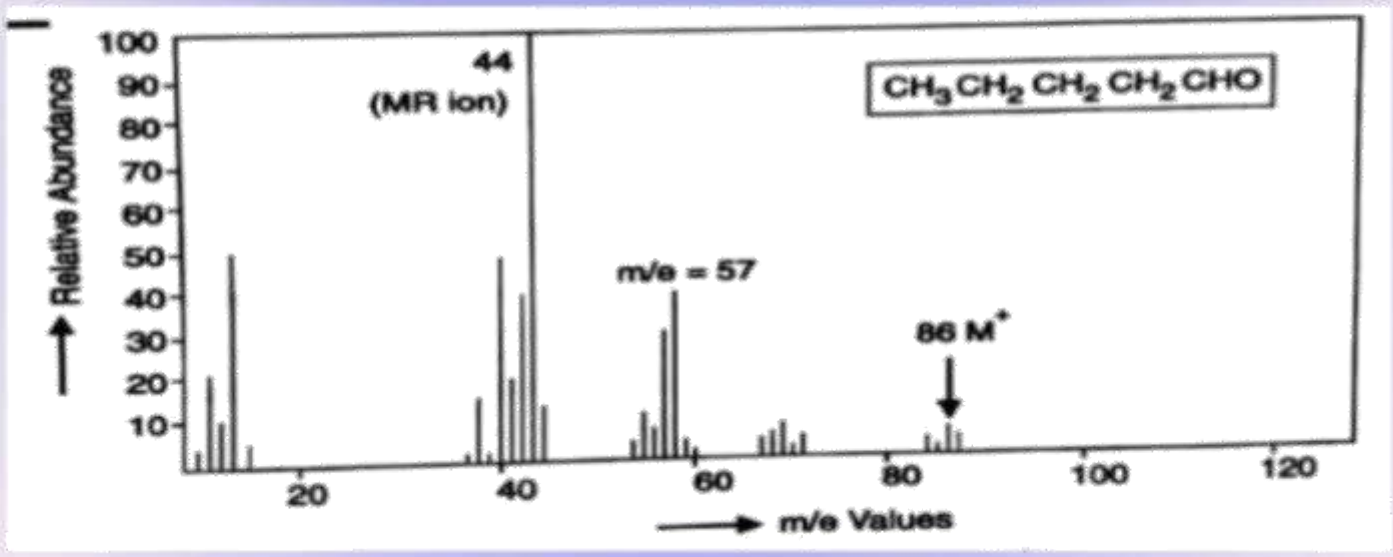
PENTANAL


CH3CH2CH2CH2CHO
M+ m/e 86
α-cleavage
H—C≡O
m/e 29
CH3CH2—CH2CH2≡CH3CH2CH—CH3
m/e 57

MCLAFFERTY REARRANGEMENT



1) Eg. Mass spectrum of Pentanal



(1) Circular bifringence and cicular dichorism!-

When a linearly polarized light beam passes through an optically active medium, it's two circularly polarized components display
(i) different refractive indices ($\eta_L \neq \eta_R$)
(ii) different absorption coefficients ($K_L \neq K_R$)
thus giving rise to two chiroptical properties of a chiral medium, known as circular bifringence and circular dichorism, respectively. These two are contributions of electronic transitions and are

CIRCULAR BIFRINGENCE:- wavelength dependent

(i) When the left and right circularly polarized components of a beam of a plane polarized light are transmitted, with equal speed through a medium, no rotation of the plane of polarization will be observed.

(ii) However if the plane polarized light passes through an optically active medium such as I, in which the polarizibilities of the atoms or groups decrease ~~in the order~~ then the two component vectors pass through the medium with unequal speeds.

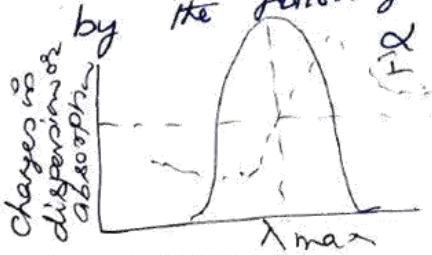
(iii) Upon emerging from such a medium, the two components are no longer in phase and the resultant vector has been rotated through an angle with respect to the original plane of polarization.

(iv) Such a medium is said to be circularly bifringent and the property of the medium to rotate the original plane of polarization is called circular bifringence

(v) If the right circularly polarized ~~light~~ component moves faster, the medium is dextro-rotatory (α is +ve). If the left circularly polarized component moves faster, the medium is laevorotatory (α is -ve)

(vi) The angle of rotation α is given by the following equation.

$$\alpha = \frac{\pi}{\lambda_{vac}} (\eta_r - \eta_l)$$



λ_{vac} = Vacuum wavelength of the light employed

n_r and n_l = Refractive indices of the medium with respect to the right and left circularly polarized components respectively

CIRCULAR DICHORISM:-

Definition:-

The measurement of unequal absorption of right and left circularly polarized components of a beam is linearly polarized light is known as circular dichorism.

(1) The optically active medium has unequal molar absorption coefficients for left and right circularly polarized components. The difference in the molecular extinction coefficients of RCP and LCP rays ($\Delta\varepsilon$) is called as differential dichroic absorption.

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R \neq 0$$

(2) Upon emerging from the optically active medium, the two circularly polarized components not only are out of phase but are of unequal amplitudes. (i.e) the component are absorbed to different extents.

(3) If the LCP component is absorbed more strongly (i.e) $K_L > K_R$, its electric field vector E_L will be smaller E_R..

(4) The emergent beam is no longer circularly polarized but it is elliptically polarized.

COTTON EFFECT:-

Circular dichorism is not easy to measure in the UV region, the only region where it can be important for colourless compounds, but the combination of circular dichorism and circular birefringence is known as cotton effect may be studied by plotting the change of optical rotation with wavelength.

(2) OPTICAL ROTATORY DISPERSION (ORD)

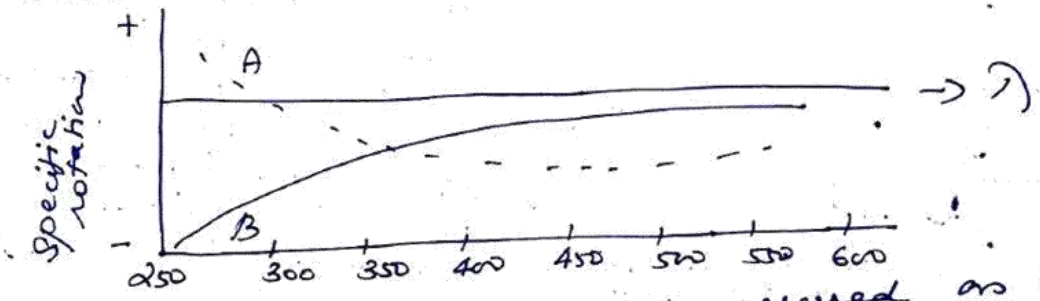
The measurement of optical rotation as a function of wavelength is known as Optical rotatory dispersion. The curves obtained are optical rotatory dispersion curves

TYPES OF OPTICAL ROTATORY DISPERSION CURVES:-

(i) Simple ORD curves
(ii) Anomalous ORD curves

SIMPLE ORD curves:-

Simple ORD curves may either be plain or normal dispersion curves. If measurement of rotation is restricted to wavelengths away from λ_{max} region, a solid curve results, showing a steady increase or decrease in optical rotation with decrease in wavelength. Such a plot is known as plain curve.



The curve A is referred as the plain positive dispersion curve because the molecular rotation increases in the positive direction in going to shorter wavelength. The curve B is referred to as a plain negative dispersion curve. (Molecular rotation increases in the negative direction).

The plain dispersion curve obeys a one term Drude equation. $\alpha = K/\lambda^2 - \lambda_0^2$

K & λ_0 are empirical constants

λ = wavelength at which the specific rotation is measured

λ_0 = wavelength due to absorption maximum.

ANOMOCOUS ORD CURVES:-

(i) The ORD curves containing both the peak and the trough are called as anomalous curves. The term anomalous is used because the curves do not obey the one term Drude equation.

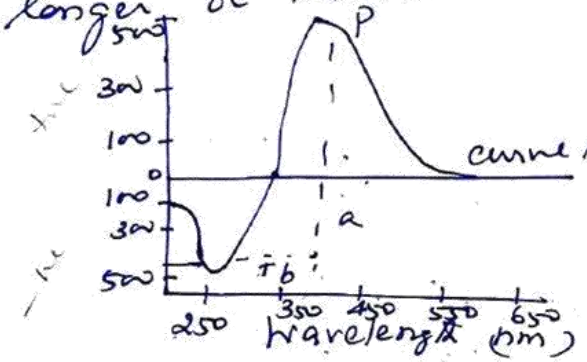
(ii) Anomolous curves are of two types.

(a) Single Cotton effect curves

(b) Multiple " "

(iii) SINGLE COTTON EFFECT CURVES:-

Single Cotton effect curves are defined as positive or negative, depending upon whether the peak occurs respectively at longer or shorter wavelength than the trough.

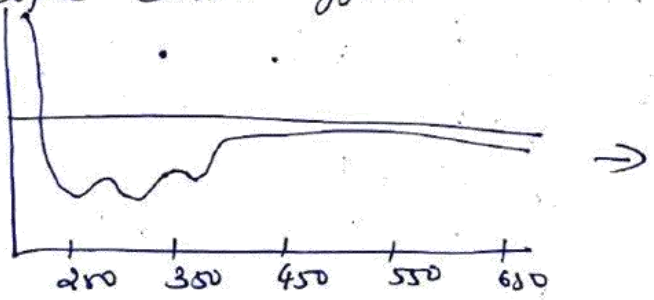


In the following positive single cotton effect curve, the vertical distance (a) between the peak and trough is the amplitude and the horizontal distance is the breadth.

Positive Cotton effect curve.

(iv) If the peak occurs at shorter wavelength than the trough, it is negative single cotton effect curve.

(v) Muliple Cotton effect curve:-



Multiple Cotton Effect curves exhibits several peaks and troughs with shoulders and inflections.

SIGNIFICANCE OF COTTON EFFECT CURVES IN STEREOCHEMISTRY:-

(i) Cotton effect curves are obtained for an optically active ketone undergoing $n-\pi^*$ transition.

(ii) Cotton effect curves can be correlated with many features of the stereochemistry around chromophore.

(iii) The $\pi-\pi^*$ transitions of conjugated ketones are of much higher intensity than $n-\pi^*$ transitions and are more difficult to study.

(iv) Aromatic compounds, heteroaromatic systems are successfully studied as well as carbohydrates, which have absorptions only in the less accessible vacuum UV.

(3) OCTANT RULE:-

The absolute stereochemistry of substituents around the chromophore can be deduced by using octant rule from the sign of the COTTON EFFECT. Octant rule is framed as follows.

(1) The space around the carbonyl group is divided into eight sectors (octants) by using three orthogonal planes which are mutually perpendicular to each other say A, B and C about x, y and z axes.

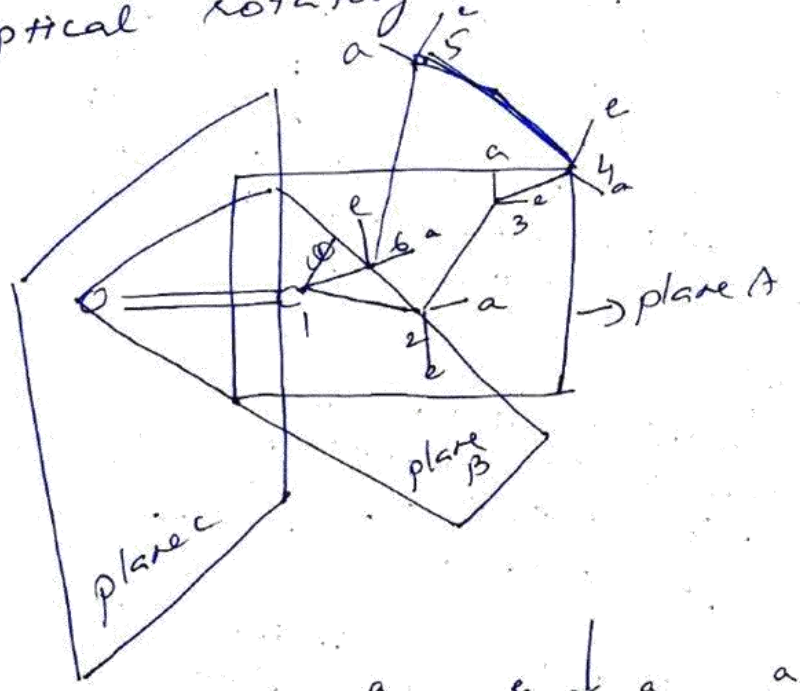
(2) Plane A defined by XY bisects the cyclohexane chair and intersect the carbonyl oxygen and carbons 1 & 4.

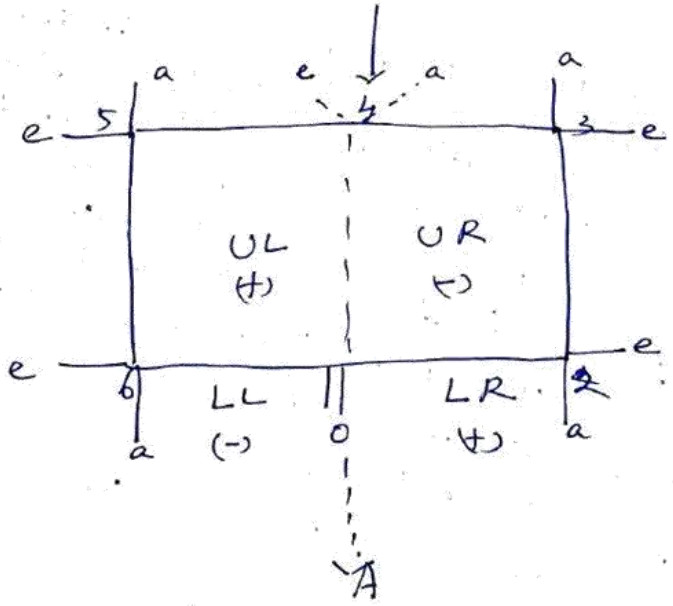
(3) Plane B perpendicular to plane A and contains C moiety and the two attached carbons C-2 & C-6.

④ Plane C is perpendicular to both the planes A + B and intersects the carbon-oxygen double bond at the mid point.

⑤ The two planes A & B thus divide the space around the carbonyl group into four quadrants designated as UL, UR, LL and LR. (Upper left, Upper right, Lower left and Lower right).

⑥ The groups that fall in these four quadrants will contribute to the sign of dispersion curve as indicated by plus and minus signs. Substituents lying on the Coordinate planes have no influence on Optical rotatory dispersion





Rear Octant
(front view)

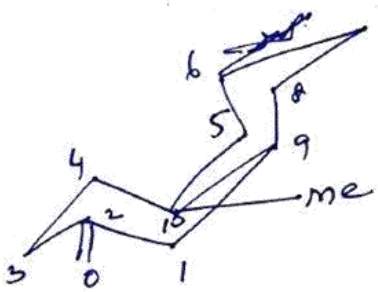
⑦ These four quadrants constitute the set of rear octants (away from the observer). On the left hand side of the plane C. There is another set of four quadrants (front) which are mirror images of the former.

⑧ The substituents lying in the front quadrants contribute oppositely. In a majority of cyclohexanones, the substituents are lying in the four rear octants only.

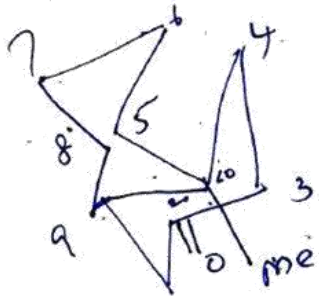
④ Determine the conformation of an organic compound by using octant rule / How will you determine the conformations of

(+) - cis - 10-methyl - 2 - decalone by octant rule.

① (+) - cis - 10-methyl-2-decalone may exist in either of the two conformations I & II which exhibit different contributions to the cotton effect and hence can be identified,

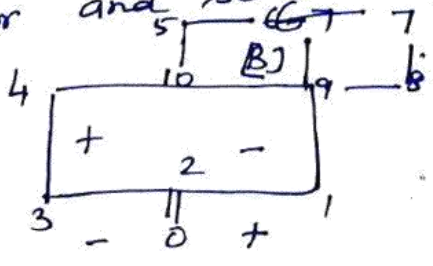


I)



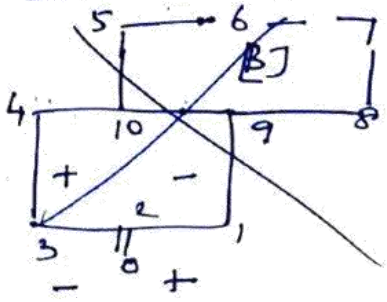
II

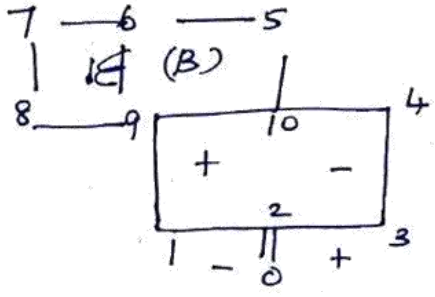
② Conformation (I), if it is put in a box diagram, according to Octant rule (i.e) in the projected form, ring (B) is in negative sector and so it displays -ve cotton effect.



I

(-ve cotton effect





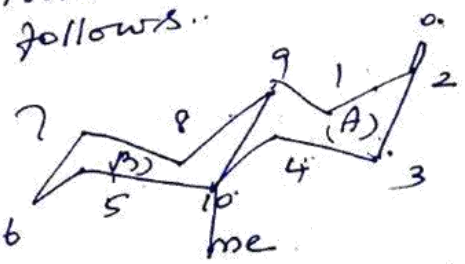
II
(+ve cotton effect)

(3) Conformation (II), if it is put in projected form, according to Octant rule, ring (B) is in (+ve) sector and so conformation (II) displays (+ve) cotton effect.

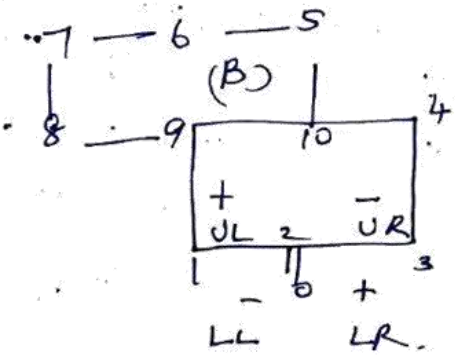
(4) Actually (+)-cis-10-methyl-2-decolone give (+ve) cotton effect. Hence it has conformation I

(5) Explain the cotton effect in trans-10-methyl-2-decalone / trans-10-methyl-2-decalone has +ve cotton effect. Explain.

(i) Trans-10-methyl-2-decalone is represented as follows.



(ii) If it is projected in a box diagram, according to Octant rule, ring (B) falls in UL quadrant which has +ve cotton effect



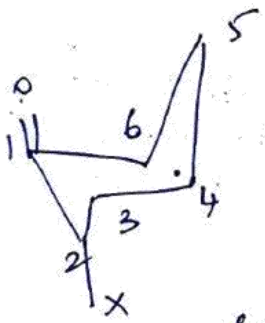
⑥ Write notes on axial haloketone rule.

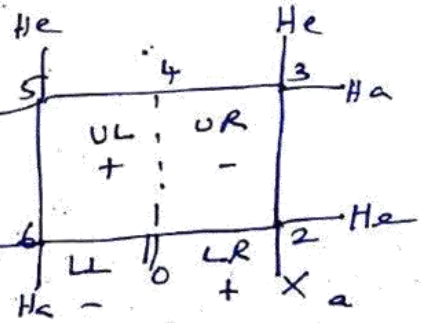
Definition:-

① Axial haloketo rule states that the introduction of an equitorial halogen in either α-position of cyclohexanone does not alter the sign of the cotton effect of the halogen-free ketone. Whereas the introduction of an axial halogen Cl/Br into the α-position may alter the sign of the cotton effect of the parent ketone.

② The axial haloketo rule applies to cyclohexanones containing an axial halogen (Cl, Br or I but not F). Polarisibility of fluorine is low compared to hydrogen.

③ When one looks along the >C=O axis as indicated in the following figure, if the halogen is on the right, there will be +ve cotton effect and if it is on the left, cotton effect is -ve.



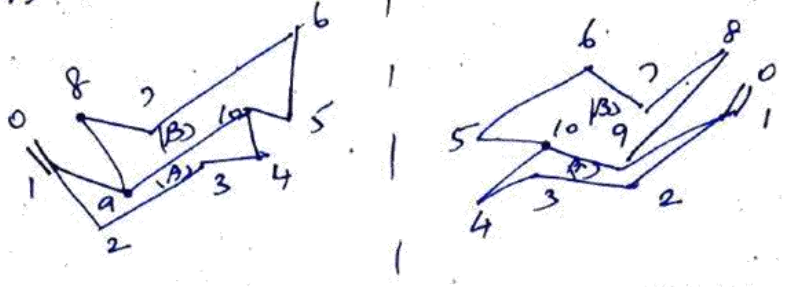


X = Any halogen Cl, Br, I

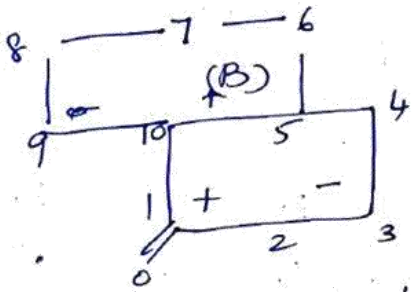
The halogen (X) in the projected structure (i.e) in the box diagram, it is in the lower right quadrant (in +ve sector) and hence it has +ve cotton effect. +ve cotton effect

(7) Define axial haloketo rule. Explain giving one example how this rule could be used for the determination of absolute configuration of an organic compound, points 1-3 in the previous question.

(4) (-)-trans-1-decalone may exist either in I & II R = H.

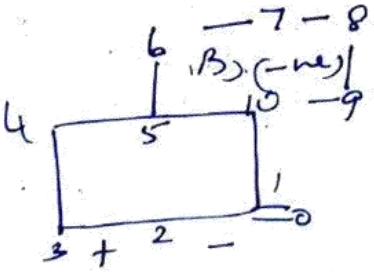


(5) Structure I), if it is given in projected form (i.e) in the box diagram ring (B) is in upper left quadrant, a (+ve) sector and it has +ve cotton effect.



+ve cotton effect

(6) Structure (II), if it is given in projected form (ie) in box diagram, ring (B) is in upper right quadrant, (-ve) sector and it has (-ve) cotton effect.



(7) On bromination, it gives (+)-trans-2-bromo-1-decalone which exhibits a strong (+ve) cotton effect. Looking at the two

Structures I & II (R = Br), I would give (+ve) cotton effect, since in this structure Br is on the right of $>C=O$ group. Structure (II) would give (-ve) cotton effect.

Thus the configuration of (-)-trans-1-decalone thus corresponds to I. R = H.

4. SECONDARY ION MASS SPECTROSCOPY:- (SIMS)

(i) It involves the generation of beams of ions including Xe^+ / Ne^+ / Ar^+.

(ii) This ion beam is directed on the target molecule

(iii) The energy of the ions transferred to the molecule, causing it to turn to ionise and hence it is called as secondary ion.

Decomposition of diazo compounds:-

Diazomethane:- (CH_2N_2)

(1) Reaction with halogen acids:-

Diazomethane reacts with halogen acids to form alkylhalides.

$$CH_2N_2 + HCl \rightarrow CH_3Cl + N_2$$
(methylchloride)

(2) Reaction with fatty acids:-

$$CH_3COOH + CH_2N_2 + CH_3COOCH_3 + N_2$$
Acetic acid — methylacetate.

(3) Reaction with phenols:-

$$C_6H_5OH + CH_2N_2 \rightarrow C_6H_5OCH_3 + N_2$$
phenol — anisole

(4) Reaction with alcohol:-

$$CH_3-CH_2-OH + CH_2N_2 \xrightarrow{Al(OR)_3} CH_3-CH_2-O-CH_3 + N_2$$
Ethyl alcohol — Ethylmethylether.

(5) Reaction with aldehydes:-

$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_2N_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + N_2$$
Acetaldehyde — Acetone.

(6) Reaction with Ketones:-

$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + CH_2N_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + N_2$$
Acetone — Ethylmethyl Ketone

(7) Reaction with amines:-

$$H_3C-NH_2 + CH_2N_2 \rightarrow H_3C-NH-CH_3 + N_2$$
Methylamine — N-methyl methylamine

⑧ Reaction with amides:-

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + CH_2N_2 \Rightarrow R-\underset{\underset{O}{\|}}{C}-NH-CH_3 + N_2$$

N-methylamide

$$H_3C-\underset{\underset{O}{\|}}{C}-NH_2 + CH_2N_2 \Rightarrow CH_3-\underset{\underset{O}{\|}}{C}-NH-CH_3 + N_2$$

N-methylacetamide

⑨ Arndt Eistert synthesis:-

Diazomethane reacts with acid chlorides to form diazoketones. These diazoketones when warmed with water in the presence of silver catalyst decompose to give higher carboxylic acid. This reaction is used to convert a carboxylic acid into its next higher homologue and is known as Arndt Eistert synthesis.

$$H_3C-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{PCl_5} H_3C-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{CH_2N_2} H_3C-\underset{\underset{O}{\|}}{C}-CHN_2$$

Acetylchloride

Diacetyldiazomethane

$$\xrightarrow[Ag\ /\ \Delta]{H_2O} H_3C-CH_2-COOH + N_2$$

propionic acid.

⑩ Reaction with ethylene and acetylene:-
Preparation of heterocyclic compounds:-

(i) $H_2C=CH_2 + CH_2N_2 \Rightarrow$ Pyrazoline

(ii) $HC\equiv CH + CH_2N_2 \Rightarrow$ Pyrazole.

(11) Reduction:-

$H_2CN_2 + 4[H] \xrightarrow{Na/Hg} H_3C-NH-NH_2$

Methylhydrazine.

Diazoacetic ester / Ethyldiazoacetate:-

(1) Reaction with halogen acids:-

$N_2CH\cdot COOEt + conc\ HCl \xrightarrow{\Delta} N_2 + Cl\cdot CH_2\cdot COOEt$

Ethylchloroacetate

$\downarrow HCl/H_2O$

$ClCH_2COOH$

Chloroacetic acid.

(2) Reaction with water:-

$N_2CH\cdot COOEt + H_2O \xrightarrow[\Delta]{dil\ HCl} N_2 + HO\cdot CH_2\cdot COOEt$

Ethyl Glycollate.

$\downarrow H_2O$ (Hydrolysis)

$HO\cdot CH_2\cdot COOH$

Glycollic acid

(3) Reaction with compounds containing active hydrogen atoms:-

(a) $H_3C\cdot COOH + N_2CH\cdot COOEt \rightarrow H_3C\cdot C(=O)\cdot O\cdot CH_2\cdot COOEt + N_2$

Acetic acid — Ethylacetylglycolate.

(b) (6) $C_2H_5OH + N_2CH\cdot COOEt \rightarrow C_2H_5O\cdot CH_2\cdot COOC_2H_5 + N_2$

Ethanol — 2-Ethoxyethylacetate

(4) Reaction with iodine:-

$I_2 + N_2CH\cdot COOEt \Rightarrow I_2\cdot CH\cdot COOEt + N_2$.

Ethyldiiodoacetate

(5) SYNTHESIS OF HETEROCYCLIC COMPOUNDS:-

(i) $H_2C(=CH_2) + N_2CH\cdot COOEt \Rightarrow$ Pyrazolene-3-carboxylic ester.

(ii) $HC\equiv CH + N_2CH\cdot COOEt \Rightarrow$ Pyrazole-3-carboxylic ester

⑥ Reduction:-

When reduced with Zn/CH3COOH, it gives ammonia and glycine ester.

$N_2CHCOOEt + 6[H] \xrightarrow[-NH_3]{Zn/CH_3COOH} H_2N-CH_2-COOEt$ Ethyl Glycine ester. $+ NH_3$

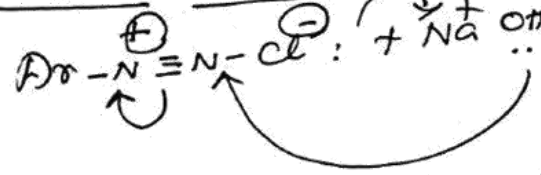
GOMBERG REACTION:-

Treatment of diazonium salts with benzene/derivatives of benzene in the presence of sodium hydroxide to form diaryl compound. Yields are usually less than 40%.

$ArN_2^+Cl^- + C_6H_6 \xrightarrow{OH^-} Ar-C_6H_5 + N_2\uparrow + HCl$.

Mechanism:-

STEP I:- Aromatic nucleophilic substitution:-



$Ar-N=N-OH + NaCl$

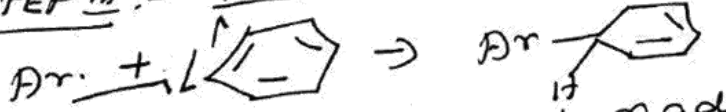
Diazohydroxide.

STEP II:- Formation of aryl radical:-

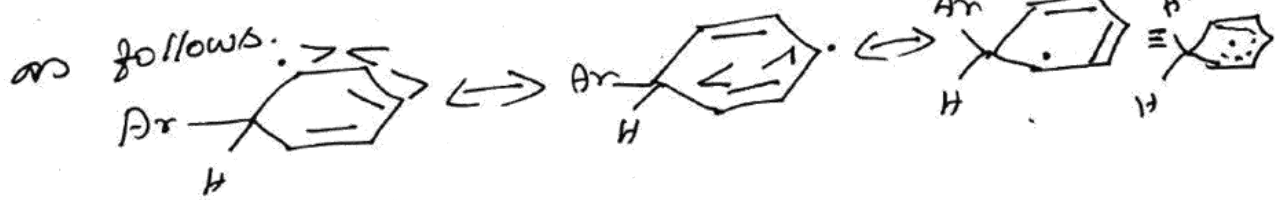
$Ar-N=N-OH \rightleftharpoons Ar\cdot + N_2 + \dot{O}H$

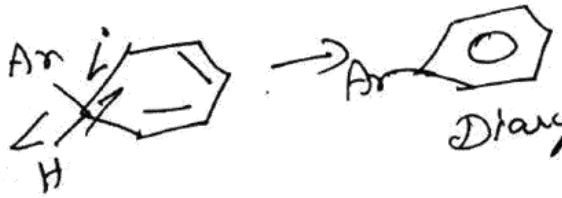
Diazohydroxide

STEP III:- Formation of diaryl:-



The formed radical is stabilised as follows:

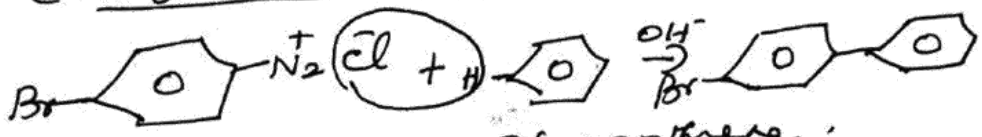




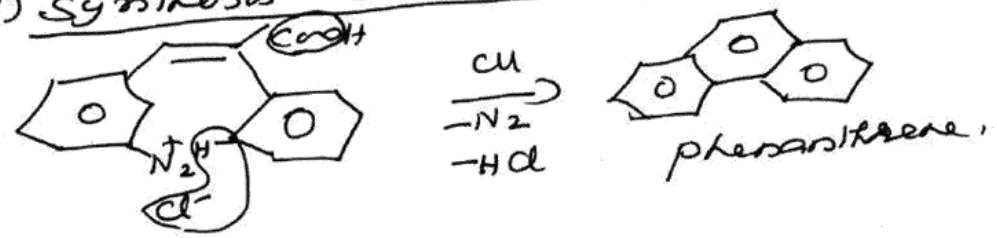
Diaryl.

APPLICATIONS:-

(i) Synthesis of p-bromodiphenyl:-



(ii) Synthesis of phenanthrene:-



Molecular ion & its peak:-

① The electron bombardment with energy 10-15 eV removes one electron from the organic molecule in its vapour phase and the ion formed is known as molecular ion/parent ion.

② The highest occupied orbital of aromatic system and non-bonding electron orbitals on oxygen and nitrogen atoms readily lose one electron and form molecular ion.

③ The mass of the parent ion gives the molecular mass of the sample.

④ The stability of the parent ion decides its relative abundance.

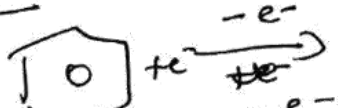
⑤ The peak intensity of the molecular ion differ from one compound to another.

⑥ In some cases, parent ion peak is not formed since the rate of decomposition of the parent ion is too high for its detection.

⑦ The rate of decomposition of the molecular ion increases with increase in molecular size.

Examples:-

(i)



(ii) $R-\ddot{O}-H + e^- \xrightarrow{-e^-} R-\overset{+}{\ddot{O}}-H + 2e^-$

Significance of parent ion peak:-

(1) The molecular ion peak in aromatic compounds is relatively much intense due to the presence of π electron system.
(2) Conjugated olefins show more intense molecular ion peak compared to the non-conjugated olefins with same number of unsaturation
(3) Unsaturated compounds give more intense peak compared to the saturated or the cyclic molecule.
(4) The relative abundance of the saturated hydrocarbon is more than the corresponding branched chain compound with the same number of carbon atom.
(5) The ~~relative abundance of the~~ substituents like OH, OR, NH_2 etc., which lower the ionisation potential of the aromatic compounds and increase their relative abundance.
(6) But the groups like NO_2, CN etc., decrease the relative abundance of aromatic compounds since they increase the ionisation potential.
(6) Absence of molecular ion peak in the mass spectrum indicates that the compound under examination is highly branched.
(7) In case of chloro/bromo compounds isotope peaks are also formed along with molecular ion peak. In case of bromo compounds M^+ and $(M^+ + 2)$ peaks are formed in the intensity ratio 1:1. In case of chloro compounds M^+ and $(M^+ + 2)$ peaks are formed in the intensity ratio 1:3.

PERIYAR ARTS COLLEGE CUDDALORE-1
P.G. DEPARTMENT OF CHEMISTRY
II M.Sc, CHEMISTRY
ORGANIC CHEMISTRY - III

ASSIGNMENT - II

MASS SPECTRAL PROBLEMS:-

Date to be submitted on or before 30.09.2020.

(1) Explain the mass spectral fragmentation pattern of benzyl radical ion (m/e = 108)

(2) Give the complete fragmentation of the following organic compounds:-

(i)

(ii) $H_3C - CH_2 - CH(CH_3) - CH_2 - COOH$

(iii) pentanal.

(3) How will you distinguish 2-pentanone and 2-hexanone by mass spectra.

(4) Discuss the mass spectrum of phenylacetic acid.

(5) Explain the mass spectral peaks of butyraldehyde.

All the best
Dr.
23/09/20