DIAS

All India TEST – SERIES CSE – 2024

Organic-III (Test-6)

Syllabus -: Polymer, Pericyclic, Photochemistry & Spectroscopy.

Instructions:-

1. Attempt five questions selecting at least one question each section. apart from question 1&5 which is compulsory.
2. Write answer in space provided for this purpose only.
3. Total time allowed is 3hr and Marks is 250.

Information:

Name of student:- Vaibhavi Patel

UPSC Roll no:-

Mobile Number. 9911883)

Date :- 29 August, 24

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	28		23	28	32			37

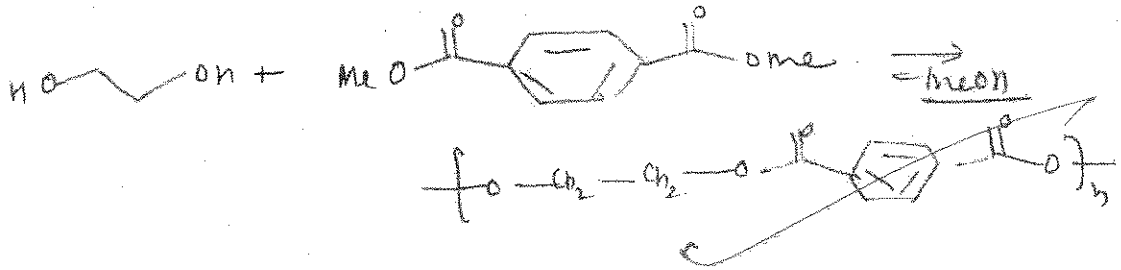
Signature of invigilator

Signature of Examiner

Section-A

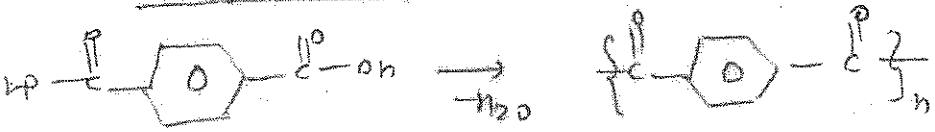
Q 1 (a) (i) For synthesis of polyester, glycol is treated with dimethyl terphthalate but not phthalic acid. Explain. (5)

Synthesis of polyester



Reasons are —

1. Terephthalic acid may polymerise itself by loss of water



2. Energetics of polymerisation more favourable with dimethylterephthalate. (low temperature requirement)

3. Product is easier to separate as no H_2O formed.

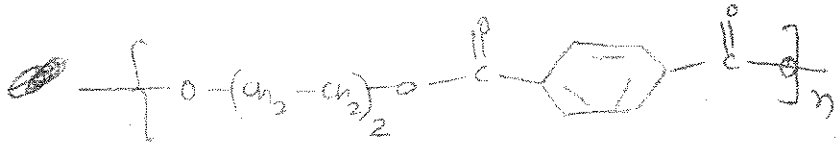
(ii) What is major point of difference between structure of RNA&DNA. (10)

Both are biopolymer formed by assembly of Nucleotide

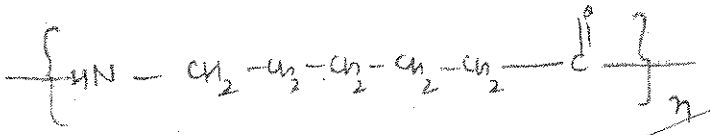
	DNA	RNA
1) Sugar	DNA has Deoxy-ribose sugar	Ribose sugar (OH group at 2' carbon)
2) Base	Nucleotide has Adenine, Thymine, guanine, cytosine	Adenine, Uracil, guanine, cytosine
3) Structure	Double-stranded (usually)	single stranded usually
4) Stability	more stable	less due to 'OH' group at 2'OH
	more UV sensitive	less sensitive to UV
5) Types	one main type	There main type - m-RNA, t-RNA, r-RNA
6) Function	store genetic information & transfer to next generation (Because	Role in protein synthesis (Translation)
7) Location	usually nucleus, mitochondria	Present in nucleus, cytoplasm, ribosome
8) Size	million base pair	Short (100-2000) nucleotide
9 Generation	Self-replication	Transcription process.

(iii) Write down structure of repeat unit of PBT; Nylon – 6; PVC. (5)

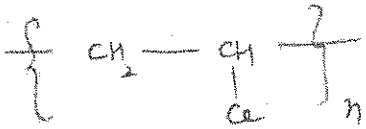
1) Polybutylene terephthalate



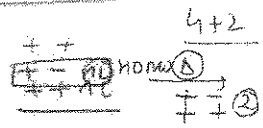
2) Nylon-6



3) PVC



(b) Identify the reaction and predict the products A and B based on FMO approach. Give suitable justification for which product is major. (15)

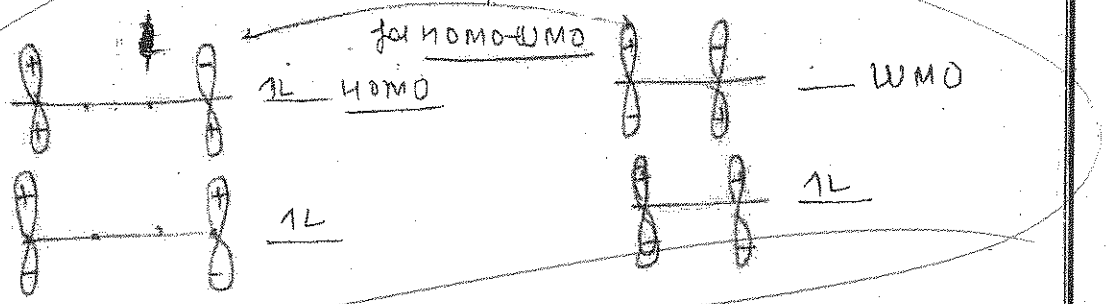


Pericyclic

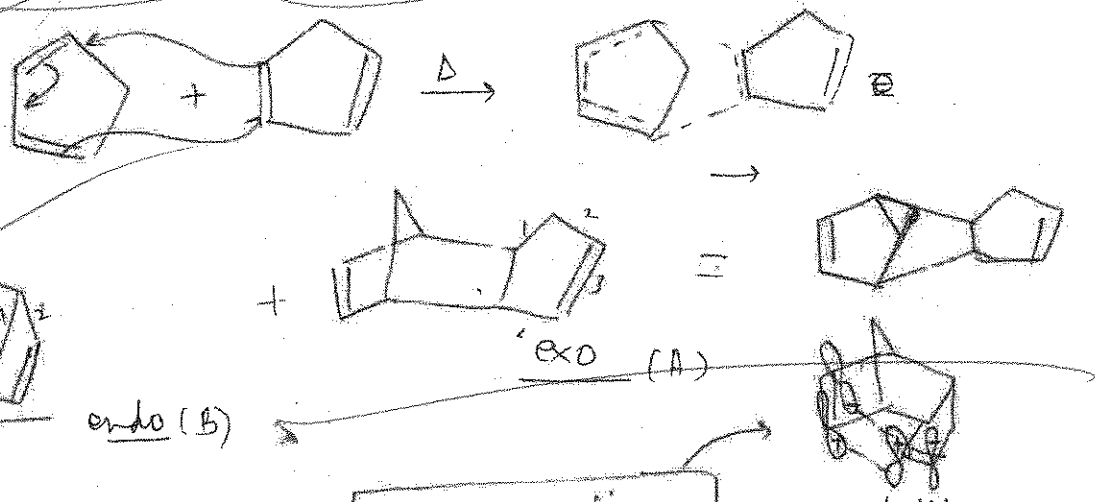
- It is a cycloaddition reaction.

FMO approach - the diene and dienophile must have its frontier orbital in same plane during cycloaddition

Here, Diene (pentadiene) Dienophile (ethene)



Reaction

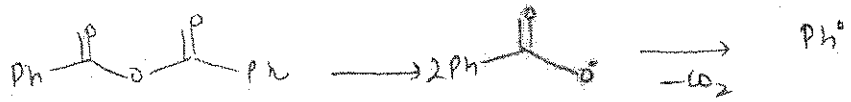


Endo Product is major because secondary interaction of p orbital on dienophile reduce TS energy.

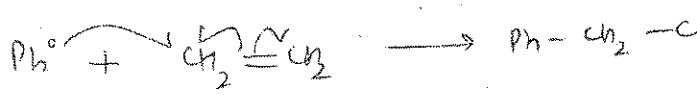
(c) Explain the mechanism of free radical polymerization of ethylene. How will you explain the formation of branching in the resulting polymer? (15)

Free radical polymerisation involve three steps - initiation, propagation, termination

Step1 - Initiation by a radical initiator

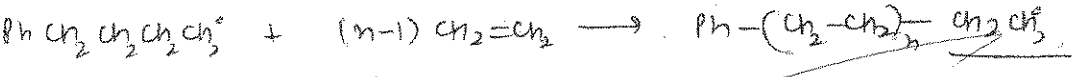


1. Benzoyl peroxide



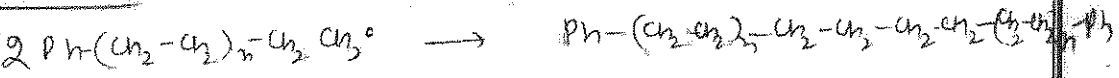
Step2 propagation

1. 

2. 

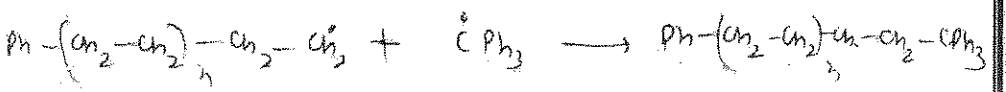
Step3 Termination

1) disproportionation -



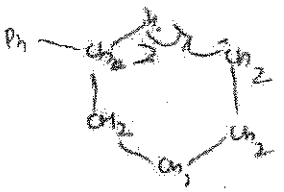
2) disproportionation

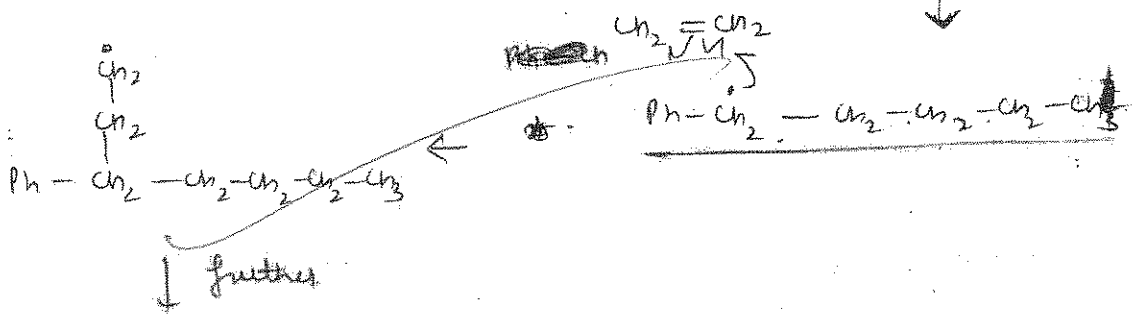
3) extend agent

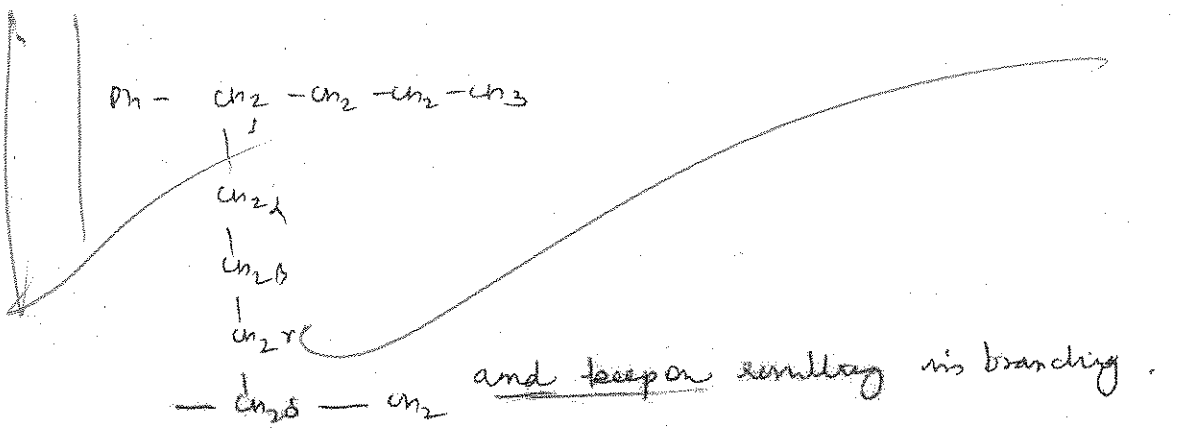


Formation of Branching

1) It happens due to Back biting (γ-H abstraction by radical)







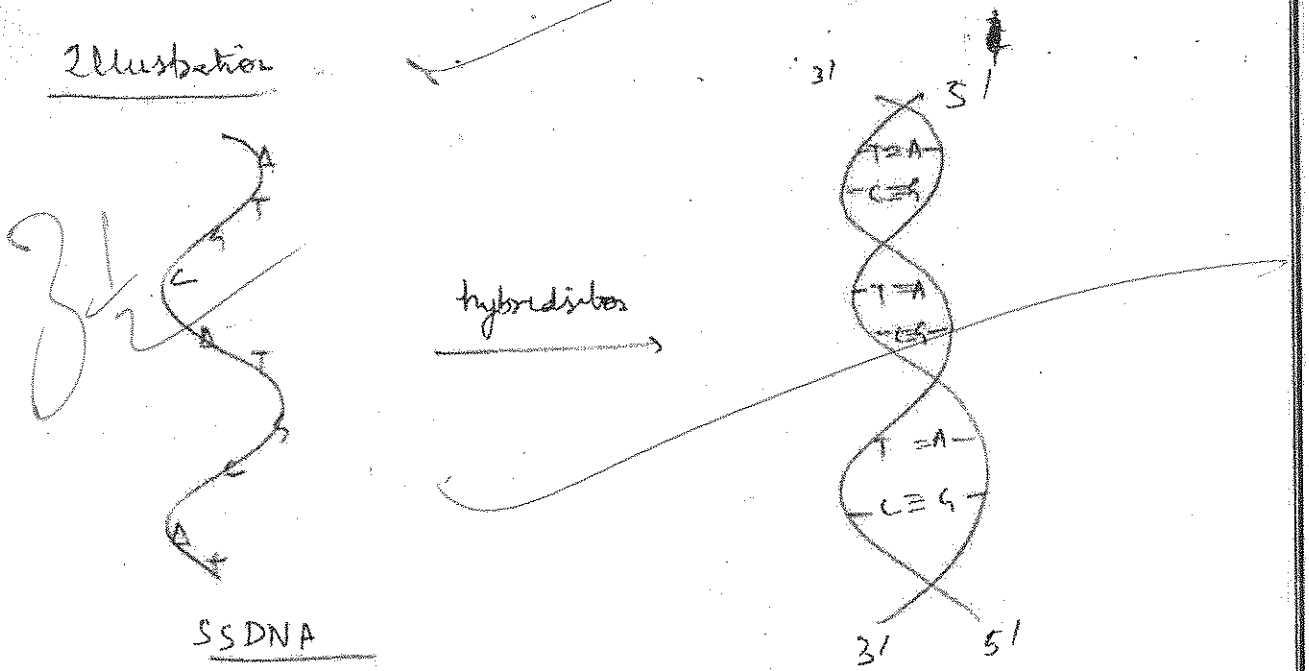
and keep on repeating this branching.

3(a) (i) What is the hybridization of DNA? (5)

Hybridisation of DNA – It is conversion of single strand dna (ssDNA) to double stranded dna.

Reason for hybridisation – Base pairing and stacking interaction are main driving factor. to achieve more energetically stable structure.

Illustration

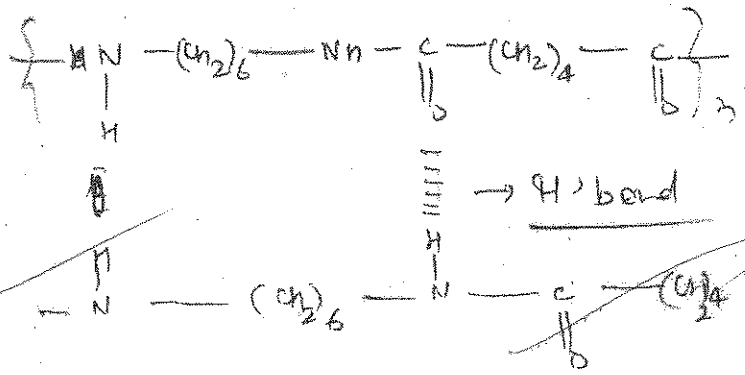


(ii) Mechanical strength of Nylon is better than polyester. Explain. (5)

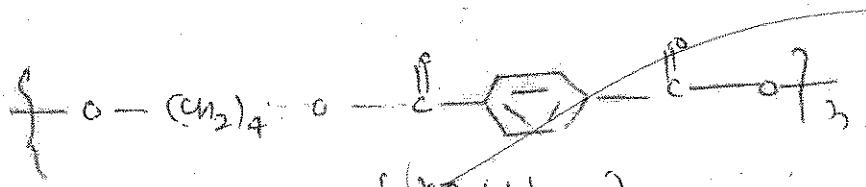
Nylon is a polyamide (eg Nylon 6,6). It has higher mechanical strength due to formation of H-bonds ~~cross linking~~. and achieving more crystallinity. No, such 'H' bonding in polyester

Illustration.

$NH_2-(CH_2)_6-NH_2$



polyester

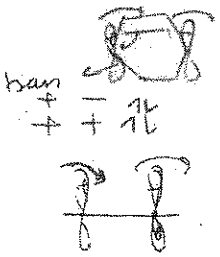


(b) Dewar benzene is less stable than its isomer benzene by 60 kcal/mol. nevertheless, its conversion into benzene is extremely slow with an activation energy of about 37 kcal/mol. explain this observation. **(10)**

Dewar Benzene –

Less stable – due to ring strain (two fused 4 membered ring) and no aromaticity.

Conversion into benzene is slow.



Electrocyclic opening.

$\xrightarrow{\Delta}$ conrotatory

bars bond

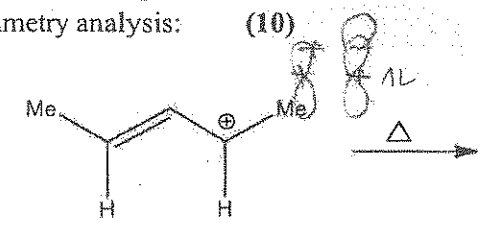
↓

Energetically not favorable

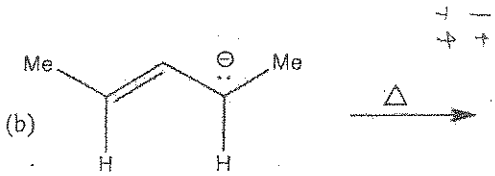
So, reaction is slow

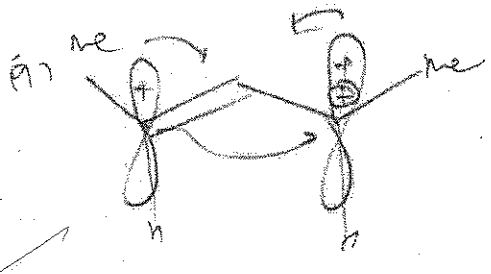
(c) Predict the product in each of the following reactions and explain these by orbital symmetry analysis: **(10)**

(a)



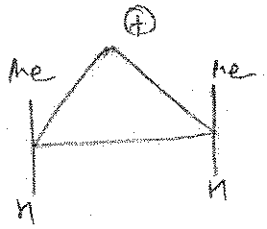
(b)





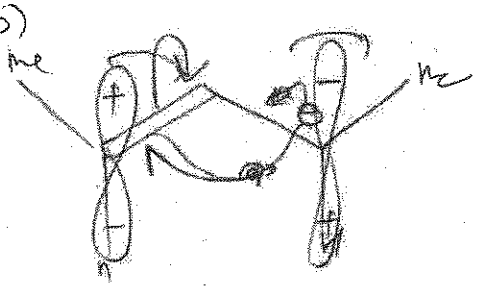
disrotatory

(2π system)



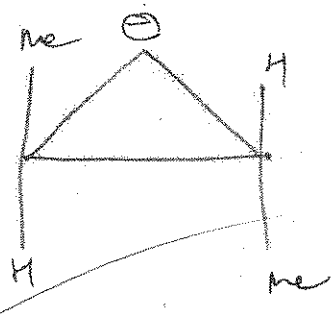
(cis)

(b)



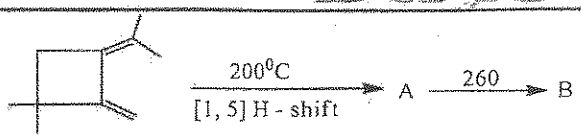
conrotatory

(4π system)



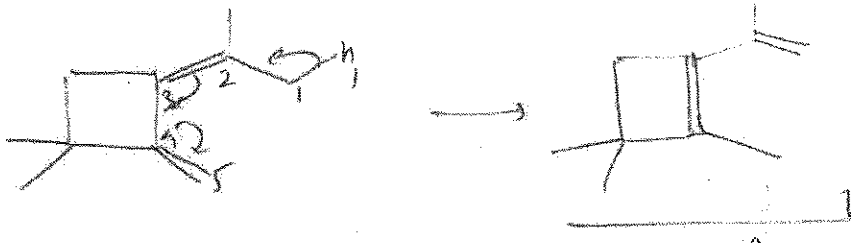
(trans)

(d) Mention the reagent(s) and write the mechanism for the following conversion: **(10)**

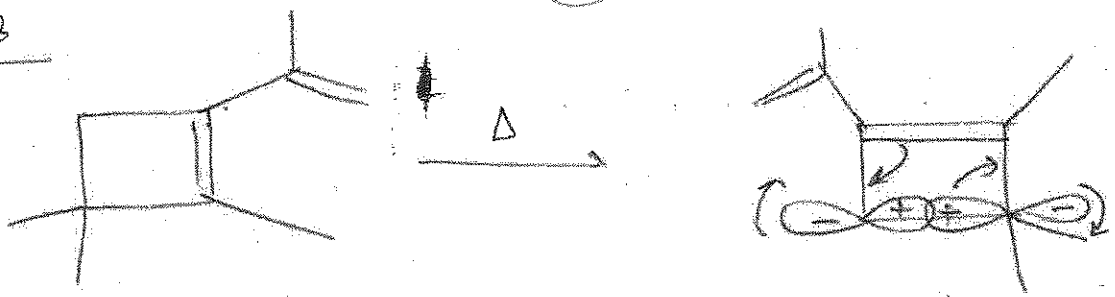


(10)

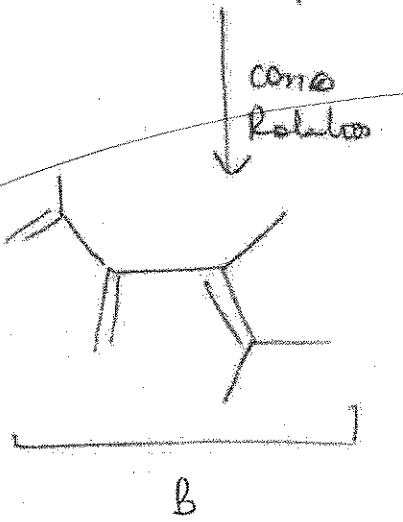
Product A – [1,5]H shift (Sigmatropic Reaction)



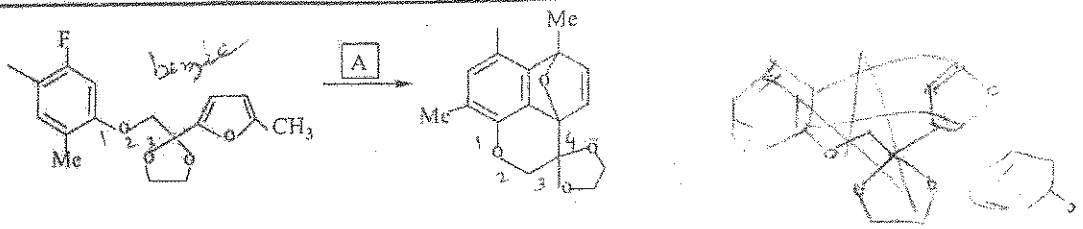
Product B



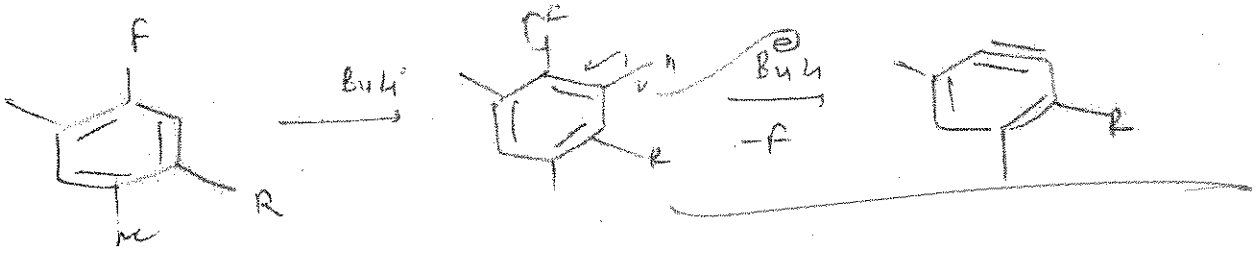
It will cause electrocyclic ring opening as a result thermal condition (2+2) cycloaddition would not take place



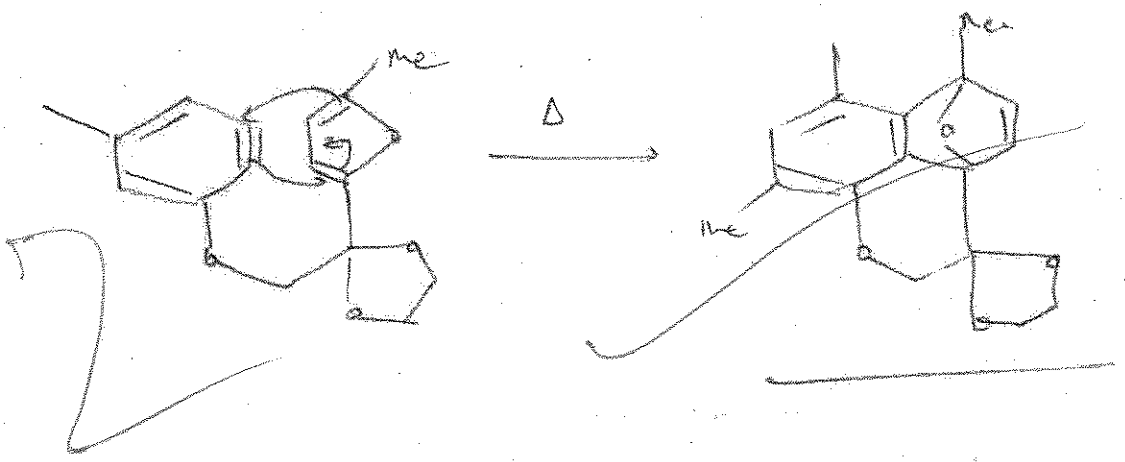
4(a). Provide structure for the compounds A- G in the following reaction sequence : (20)



Step1 Jaramtra Benzyne

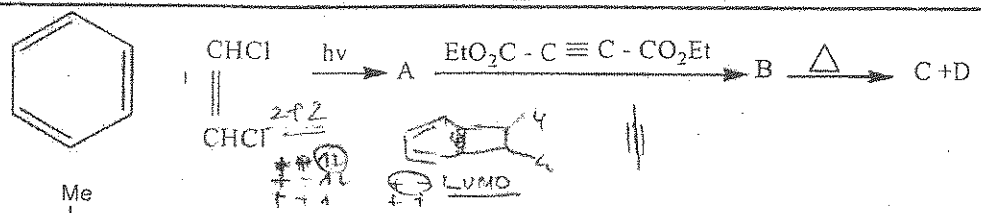


Step2 (4+2) cycloaddition

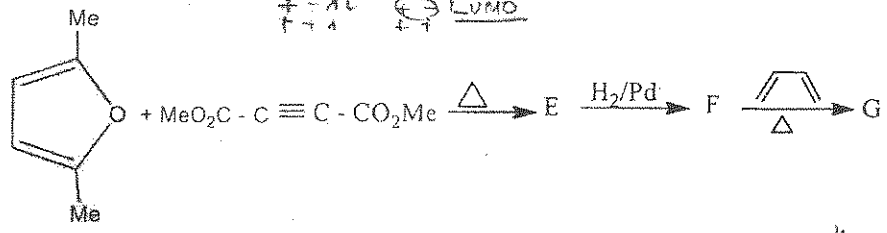


(e) The following transformation proceeds by the indicated. Give the structure of A and B.

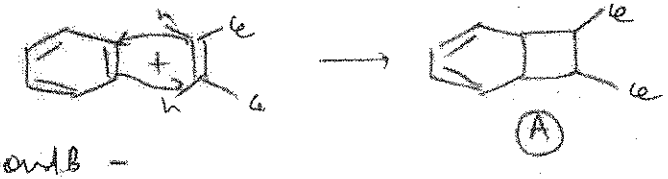
(i)



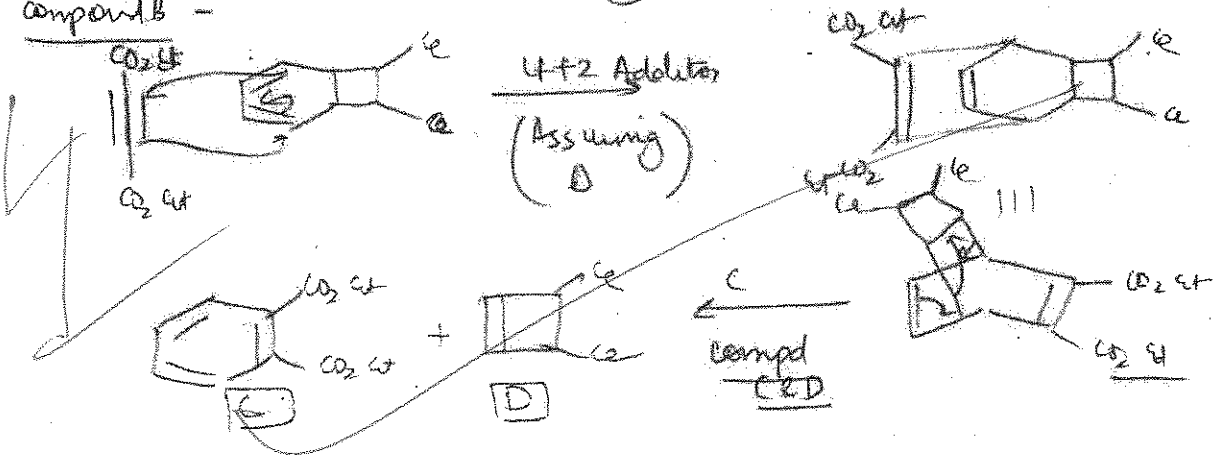
(ii)



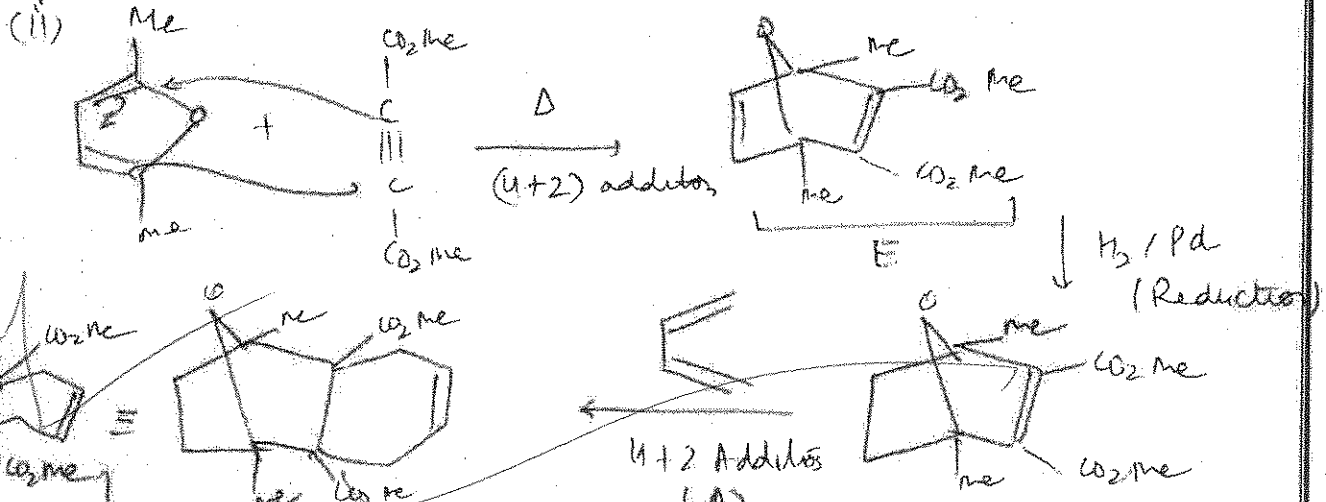
(i) Compound A – under hν it will be 2+2 cycloaddition



compound B –



(ii)



(b) Comment on unique role of cysteine and cysteine in protein structure. **(10)**

Role of cysteine – it is an amino acid that has 'SH' substituent and during secondary structure / folding of protein it provides stability & support by disulphide linkge (S — S)

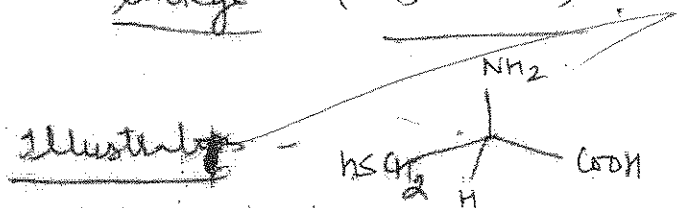
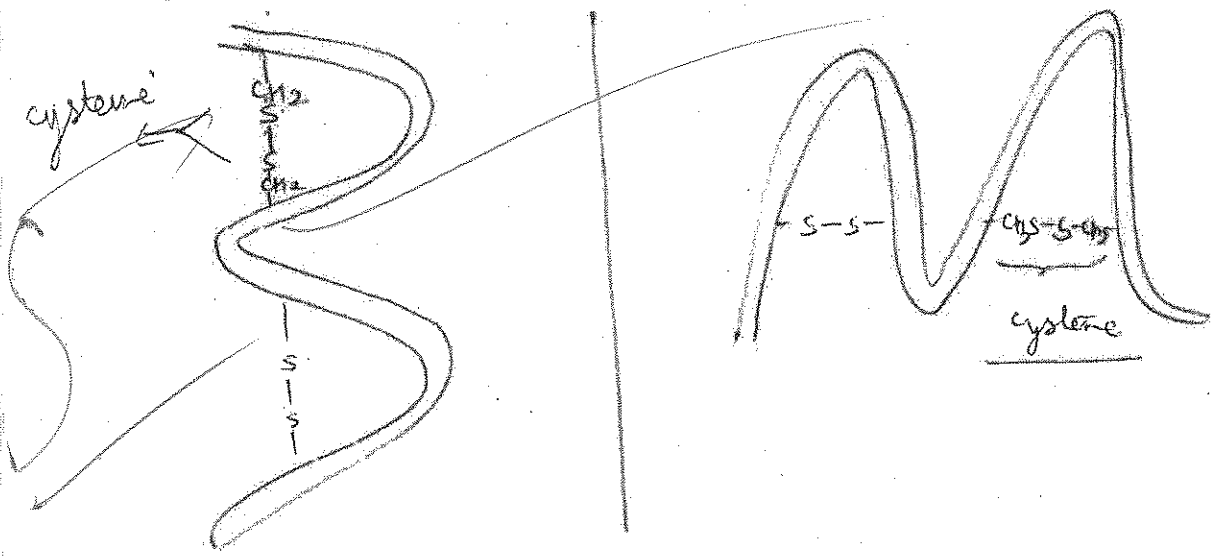


Illustration –

α-helix structure

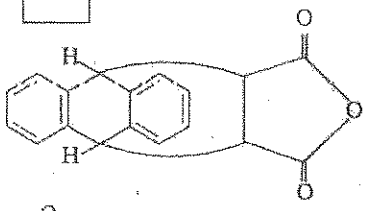
β pleated structure

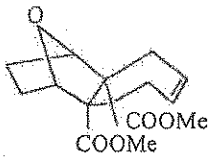


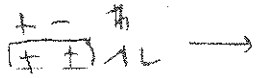
(c) What are principal forces maintaining the secondary structure of proteins. **(10)**

(i) 

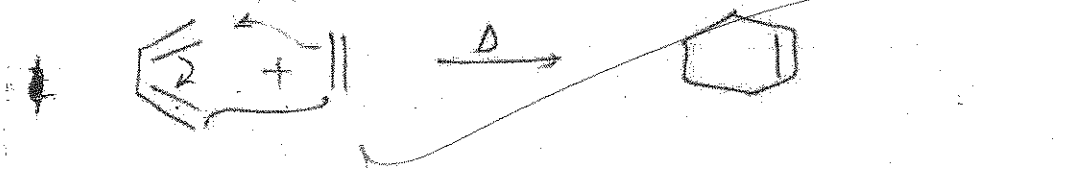
(ii) 

(iii) 

(iv) 

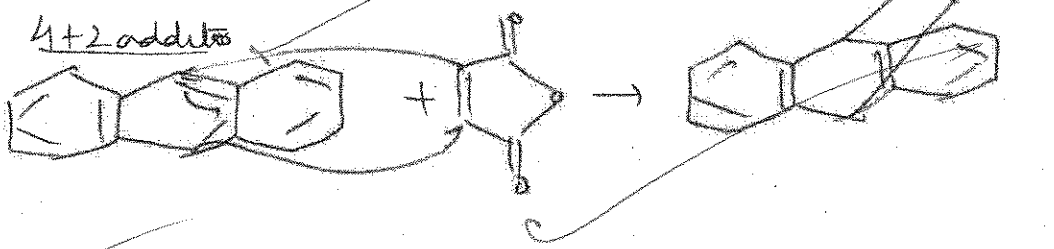


(i) formed by Diels Alder addition



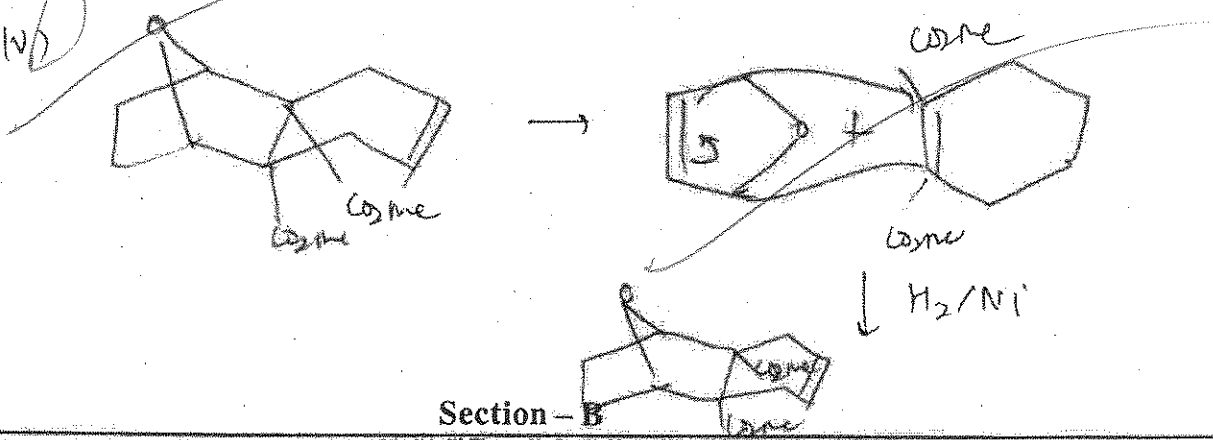
(ii) 2+2 cycloaddition

4+2 adduct



(iii)

(iv)



Section – B

Secondary structure - it is formed by folding of primary amino chain structure of protein. Various forces play role.

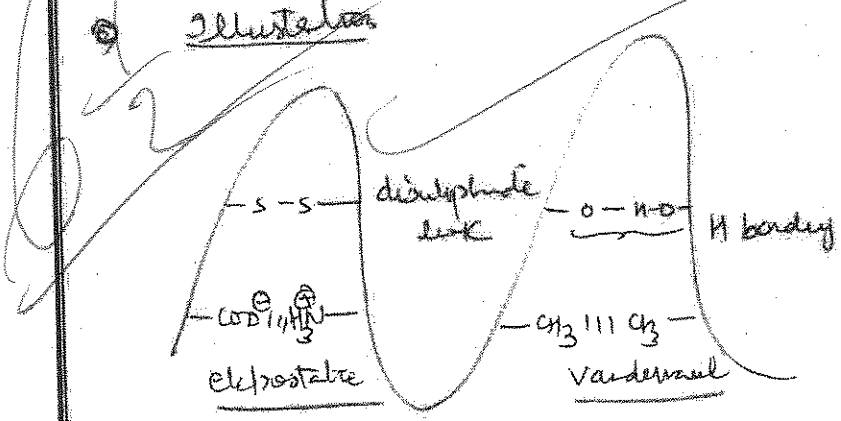
1) H-bonding eg - serine amino acid 'H' bond

2) Electrostatic attraction - due to amino acid existing as zwitter ion eg - between aspartic & glutamic acid

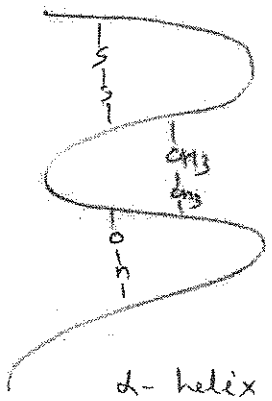
3) Vanderwaal interaction - between alkyl Rendus of amino acid as - leucine & Valine

4) Disulphide linkage - as - between cysteine

5) Illustration



β pleated structure
eg - Myoglobin



α - helix
eg - Keratin

(d) How do you prepare the following compounds? **(10)**

5(a) An organic compound ($C_6H_{12}O$) showed two signals in its ^{1}H-NMR spectrum at δ 1.0 (9H, s) and δ2.0 (3H, s). An intense IR band of this compound appears at 1715 cm^{-1}. However, there is no absorption in the range 2,700-2,860 cm^{-1}. Determine the structure of the compound. **(10)**

Given formula, $C_6H_{12}O$

1. degree of unsaturation = no of C − $\frac{\text{hydrogen}}{2}$ + 1 = $6 - \frac{12}{2} + 1$ = 1

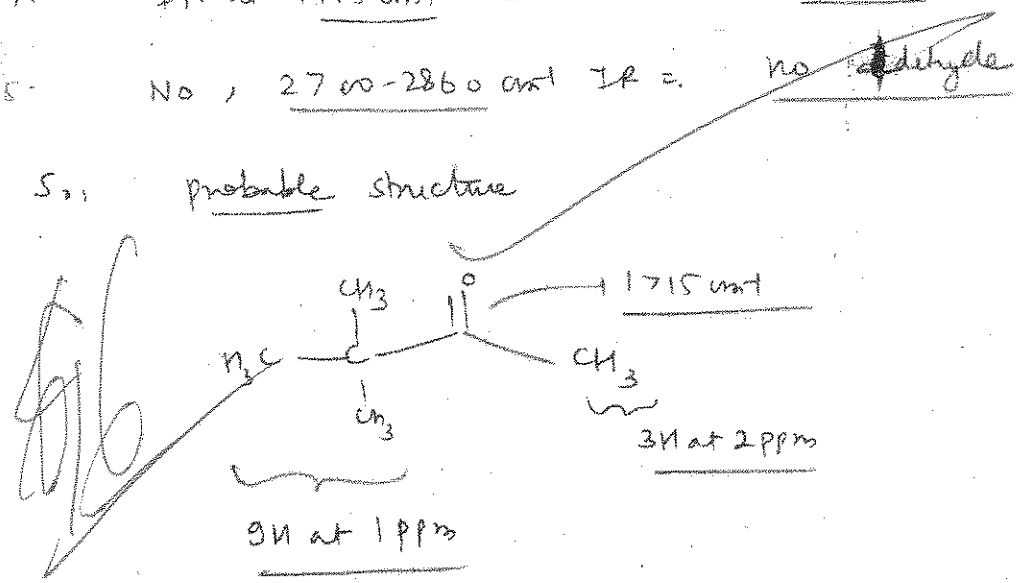
2. 9H singlet = $CH_3-C(CH_3)_2-$

3. 3H singlet = CH_3-

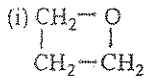
4. IR at 1715 cm^{-1} = indicate ketone

5. No, 2700-2860 cm^{-1} IR = no aldehyde.

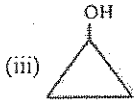
Sol: probable structure



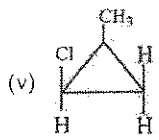
(b)Write number of major peak in H–decoupled spectra of following compounds. **(10)**

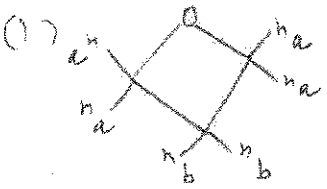
(i) 

(ii) $CH_2=CH-CH_2OH$

(iii) 

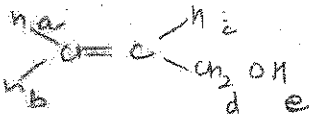
(iv) $CH_3-O-CH=CH_2$

(v) 

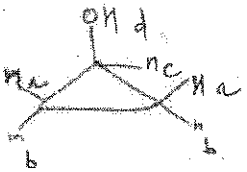
(1) 

No of peaks = 2

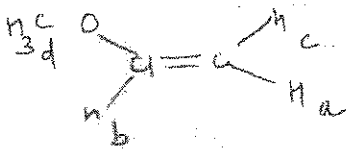
Reason 2 Chemically different H are there = 4 Ha, 2 Hb

(2) $CH_2=CH-CH_2-OH$ = 

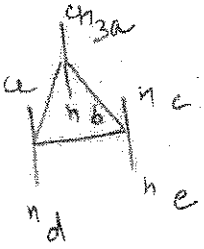
No of peak = 5

(3) 

= No of peak = 4

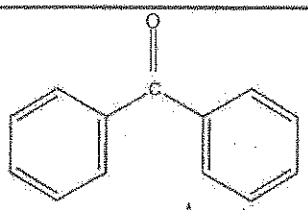
(4) $CH_3-O-CH=CH_2$ = 

= 4 peak

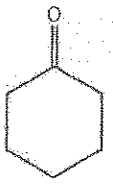
(5) 

= 5 peaks

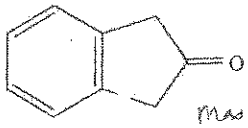
(c) Arrange the following carbonyl compounds in order of their increasing carbonyl stretching frequency. Justify your answer. **(10)**



I least



II medium



III max

① Order of increasing carbonyl frequency

(max) III > II > I

② Justification –

between III and II – III has 5 member ring, so, less internal angle and high 's' character in carbonyl bond than II

→ more 's' character

between II and I

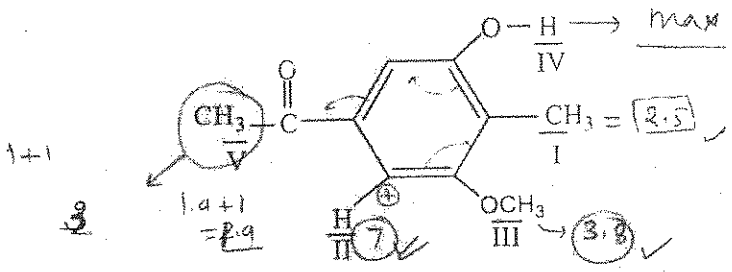
1) In the π-electron of carbonyl are delocalised in phenyl group so, bond strength decrease hence, stretching frequency

delocalisation

So, II > I

overall I < II < III

(d) In the given compound we have different underlined proton arranged them in increasing order of decreasing δ value in NMR with proper reasoning in minimum words. (10)



Increasing order

V < I < III < II < IV (considering H bonding)

Reasoning

V – $CH_3-C(=O)-$ = here, carbonyl deshielding effect is low

So, δ expected = 1.9

I –  = Due to deshielding effect of π electron circulation

δ exp = 2.15

III – OCH_3 = due to deshielding effect of E.Neg Oxygen

δ = 3.8

II – H– = due to π circulation of ring having deshielding effect + carbonyl exerts (+) charge due to delocalisation

δ exp = 7.2

IV – OH = absorbs in broad range (4–12) ppm

= E. Negative 'O' pulls electron and deshield, hence downfield

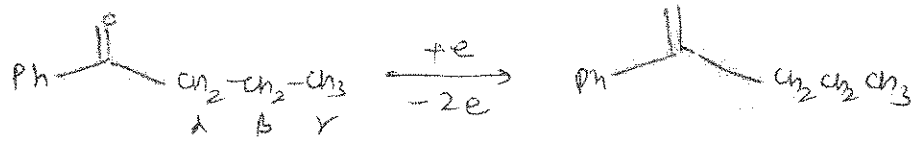
H bonding = 12 ppm

No H bonding = 4–5 ppm.

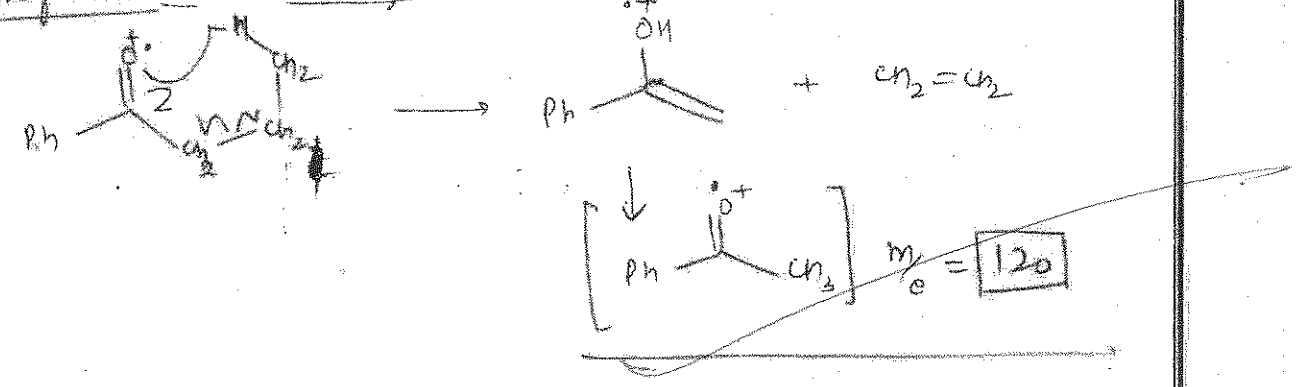
(e) Mass spectrum of Butyrophenone shows two peaks m/z 106 and 120 due to McLafferty rearrangement. Justify your answer. (10)

McLafferty rearrangement involves abstraction of 'H' from 'γ' position.

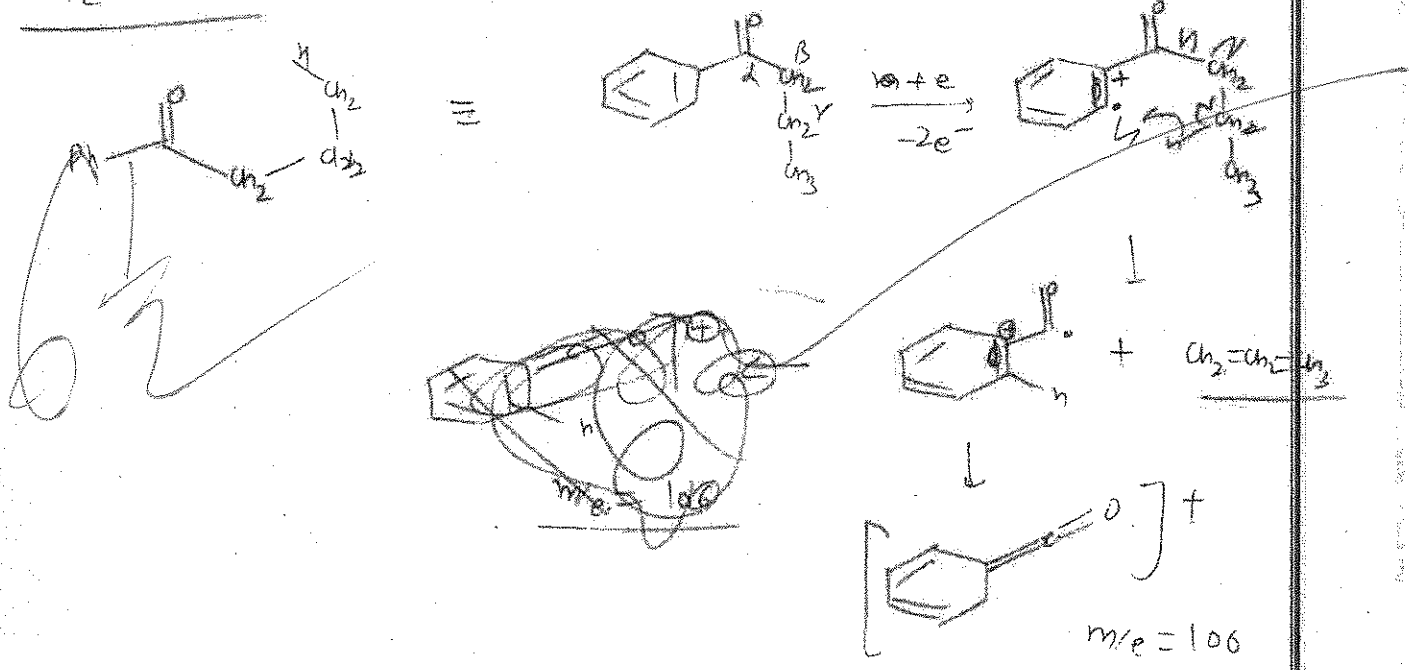
Butyrophenone



γ-H migration - β cleavage



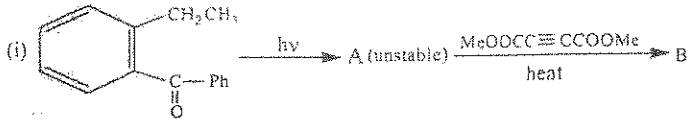
m/e at 106

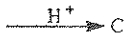


m/e = 106

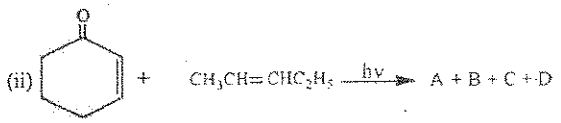
6(a) Write down product (s) and discuss mechanism for formation of product. (30)

(i)

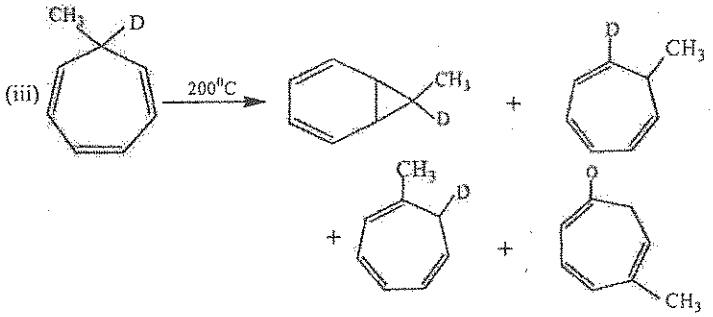




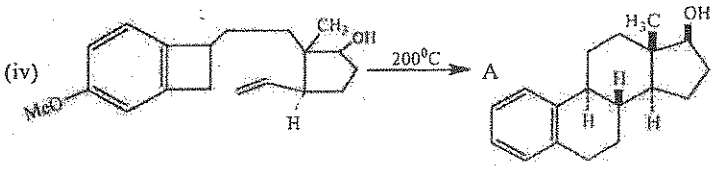
(ii)



(iii)



(iv)



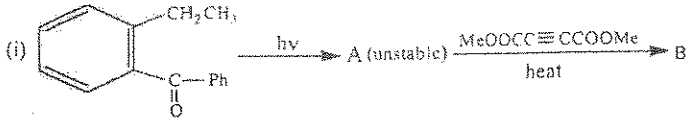
(g) How IR spectroscopy can be used to study the progress of the following transformations? **(10)**

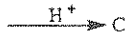
(i) $Ph - \overset{\overset{O}{\|}}{C} - CH_2CH_2CO_2Et \xrightarrow{[H]} Ph - \overset{\overset{OH}{|}}{CH} - CH_2CH_2CO_2Et$

(ii) $PhCH = NR \xrightarrow{[H]} PhCH_2NHR$

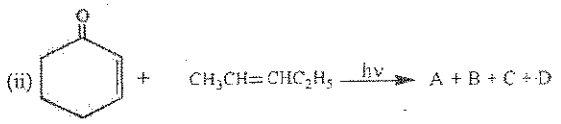
6(a) Write down product (s) and discuss mechanism for formation of product. (30)

(i)

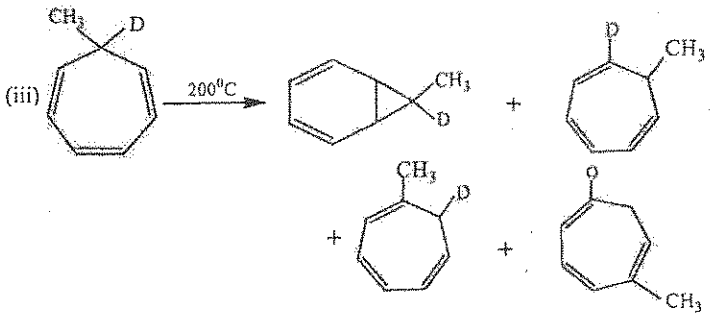




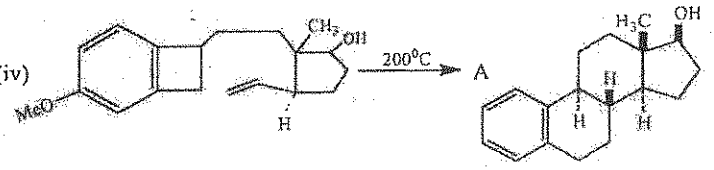
(ii)



(iii)



(iv)



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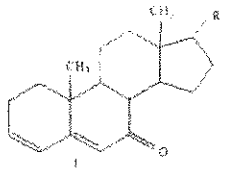
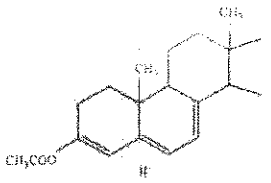
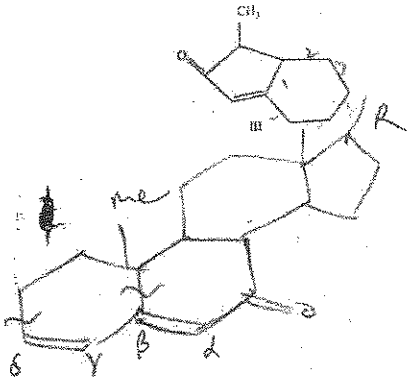
(ii) $PhCH = NR \xrightarrow{[H]} PhCH_2NHR$

8(a) Using Woodward's rules, calculate the λ_{max} value for the following compounds: (15)





(I)



Base value = 215

one exo β bond = 5

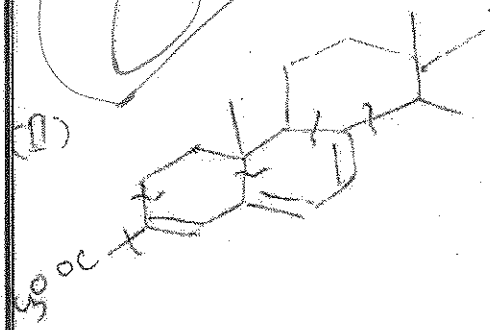
one extended double bond = 30

β Reside = 12

δ Residue = 18

= 280 nm

(II)



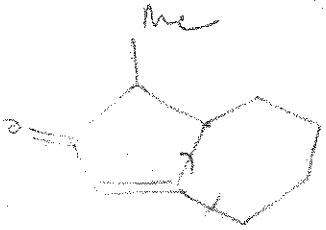
Base value = 253

exo bond = 2 × 5

Residue = 5 × 5

extended bond = 30

= 318 nm

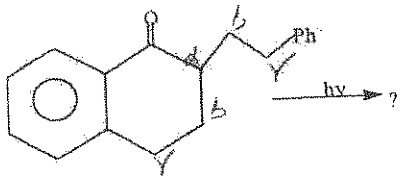


Base value = 202 nm

2 Double bond = 24 nm

= 226 nm

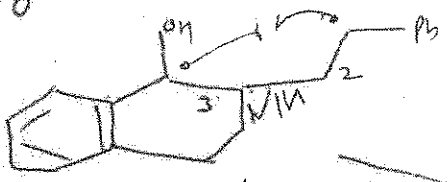
(b) Give mechanism inolved in Norrish type II reaction and predict the product the products in the following reaction: (5)



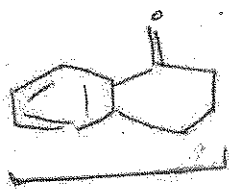
Norrish type II involve γ-H abstraction followed by β cleavage of cyclisation

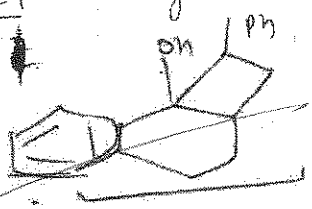
(1)

Step 1 γ-H abstraction

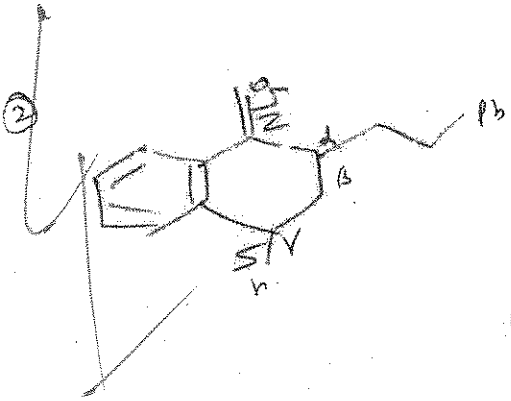


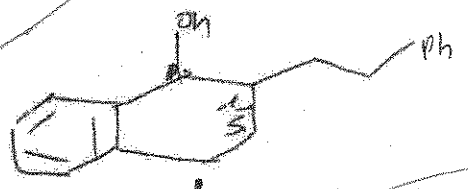
β cleavage Step 2 → cyclise





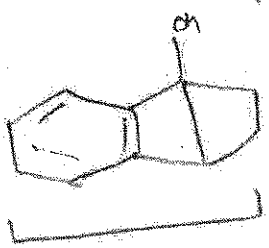
(2)

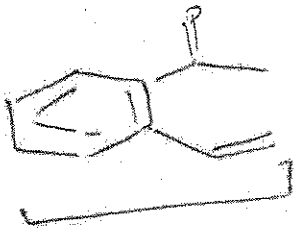




cyclise

β cleavage





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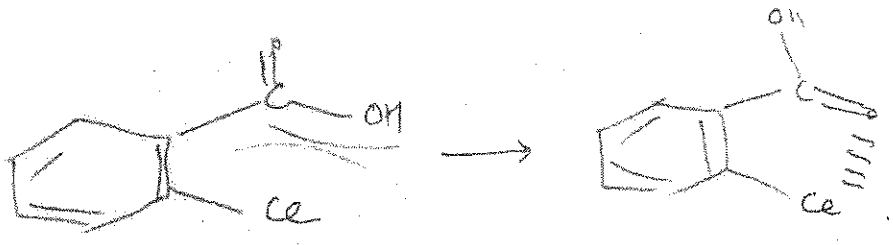
(c) Esters of o-chlorobenzoic acid show two C = O str frequencies. Explain. (5)

It is due to different electronic environment created due to Cl



Thus electronic environment causes carbonyl to exhibit 2 different frequency.

(d) Calculate C=O stretching frequency, K=12.3×10^5 dyne/cm. (5)

Given, $k = 12.3 \times 10^5$ dyne/cm

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$\frac{1}{\mu} = \frac{m_1 + m_2}{m_1 \cdot m_2} = \frac{12 \times 16}{28} = \frac{12+16 \cdot N_A}{12 \times 16}$$

$$= \frac{28\ N_A}{12 \times 16}\ g$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \times \sqrt{\frac{12.3 \times 10^5 \cdot 28 \cdot N_A (6.022 \times 10^{23})}{12 \cdot 16}}$$

$$\bar{\nu} = 1744\ cm^{-1}$$

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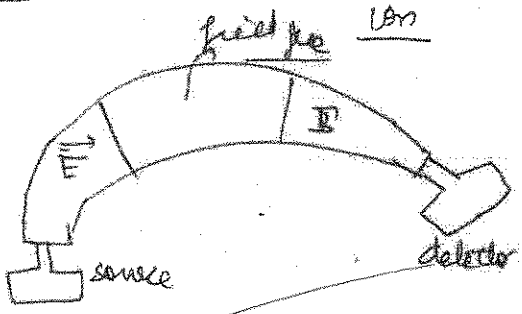
(e) What are metastable ions and how are they formed? The mass spectrum of toluene shows strong molecular ion peak at m/z 65 and its fragment at m/z 51. Calculate the value for metastable ion peak. **(10)**

Metastable ions – When some fragmentation occur in field free region then such fragment have very low Kinetic energy and are collected at detector with slow speed & broad peak called meta-stable ion

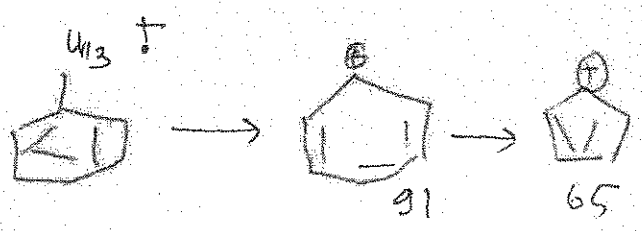


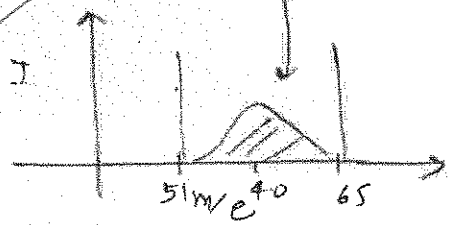
$$m^* = \frac{m_2^2}{m_1}$$

m_2 = Stable ion

m_1 = parent ion

$$m^* = \frac{65^2}{91} = \frac{51^2}{65} = 40 \text{ m/e}$$





$C_7H_{12}O_2$ 7-6+1 ⑤

(f) An organic compound ($C_7H_{12}O_2$) exhibited the following data in the ^{1}HNMR spectrum. δ 7.10 (1H, dt, J = 16 and 7.2Hz), 5.90 (1H, dt, J = 16 and 2Hz) 4.1 (2H,q, J = 7.2 Hz) 2.10 (2H,m), 1.25 (3H, t, J = 7.2 Hz) 0.90 (3H,t, J = 7.2 Hz) ppm. (10)

Double bond equivalent = $8 - \frac{12}{2} = 2$

① 7.10 (1H, dt = 16, 7.2Hz) = Trans indicate trans coupling & cis coupling of 3J coupling

② 0.9 3H(t) = CH_3-CH_2

③ 1.25 3H t = CH_3-CH_2

④ 4.1 2H/q = $CH_3-CH_2-O-C(=O)$

⑤ 5.9 (1H, J=16, 2Hz), J = 16 = trans coupling

So