

DIAS
All India TEST – SERIES CSE – 2024

Test – 8

Syllabus -: Full Syllabus Paper - 2

Q ⇒ 1, 3, 4, 5, 8

Instructions:-

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

Information:-

Name of student:- AAYUSH SAINI

UPSC Roll no:- 0841801

Mobile Number:- [REDACTED]

Date:- 2-09-24

Dias Roll No. CHTS-2401001

Official use.

Q. No	1	2	3	4	5	6	7	8
Marks	33	35	32	35	36	—	—	36

Total Marks

172

250

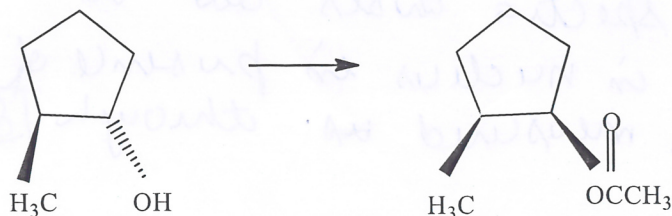
Signature of invigilator

Signature of
Examiner

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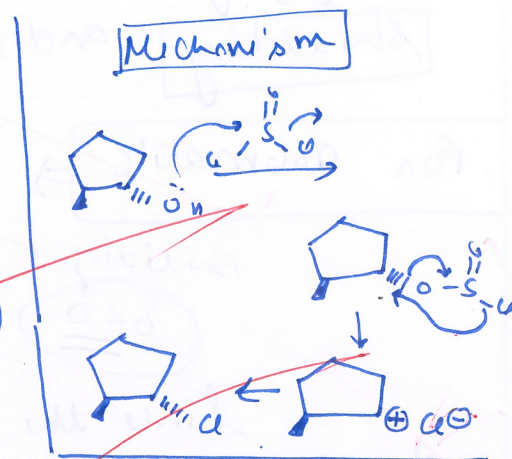
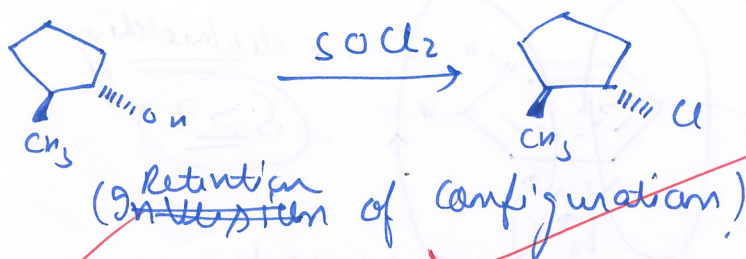
Section- A

1(a) suggest a reasonable series of synthetic transformation for covering trans-2-methylcyclopentanol to cis-2-methylcyclopentyl acetate. (10)

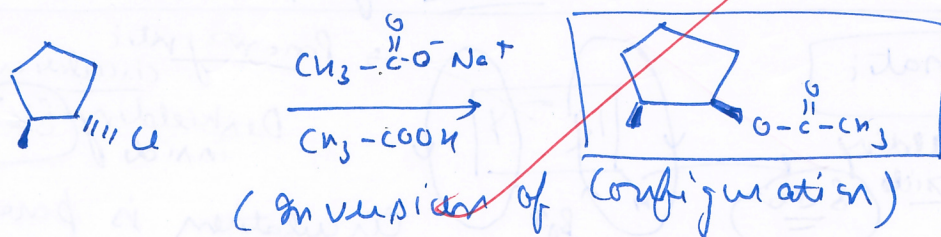


The following steps can be taken for conversion:

Step 1 $\Rightarrow$ S_N1 mechanism



Step 2 $\Rightarrow$ S_N2 attack.



Thus S_N1 followed by S_N2 could give the desired result.

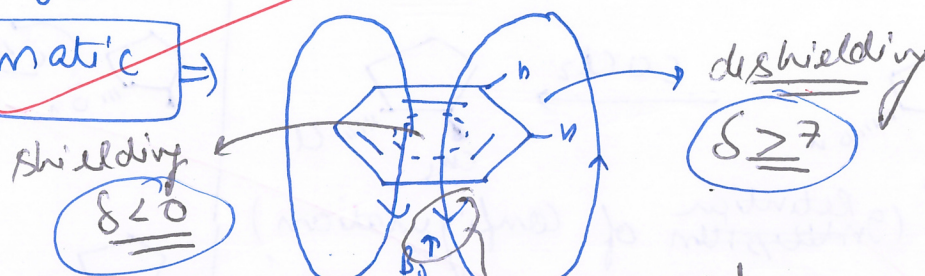
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(b) How the aromaticity of a molecule can be judged from ^1H NMR spectrum? Which thermodynamic data is concrete evidence? (10)

^1H NMR spectra arises due to flipping of proton in nucleus in presence of magnetic field. It is measured through $\delta \Rightarrow$ Chemical Shift.

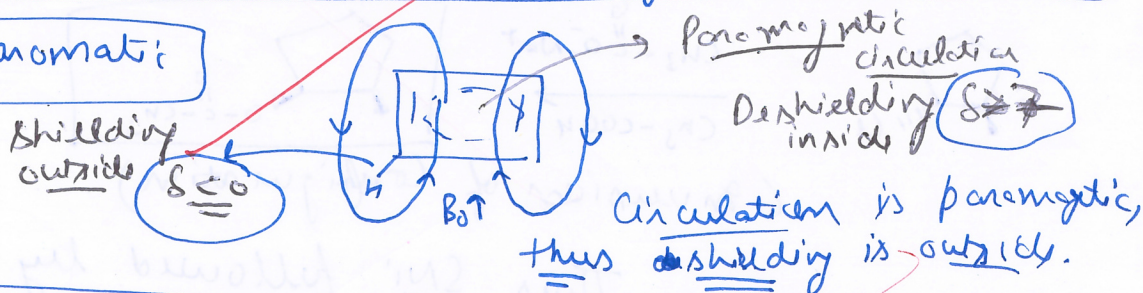
Aromaticity can be judged by analyzing δ value, which provides for shielding and deshielding information.

For aromatic $\Rightarrow$



Since the circulation is opposed diamagnetic, shielding is seen inside the ring.

For antiaromatic $\Rightarrow$



Thermodynamic data $\Rightarrow$

Resonance stabilization energy is aromatic $\Rightarrow 2\beta$ ($\beta =$ overlap energy), while is antiaromatic $\Rightarrow$ it is zero.

Further $\left. \begin{array}{l} \text{Heat of hydrogenation} \\ \text{Heat of formation} \end{array} \right\}$ provides for aromatic stability.

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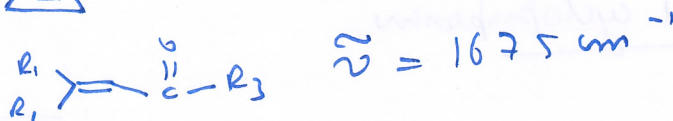
(c)(i) The C=O stretching frequency of cyclopropanone (1600 cm^{-1}) is lower than that of typical α, β unsaturated ketones (1675 cm^{-1}). (5)

In I.R spectra the carbonyl molecules lies the range of $\tilde{\nu} = 1880 - 1650\text{ cm}^{-1}$ (stretching frequency)

provided

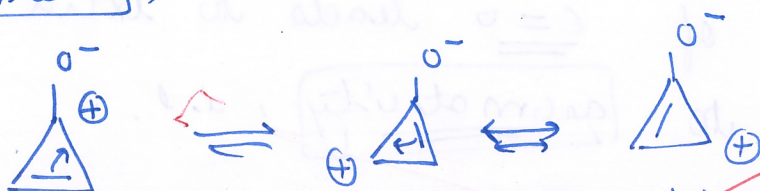


$$\tilde{\nu} = 1600\text{ cm}^{-1}$$

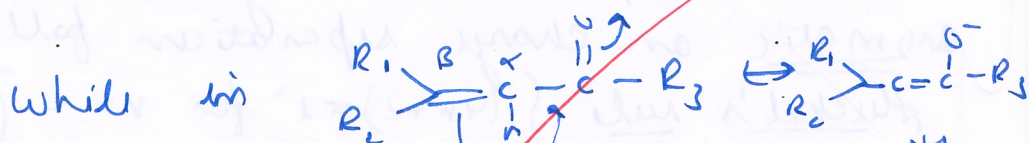


$$\tilde{\nu} = 1675\text{ cm}^{-1}$$

Mesonism $\Rightarrow$



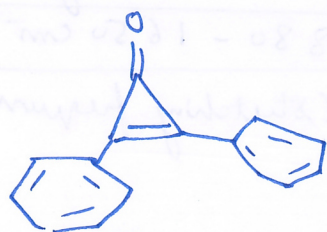
Breaking of $\text{C}=\text{O}$ provides for Aromatic Character with $(4n+2)\pi e^-$ $\{n=0\}$, validating the Huckel's rule.



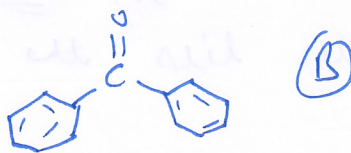
while in only simple mesomerism takes place with no extra exceptional stability.

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(ii) The dipole moment of diphenylcyclopropenone ($\mu = 5.1$ D) is substantially larger than that of benzophenone ($\mu = 3.0$ D) (5)

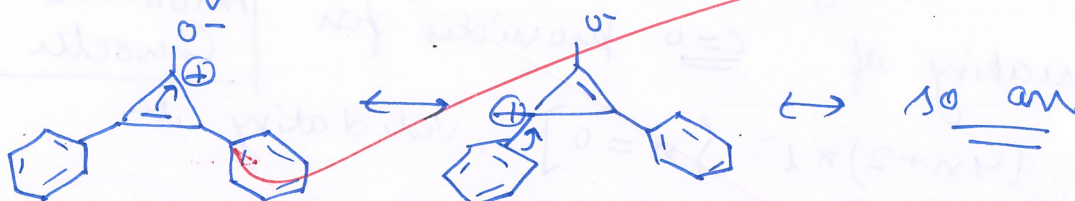


Diphenyl cyclopropenone



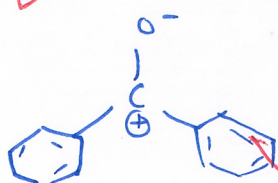
Benzophenone

In Diphenylcyclopropenone, charge ~~is~~ separation of C=O leads to extra stability due to aromaticity, i.e.



3-membered ring becomes aromatic on charge separation following Huckel's rule $\{ (4n+2) \pi e^- \text{ for } n=0 \}$

while, in benzophenone no extra stability (Normal conjugation)

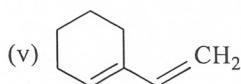
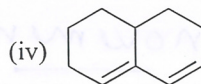
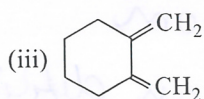
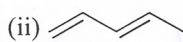
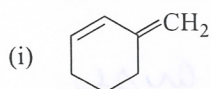


Thus

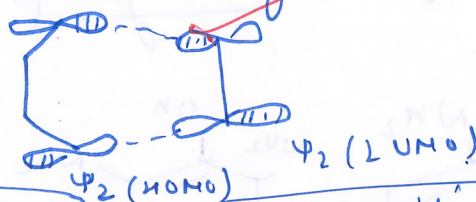
$$\underline{\underline{\mu_A > \mu_B}}$$

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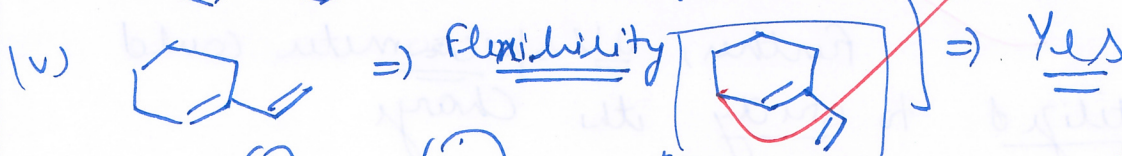
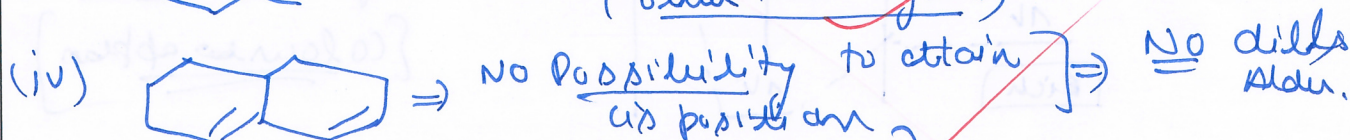
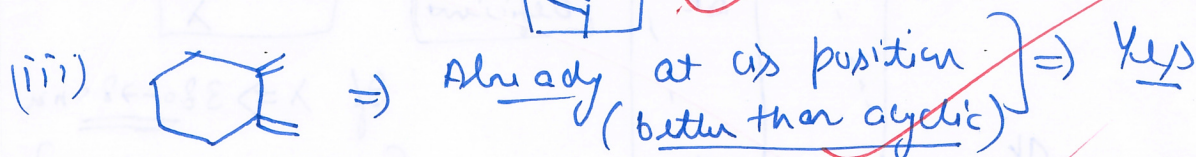
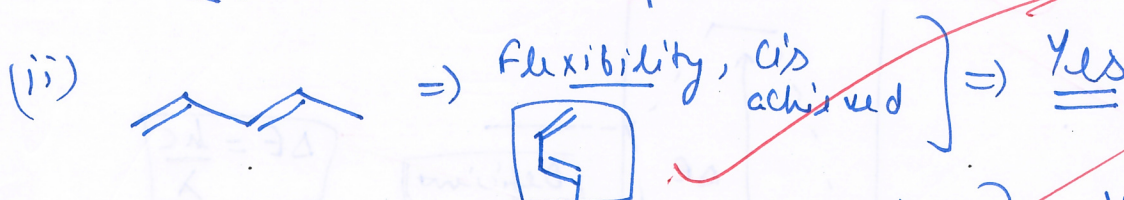
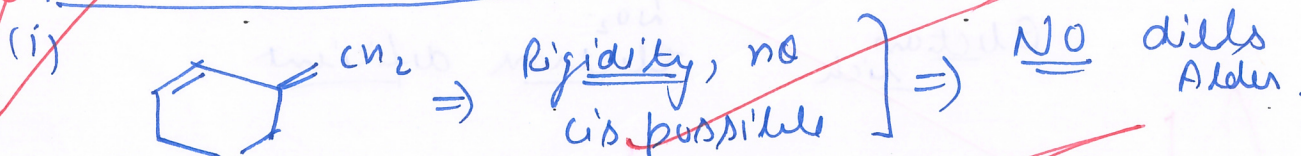
(d) Which of the following conjugated would not react with a dienophile in Diels-Alder reaction? Justify your answer: (10)



Diels Alder reaction is $[4+2]_{\pi}$ addition reaction taking place in a thermo medium



Necessary condition $\Rightarrow$ Cis position of dienophile



Thus (i), (iv) won't react with dienophile

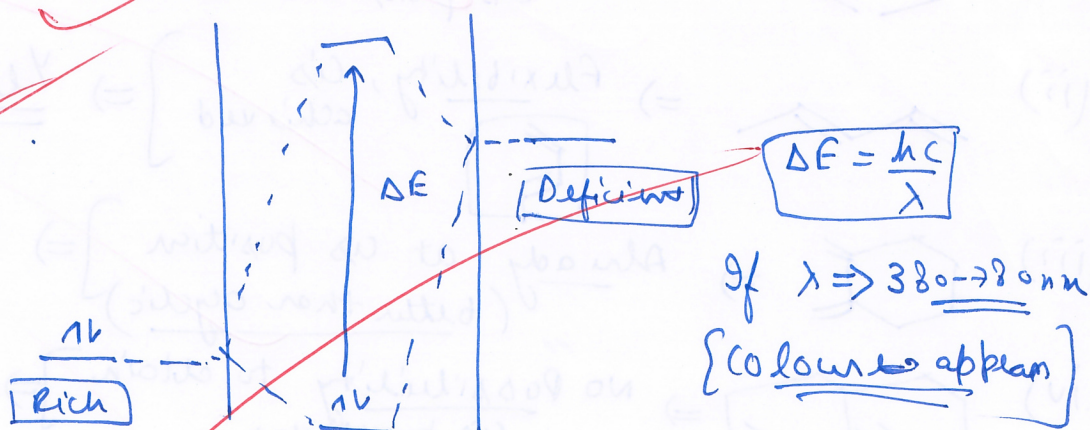
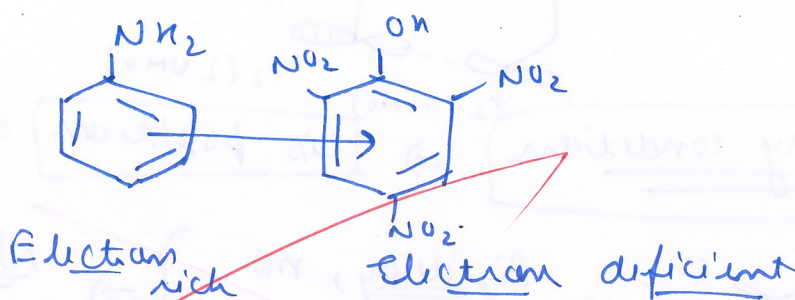
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(e) Explain charge-transfer spectra by taking a suitable donor-acceptor type complex.
(10)

Charge transfer spectra arises due to electronic movement from electron ~~deficient~~ ^{rich} molecule to electron deficient molecule.

generally lies in the range of $\Rightarrow$ UV/Visible

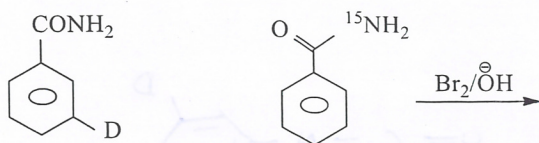
Complex



Further, UV spectrometer could be utilized to study the charge transfer spectra.

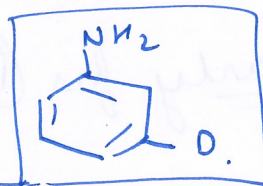
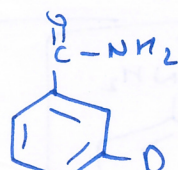
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3(a) Predict the products of the following reaction showing proper distribution of D and ^{15}N in each of these. Justify with mechanism. (15)

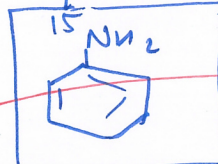
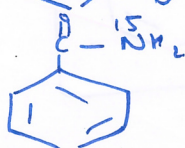


The above reaction is Hoffman
Bromamide $\text{R}-\text{C}(=\text{O})-\text{NH}_2 \xrightarrow{\text{Br}_2/\text{OH}^-} \text{R}-\text{N}(\text{H})_2$

Product of A $\Rightarrow$



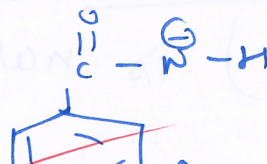
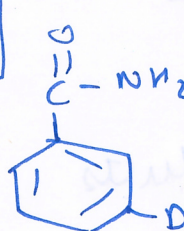
Product of B $\Rightarrow$



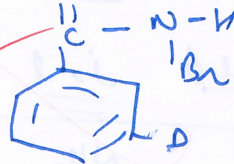
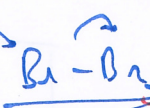
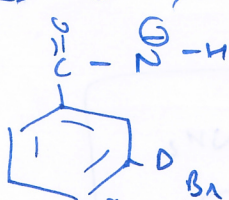
No crossover products

Mechanism

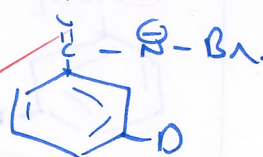
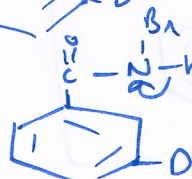
Step 1



Step 2

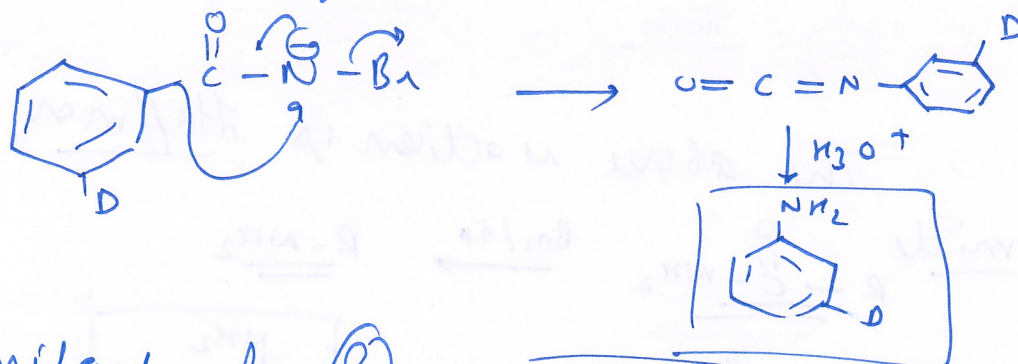


Step 3

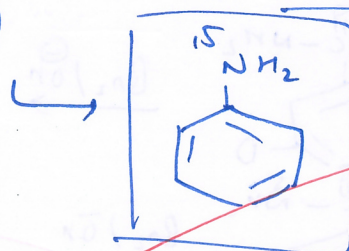


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Step 4 Rearrangement

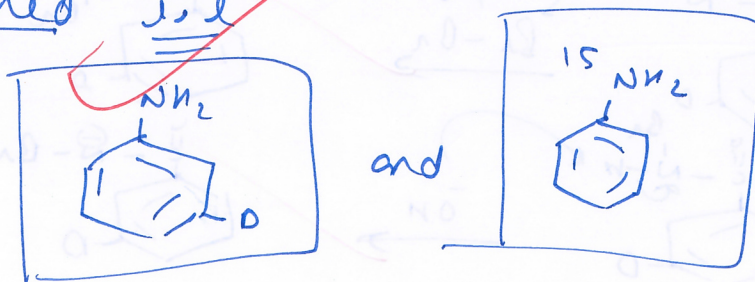


Similarly for (B)



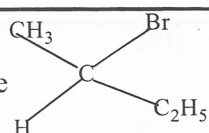
~~Since, step 4 rearrangement is intramolecular, the possibility of intermolecular attack (crossover products) is not possible.~~

~~Thus, only two products are formed is~~



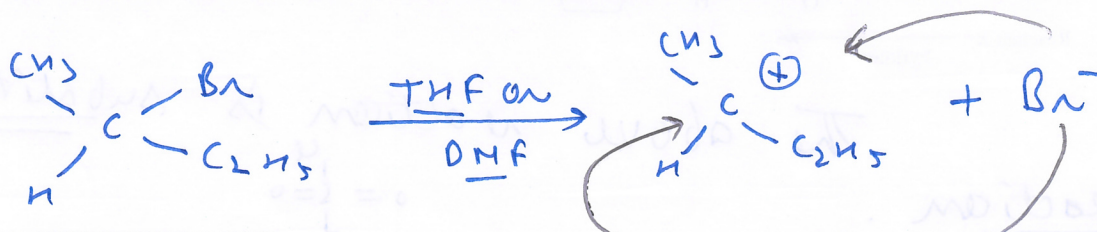
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b) Optically active

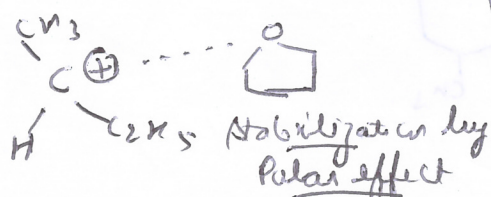
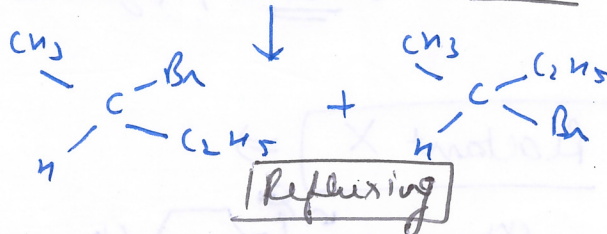


on refluxing in polar

Solvent like THF or DMF racemizes but it does not occur in cyclohexane. Explain. (10)

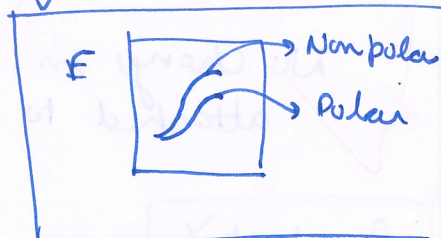


(Both side attack possible)



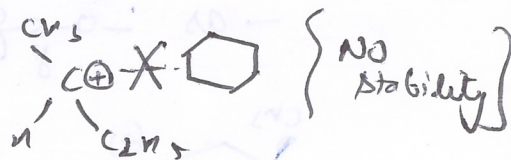
In polar solvent, carbocation formation takes place and is adequately stabilized

Since S_N1 reaction is nonstereospecific in nature, refluxing takes place.



In cyclohexane [Non Polar] $\Rightarrow$ Carbocation formation does not take place. Thus

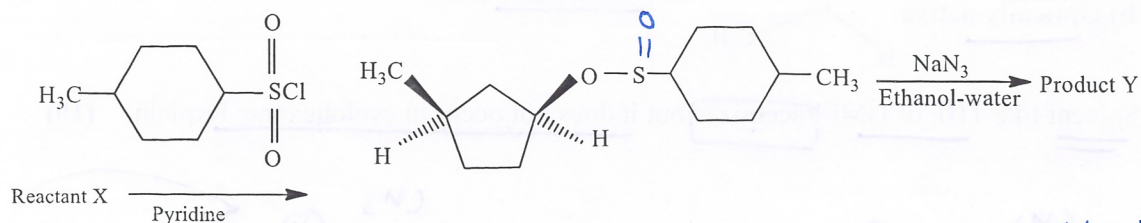
No reflux is possible.



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(c) Identify X and Y and discuss stereochemistry.

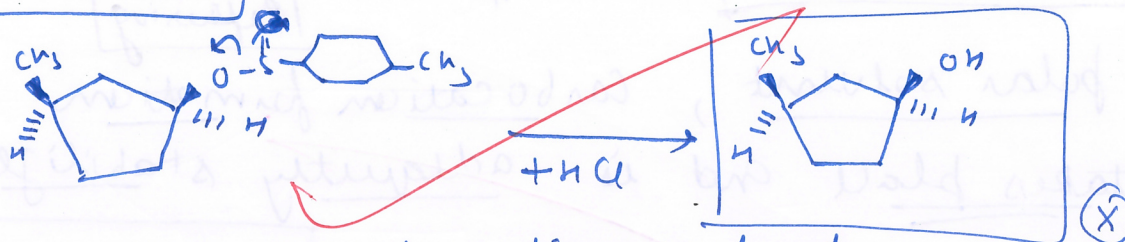
(10)



The above reaction is substitution reaction.

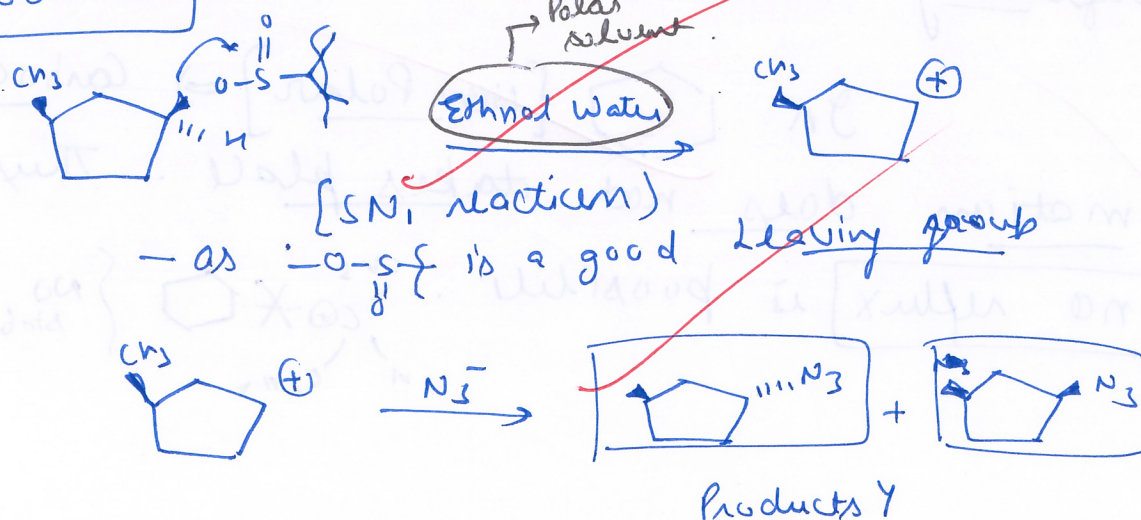
Since, pyridine +

Reactant X $\Rightarrow$



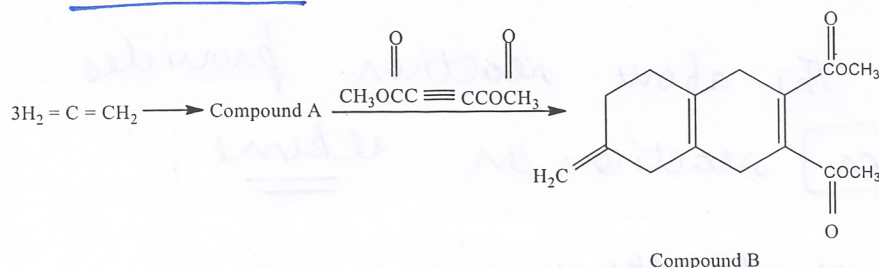
No change in configuration, as bond attached to chiral centre is intact.

Product Y



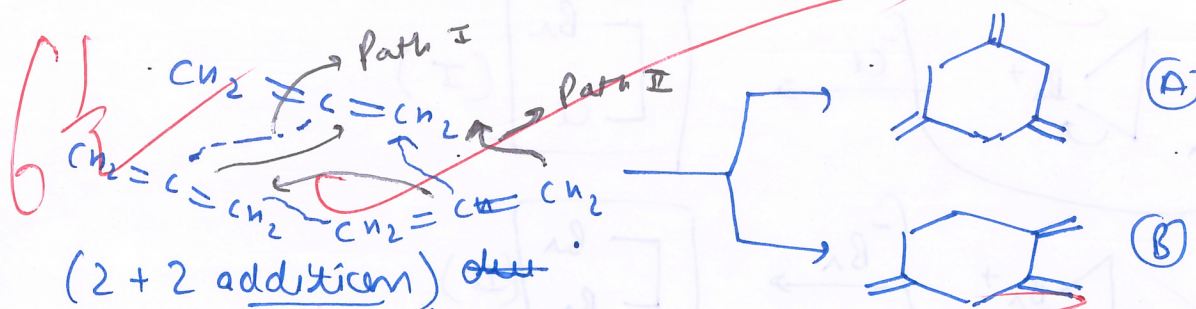
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(d) Allene can be converted to a trimer (compound A) of molecular formula C_9H_{12} . Compound A reacts with dimethyl acetylene dicarboxylate to give compound B. Deduce the structure of compound A. (10)

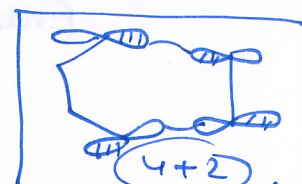
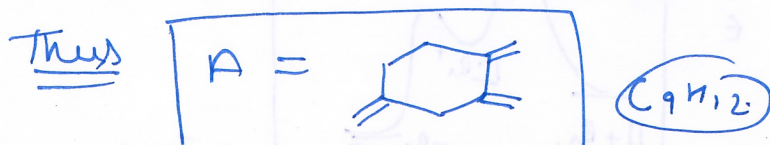
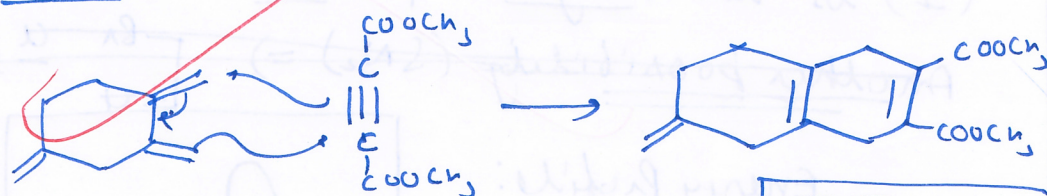


The second reaction seems to be Diels Alder in nature (4+2 addition) in thermal medium.

In first reaction, there are two possibilities of trimerization.



Since in (A), Diels Alder reaction is not feasible due to non-4's diene in (B)

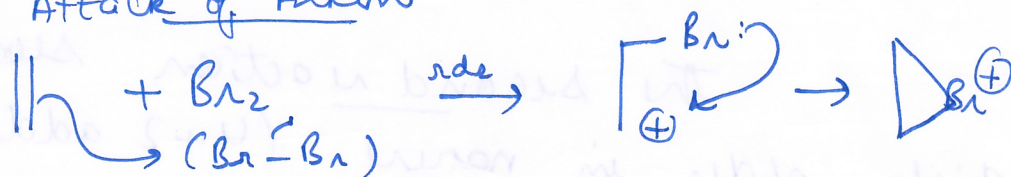


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(e) The addition of Br_2 to $\text{CH}_2 = \text{CH}_2$ in presence of excess Cl^- produces $\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$ as one of the products. Explain mechanistically. (10)

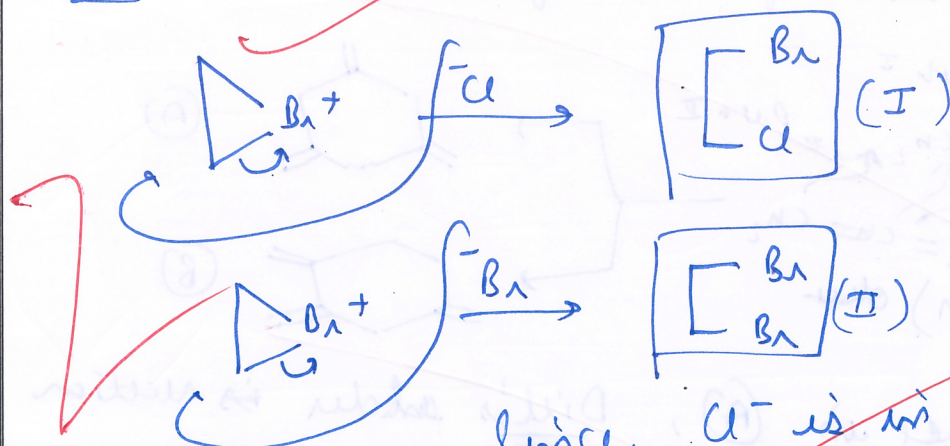
The above reaction provides for addition reaction on alkene.

Step 1 $\Rightarrow$ Attack of Alkene



(formation of cyclic bromonium ion)

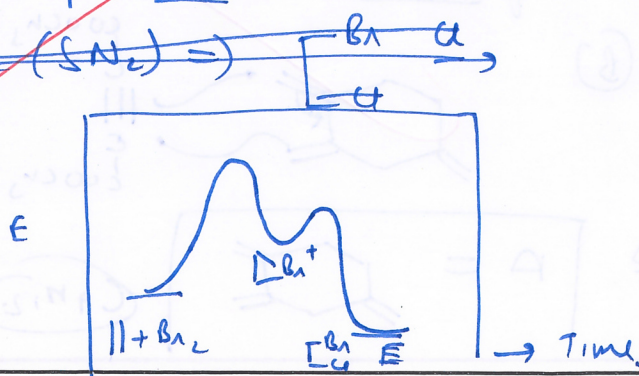
Step 2 $\Rightarrow$ Possible products



Since, Cl^- is in excess,
(I) is the major product

Another possibility ($\text{S}_{\text{N}}2$) $\Rightarrow$

Energy Profile:



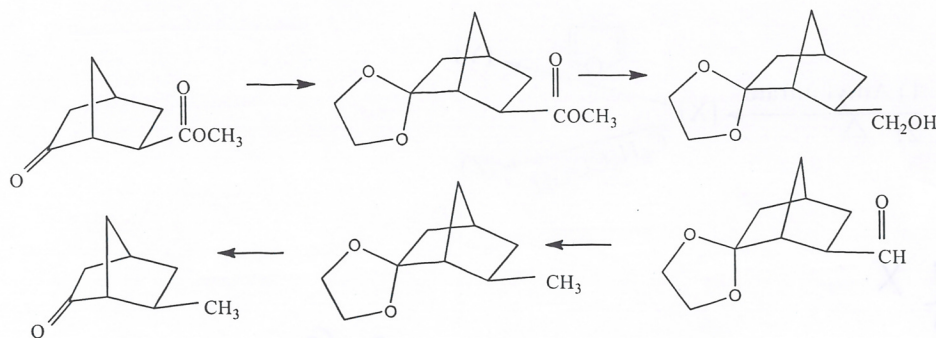
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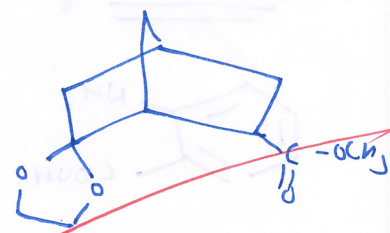
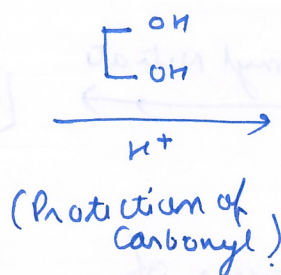
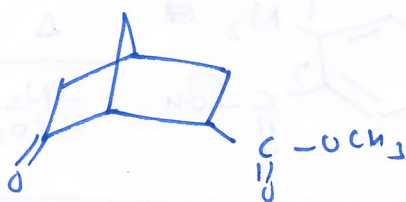
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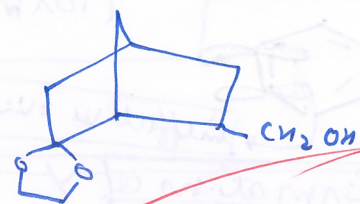
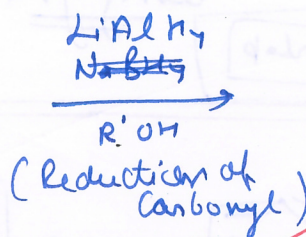
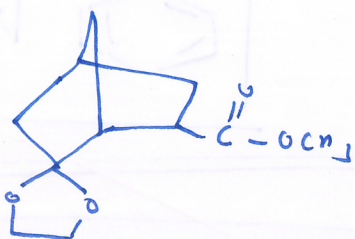
4.(a) The following five- step synthesis has been reported in the chemical literature. Suggest reagents appropriate for each step. (10)



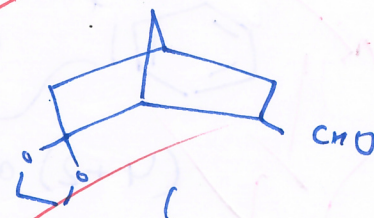
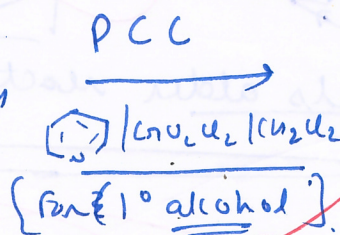
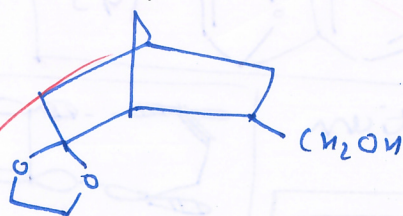
Step 1



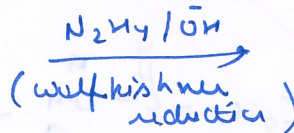
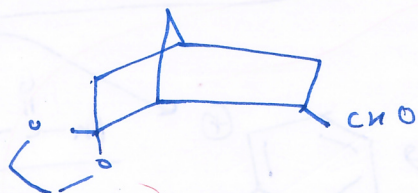
Step 2



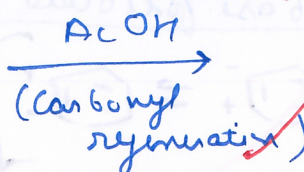
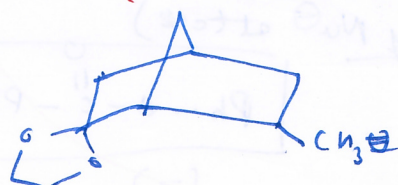
Step 3



Step 4



Step 5



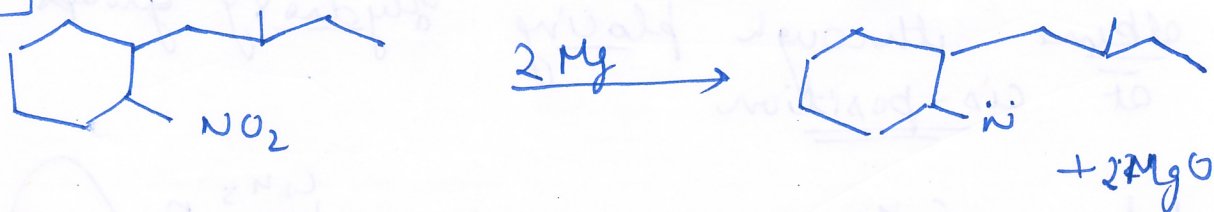
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(c) How will you carry out the following conversion? Write the steps involved in it:
(10)

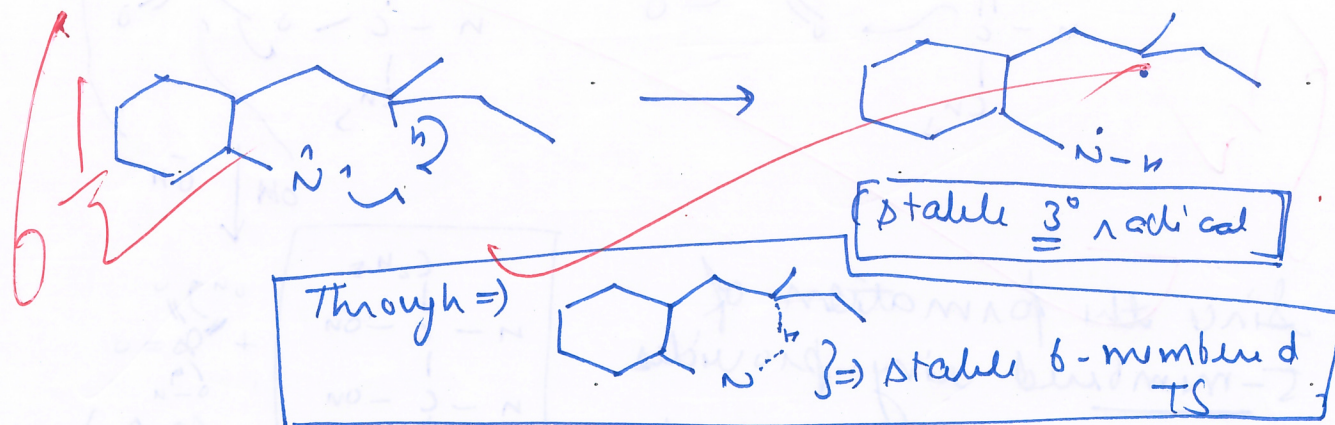


The feasibility of above reaction is through nitrene intermediate

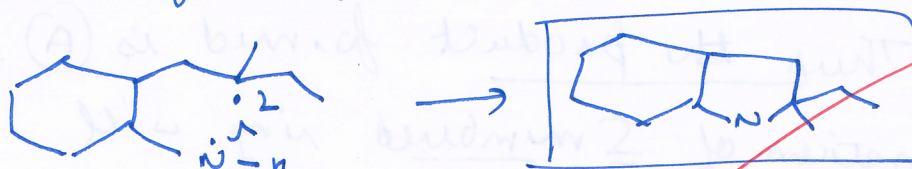
Step 1 $\Rightarrow$ Nitrene formation



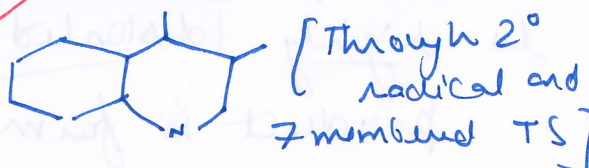
Step 2 $\Rightarrow$ Insertion reaction



Step 3 $\Rightarrow$ Ring formation

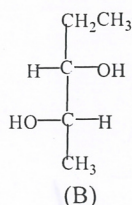
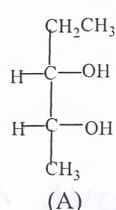


Other minor products $\Rightarrow$

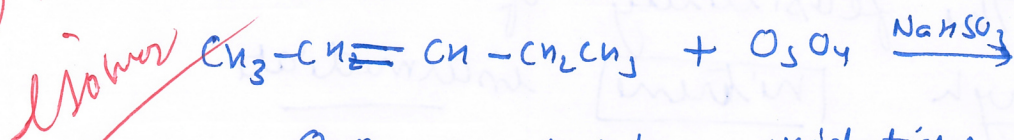


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(d) Which among the following (A or B) is formed when Pent-2-ene is oxidised by OsO_4 and NaHSO_3 ? Explain its formation with the mechanism. (10)

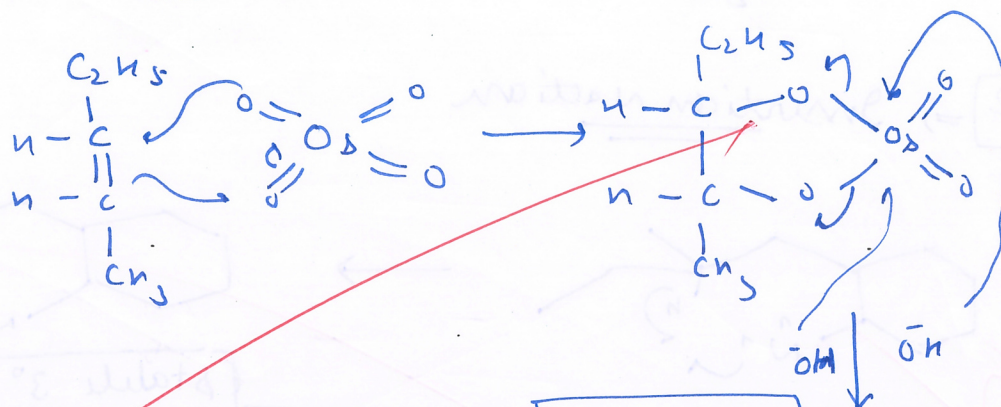


Other

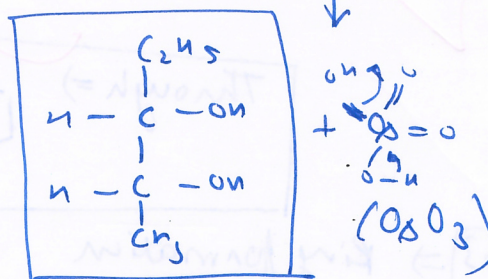


OsO_4 undertakes oxidation of alkene through placing hydroxy groups at cis-position

i.e.



Since the formation of 5-membered ring provides for cis attachment of dial.

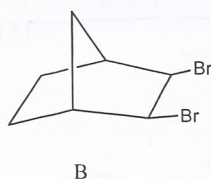
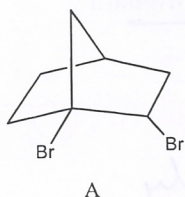


Thus the product formed is (A).

In (B), formation of 5-membered ring will be highly distorted. Thus only 1 product is formed i.e. (A).

DIAS

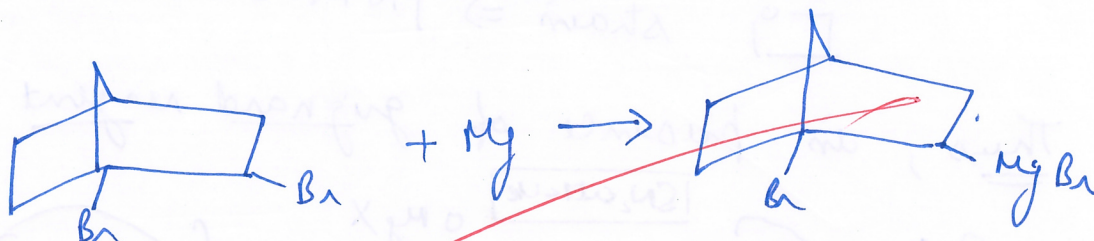
(e)(i) The dibromide A reacts with magnesium in dry ether to form a stable Grignard reagent, while the dibromide B does not. Explain. (5)



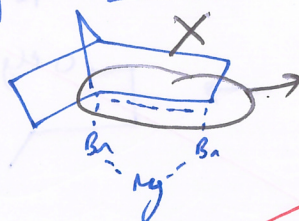
Reaction of Grignard reagent is



For A

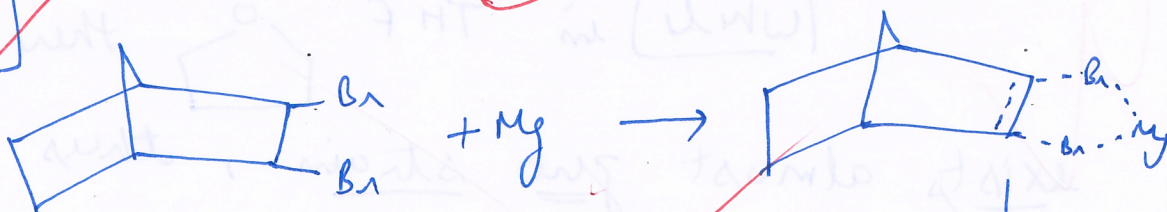


(+) No Possibility of elimination

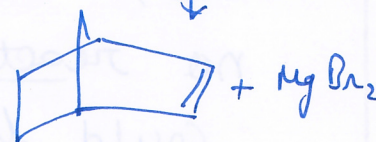


Double bond at bridgehead not possible due to non-planarity

For B



Elimination reaction takes place and Grignard reagent is not formed



DIAS

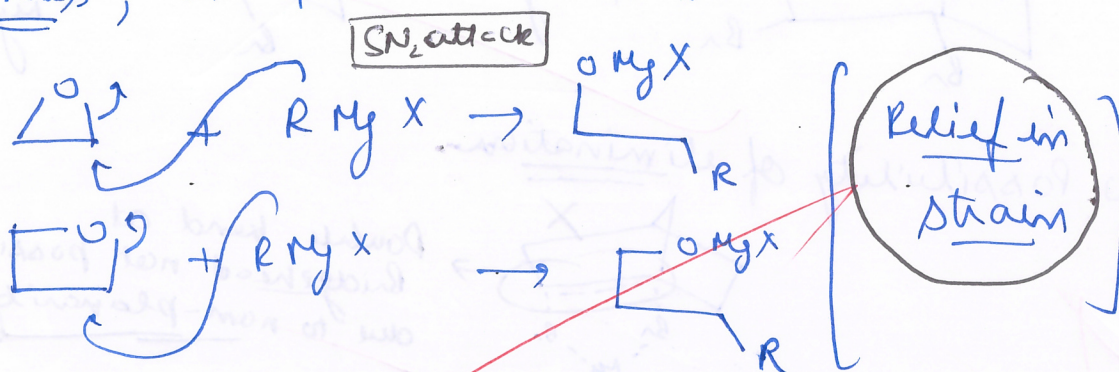
(ii) Ethylene oxide ($\triangle^{\circ}$) and trim ethylene oxide ($\square^{\circ}$) react readily with a Grignard reagent does not react with THF for which it is used as a solvent in Grignard Synthesis. Explain these observations. (5)

$\triangle^{\circ}$ and $\square^{\circ}$ are highly strained molecules

$$\triangle^{\circ} \text{ strain} \Rightarrow |109.5^{\circ} - 60^{\circ}| = 49.5^{\circ}$$

$$\square^{\circ} \text{ strain} \Rightarrow |109.5^{\circ} - 90^{\circ}| = 19.5^{\circ}$$

Thus, in presence of grignard reagent



[While] in THF $\square^{\circ}$ there

exists almost zero strain, thus

no reaction with $R-MgX$. $R-MgX$

could be efficiently used in

THF

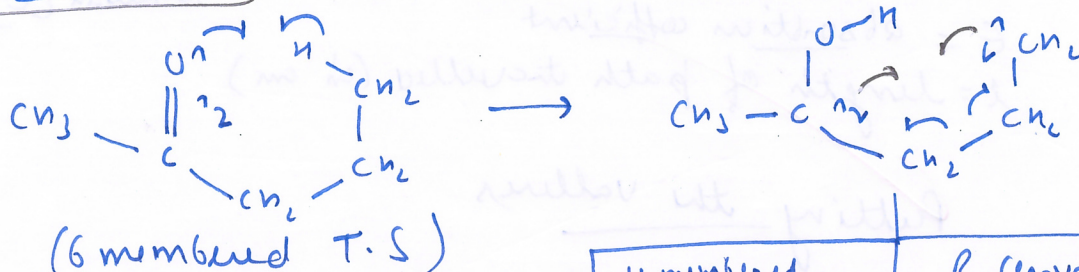
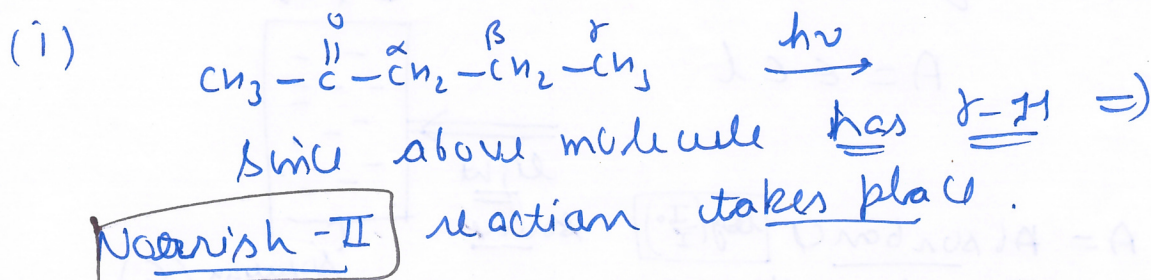
DIAS

Section-B

5(a) Write the photochemistry irradiation products of the following compounds: (10)

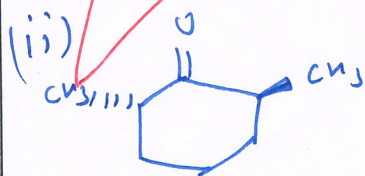
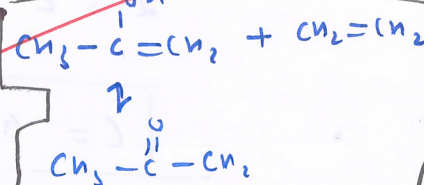
(i) 2-pentanone

(ii) trans-2,6-dimethylcyclohexanone

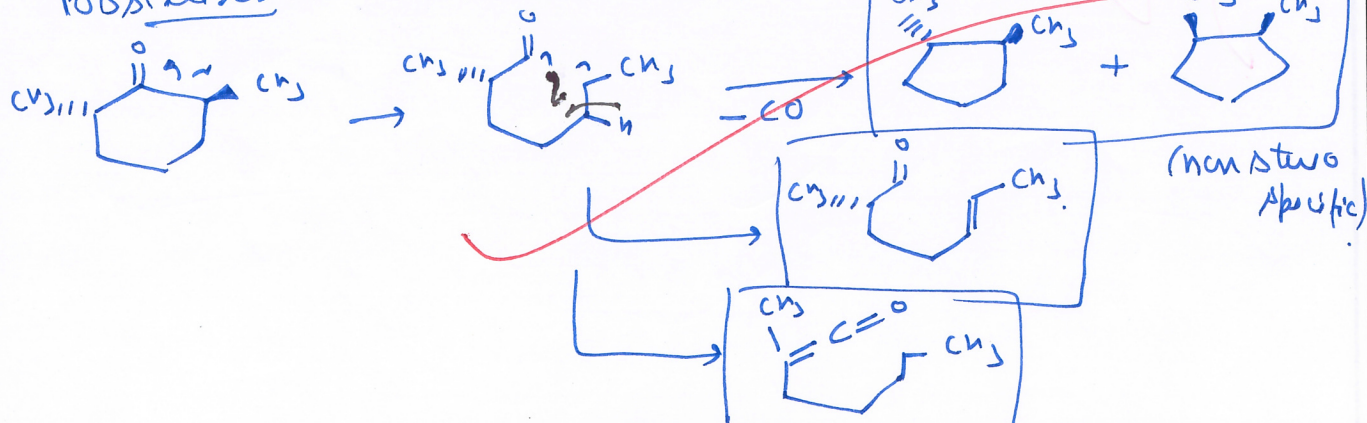


4-membered ring.

β -Cleavage



Possibilities of Norrish-I



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(b) (i) What is the concentration value for a solution of camphor $\epsilon_{\text{max}} = 14$ in hexane solution in a 10 cm cell? A at 295nm was found to be 2.52. (5)

Beer-Lambert equation provides for

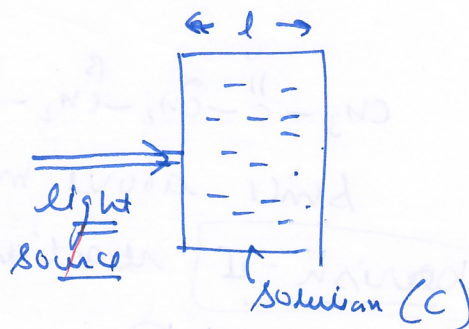
$$A = \epsilon c l$$

where

A = Absorbance $\log\left(\frac{I_0}{I}\right)$

ϵ = absorption coefficient

l = length of path travelled (in cm)



Putting the values

$$2.52 = (14) (c) (10)$$

$$c = 0.018 \text{ M}$$

3/2 ✓

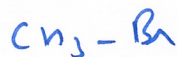
DIAS

(ii) Offer your explanation for the variation of $\lambda_{\max}$ values for the following compounds: (5)

Methyl chloride $\lambda_{\max} = 173 \text{ nm}$

Methyl bromide $\lambda_{\max} = 204 \text{ nm}$

Methyl iodide $\lambda_{\max} = 258 \text{ nm}$

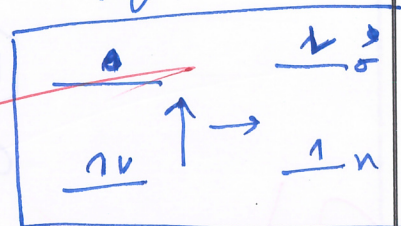
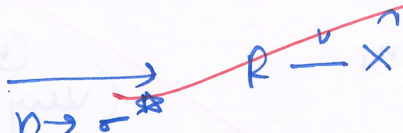
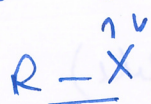


$\lambda_{\max} = 173 \text{ nm}$

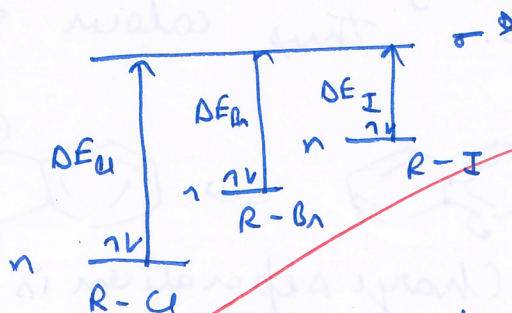
$\lambda_{\max} = 204 \text{ nm}$

$\lambda_{\max} = 258 \text{ nm}$

Since, more the electronegativity of the atom, better is its lone pair holding tendency and more energy is required for transition.



Since Electronegativity order $\text{Cl} > \text{Br} > \text{I}$



$\Delta E_{\text{Cl}} > \Delta E_{\text{Br}} > \Delta E_{\text{I}}$ (Energy required for $n \rightarrow \sigma^*$ transition)

$\therefore \lambda_{\max, \text{Cl}} < \lambda_{\max, \text{Br}} < \lambda_{\max, \text{I}}$
 $\lambda_{\max, \text{Cl}} = 173 \text{ nm}$ $\lambda_{\max, \text{Br}} = 204 \text{ nm}$ $\lambda_{\max, \text{I}} = 258 \text{ nm}$

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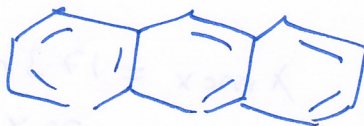
DIAS

(c) Explain the following:

(i) p-nitroaniline and anthracene both absorb near 375 nm but p-nitroaniline is yellow while anthracene is colorless. (5)

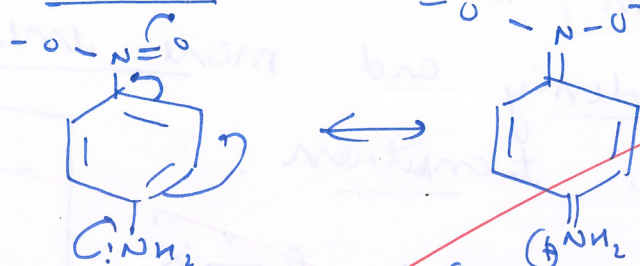


Yellow



Colorless

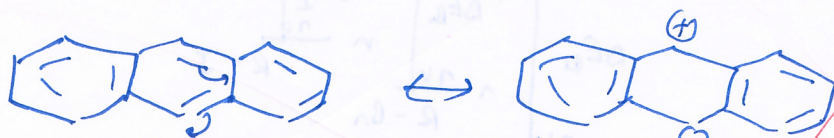
In p-nitroaniline



(very stable)

→ Charge separation leads to exceptional stability, and remains for finite amount of time. Thus colour appears

⇒ In



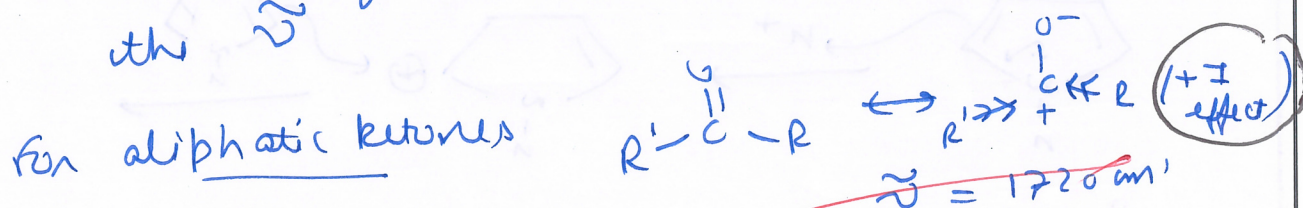
Charge separation is only for 10^{-6} s

Thus, anthracene appears colorless

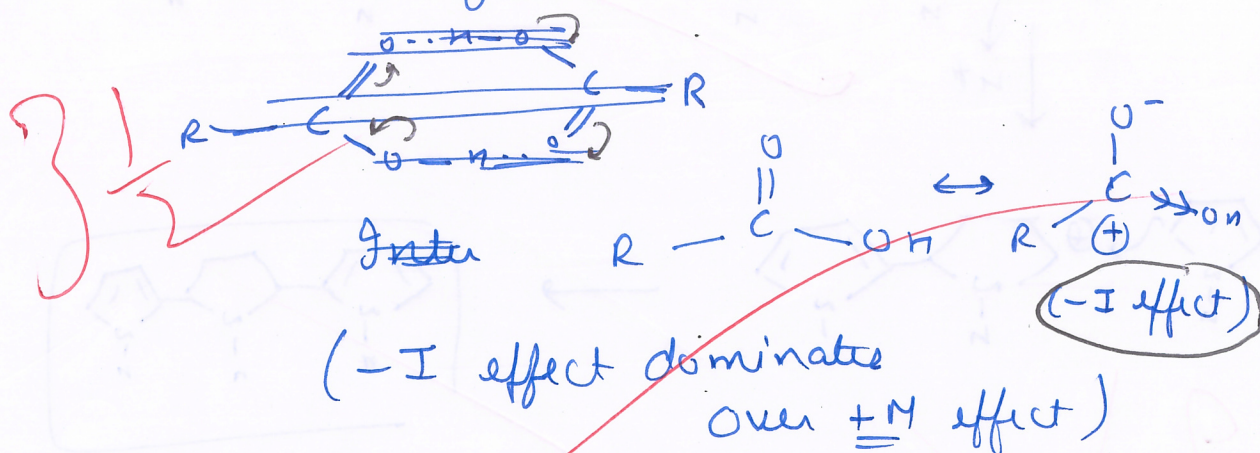
DIAS

(ii) Monomeric saturated aliphatic carboxylic acids show carbonyl stretching frequency near 1760 cm^{-1} while the saturated aliphatic ketones near 1720 cm^{-1} . (5)

IR spectra provides for $\tilde{\nu}_{\text{C=O}}$ (stretching) in the range of $1880-1650 \text{ cm}^{-1}$, when stronger the bond more would be the $\tilde{\nu}$



In case of carboxylic acid

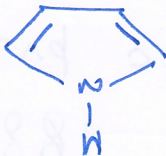


Thus, $\tilde{\nu}_{\text{C=O}}$ (carboxylic acid) > $\tilde{\nu}_{\text{C=O}}$ (ketones)

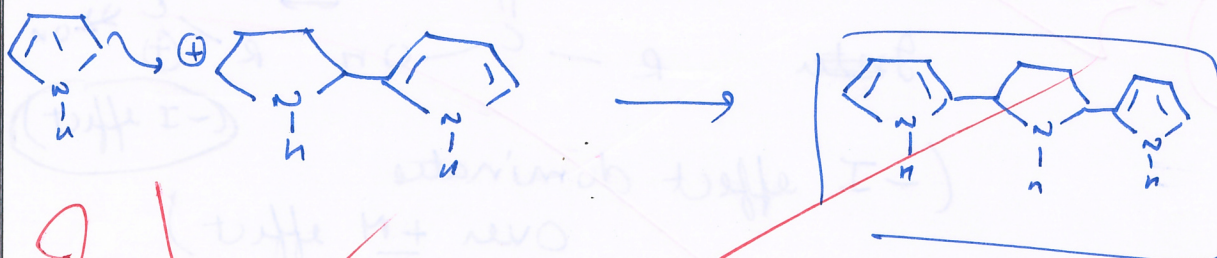
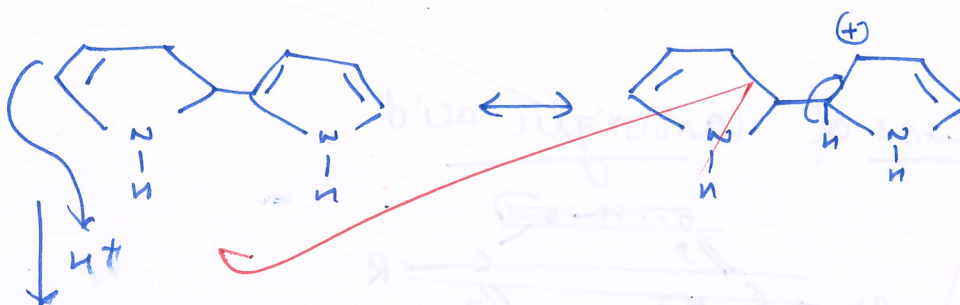
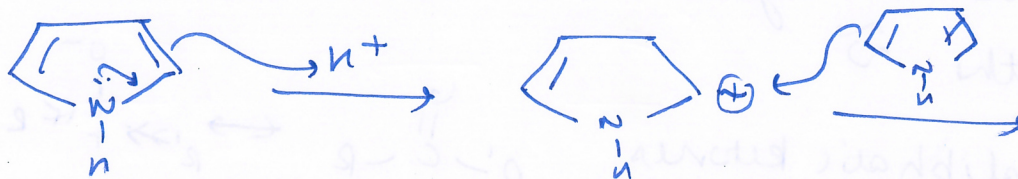
DIAS

(d)(i) Pyrrole with acid (strong) makes a red coloured compound. What is its chemical nature? (5)

Pyrrole



In presence of Acid



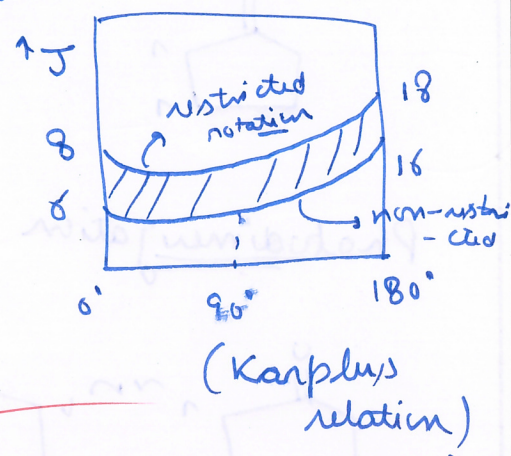
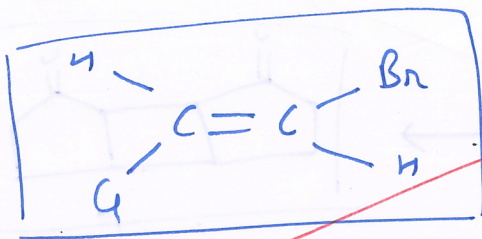
Thus, pyrrole couldn't be utilized in presence of acid

DIAS

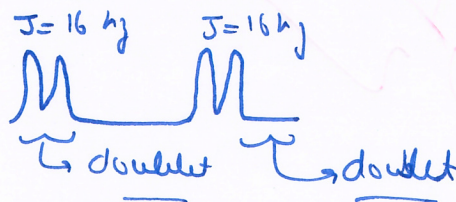
(ii) The ^1H NMR spectrum of molecular $\text{C}_2\text{H}_2\text{BrCl}$ has two doublets with $J = 16$ Hz. Write its structure with reason? (5)

$J = 16$ Hz is a rare in range $6-18$ Hz, which provides for vicinal type of coupling

Possible structure:

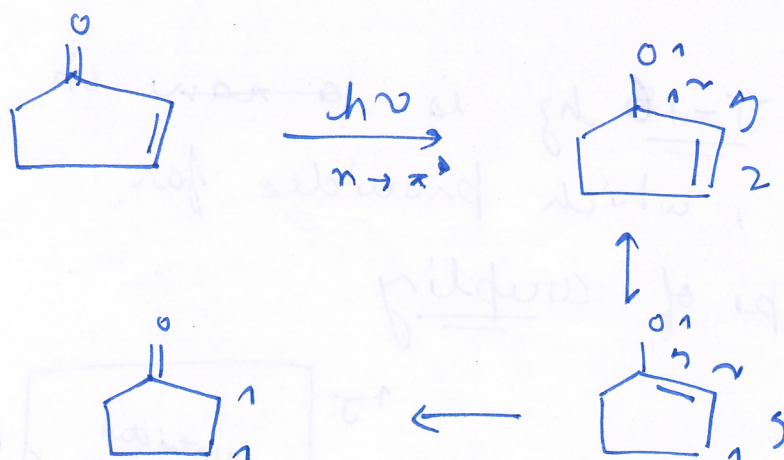


Since, both the Hs are almost at 180° providing vicinal coupling on higher side $J = 16$ Hz

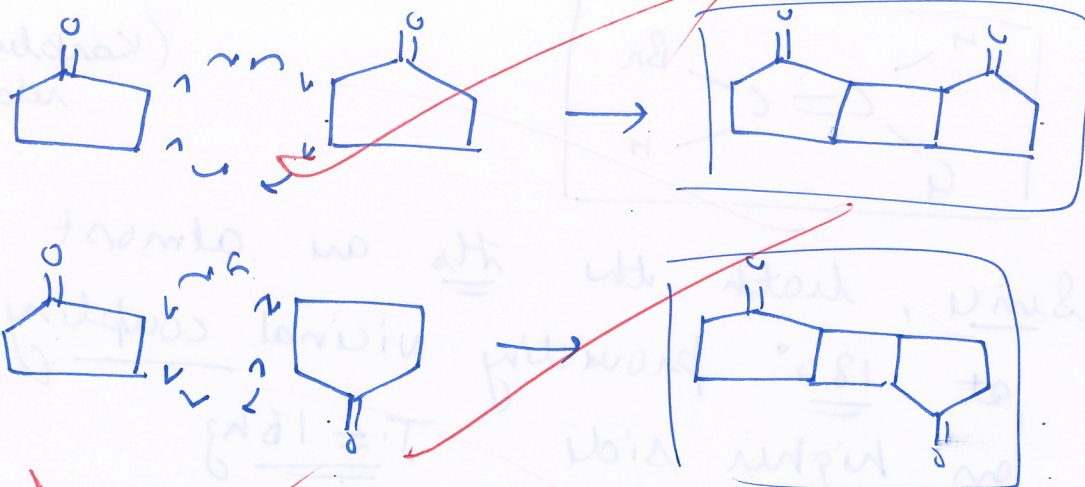


DIAS

(e)(i) What are products formed by photodimerization of cyclopent-2-en-1-one? (5)

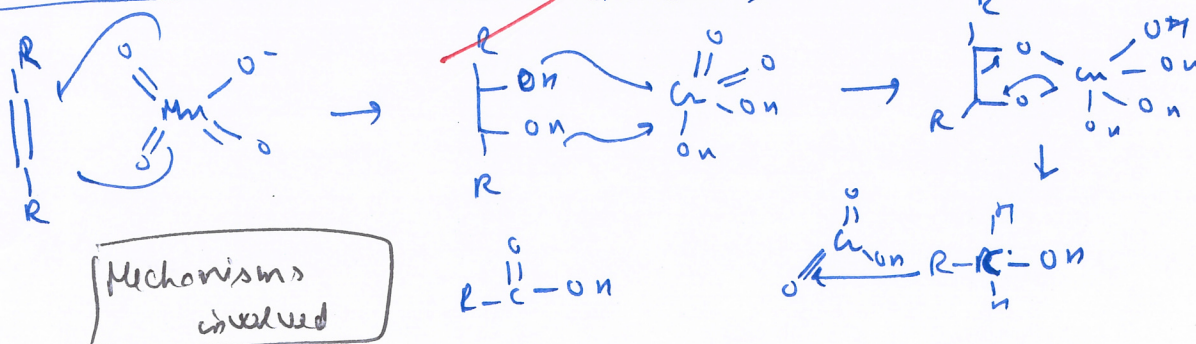
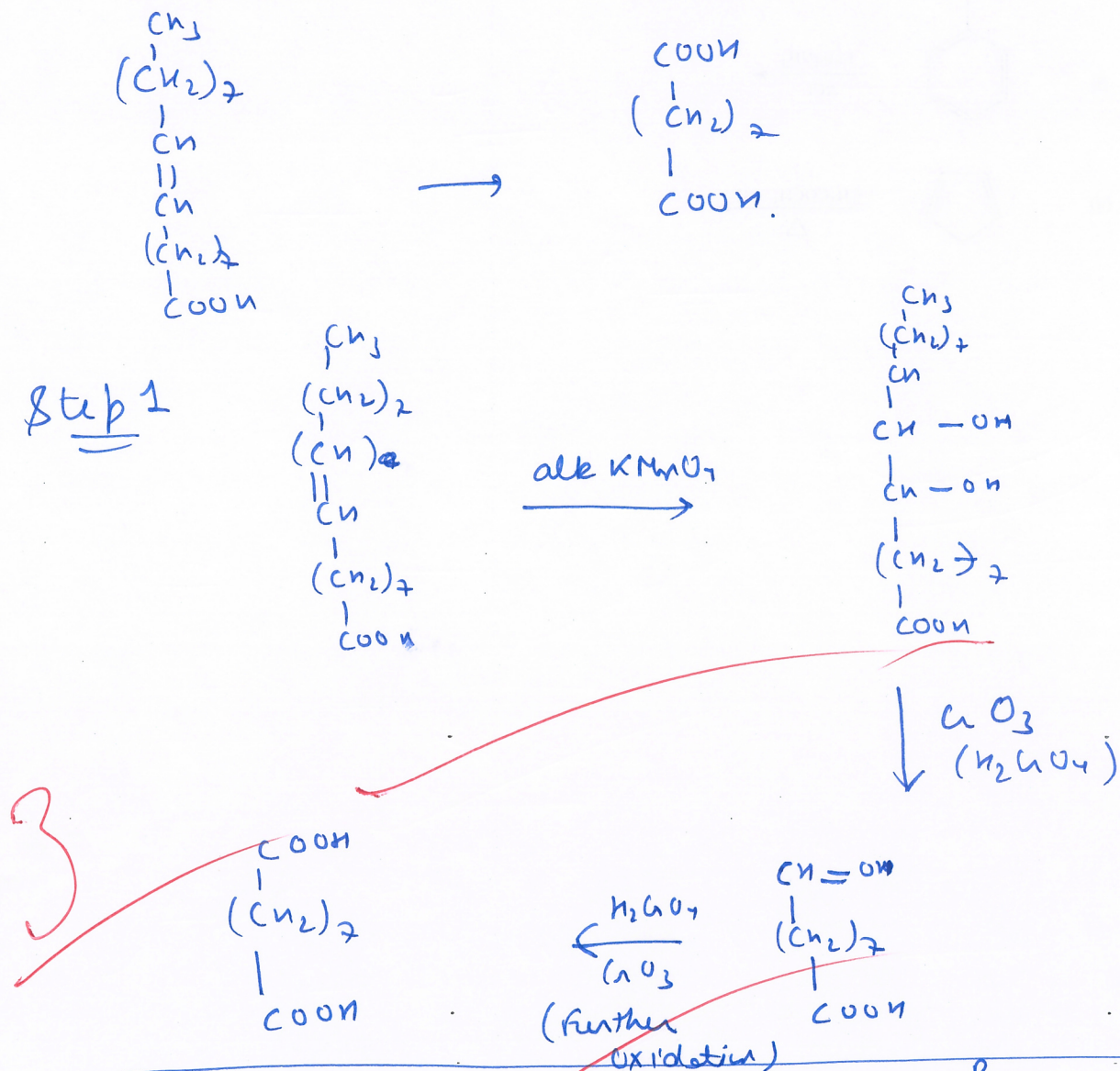


Photodimerization



DIAS

(ii) How is azelaic acid obtained from oleic acid? Azelaic acid = $\text{HOOC}(\text{CH}_2)_7\text{COOH}$
 COOH. Oleic acid = $\text{CH}_3(\text{CH}_2)_7 - \text{CH} = \text{CH}(\text{CH}_2)_7\text{COOH}$ (5)

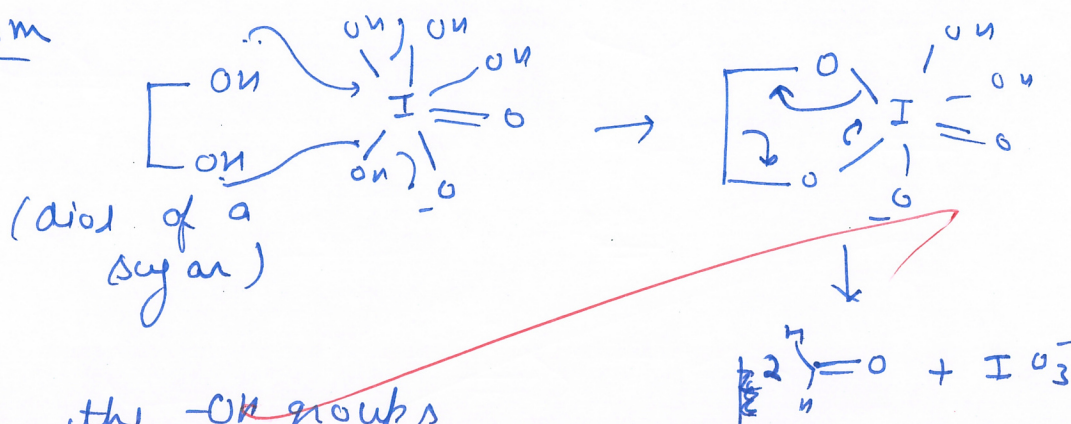


DIAS

8.(a) How malaprade oxidation is used to determine cis - glycolic units in sugars? Illustrate with one example showing mechanism. (10)

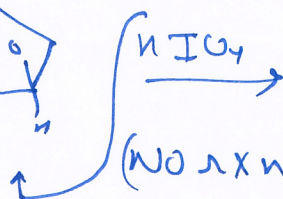
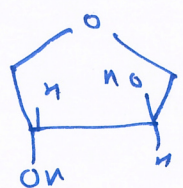
Malaprade oxidation provides for oxidation of diols located at cis-position using HIO_4

Mechanism



In Case, the ~~-OH~~ groups are not cis (trans) $\Rightarrow$ no reaction takes place

(eg)

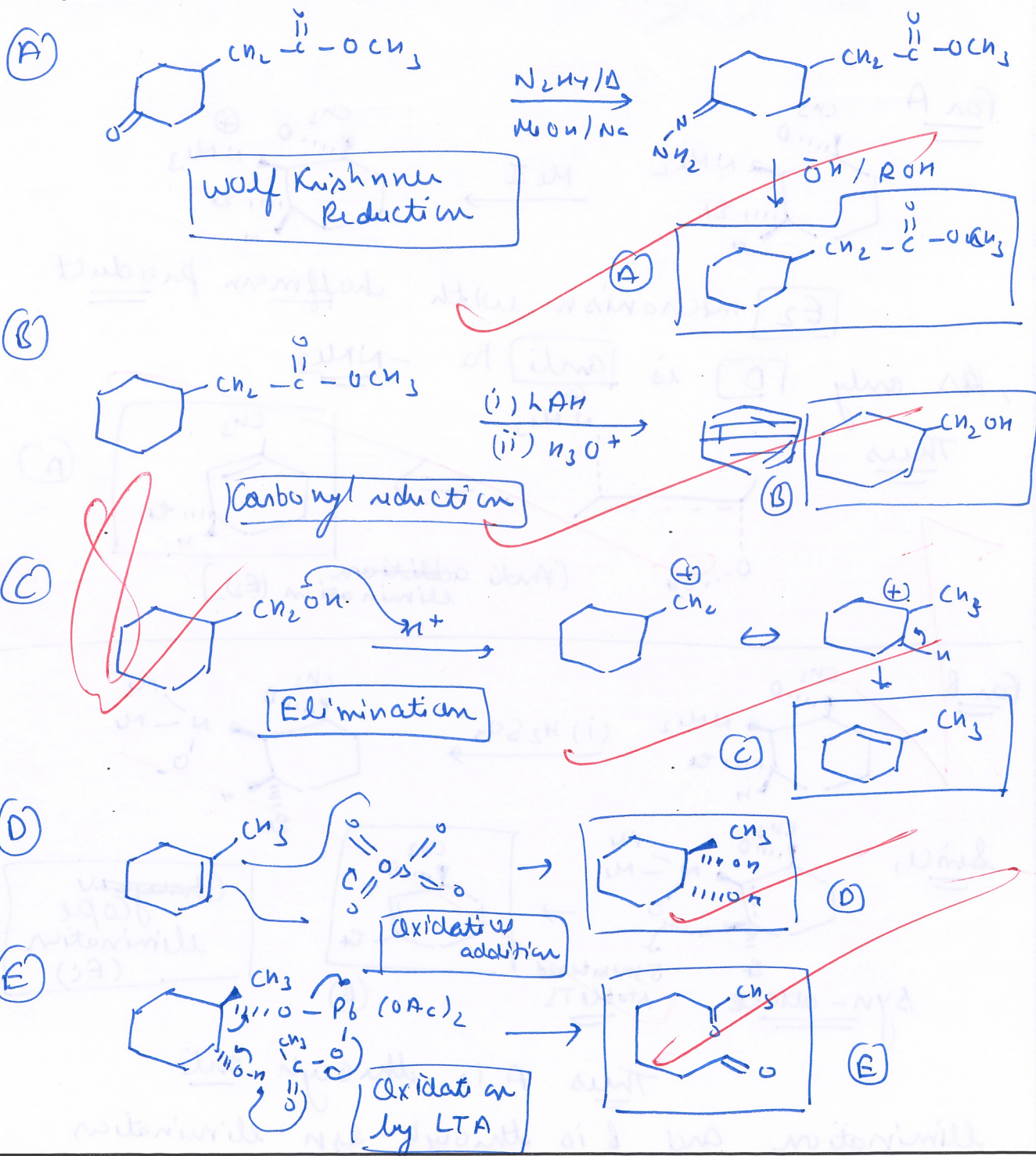
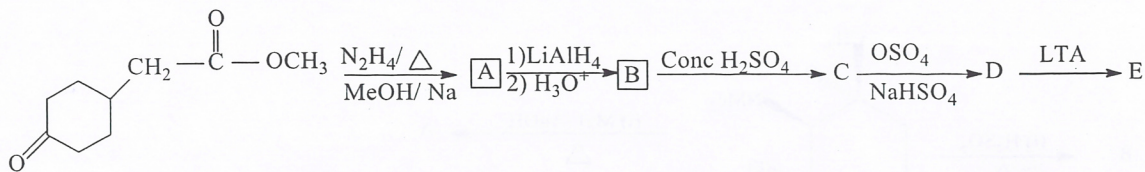


as no cis diol group. Present.

This helps in distinguishing between cis glycolic units and trans ones

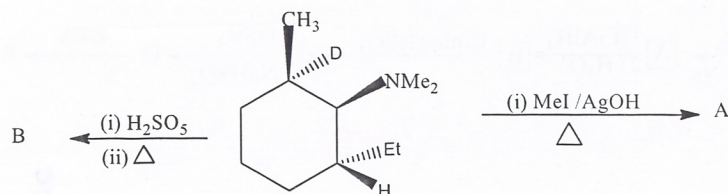
DIAS

(b) Identify the compounds A and B in the following reaction sequence: (10)

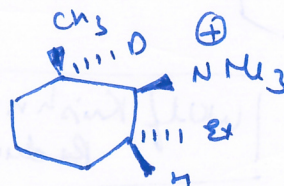
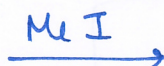
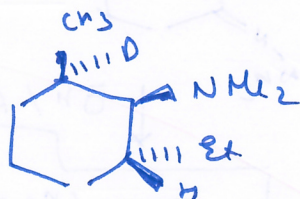


DIAS

(c) Complete the following reaction and propose a suitable mechanism. (10)



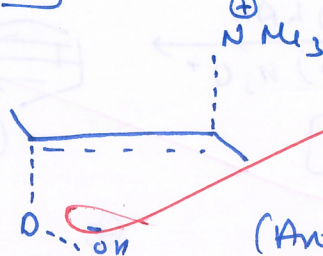
For A



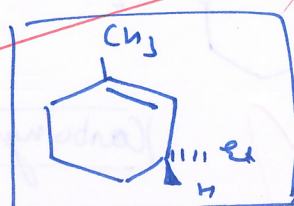
E2 mechanism with hoffmann product

, As only D is anti to $-NMe_3^+$

Thus

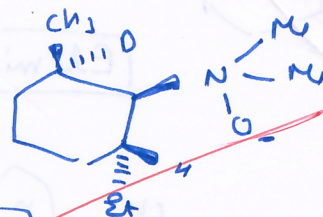
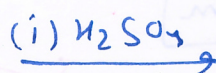
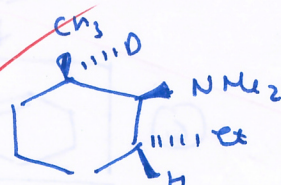


(Anti addition elimination (E2))

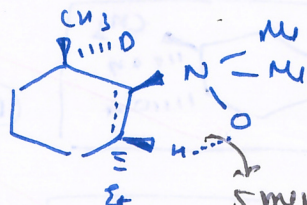


(A)

For B

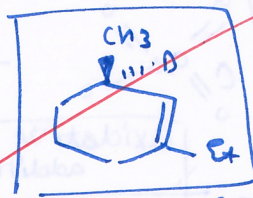


Since,



Syn-attack

Stable TS



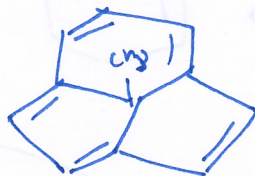
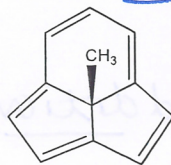
(B)

Conjugative elimination (E1c)

Thus A is through anti elimination and B is through syn elimination

DIAS

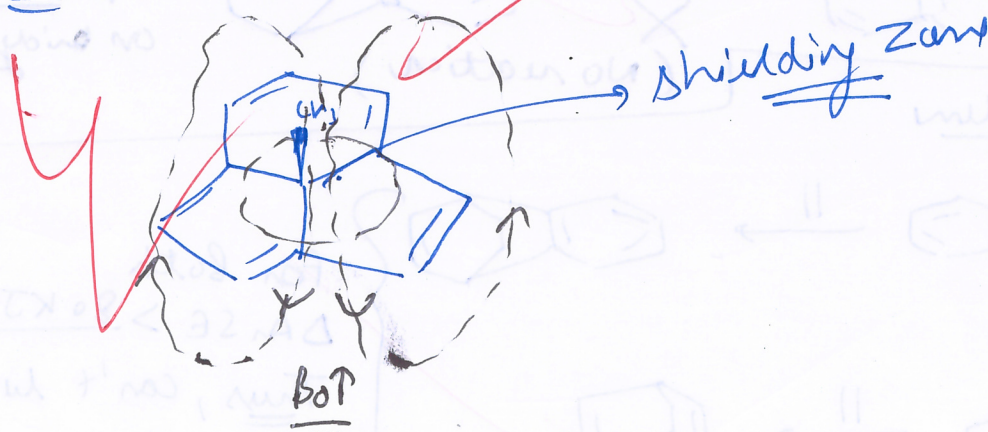
(d) (i) The methyl group in the following compound has an unusual chemical shift of δ - 1.67, about 4 ppm lower than the chemical shift of a typical allylic methyl group. (5)



Since above molecule is aromatic with $10\pi^-$ $\{(4n+2)e^- \text{ } n=2\}$

There exists, diamagnetic current inside the ring $\Rightarrow$ providing for shielding effect, thus δ value of

$-\text{Me}$ exists on the lower side

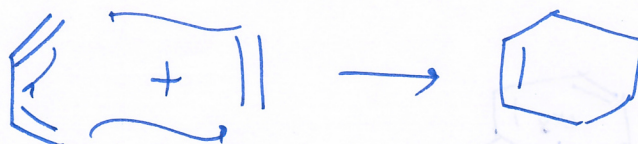


DIAS

(ii) Comment on the ability of anthracene, phenanthrene, naphthalene and benzene to act as dienes in the Diels-Alder reaction. (5)

Diels - Alder is is (4+2) addition

reaction



for Anthracene

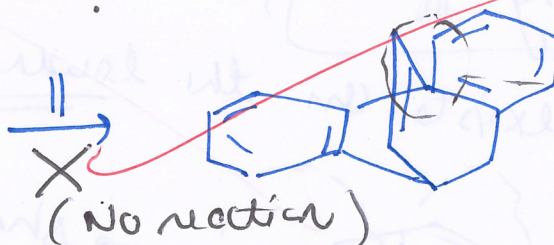


$$\Delta_{\text{ASE}} = 49 \text{ KJ/mol}$$

(Acceptable)

Since $\Delta_{\text{ASE}} < 80 \text{ KJ/mole}$
→ Acceptable limit

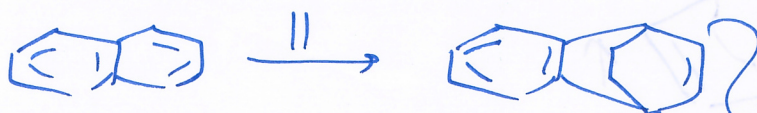
for Phenanthrene



(No reaction)

→ non planarity on bridge head

Naphalene



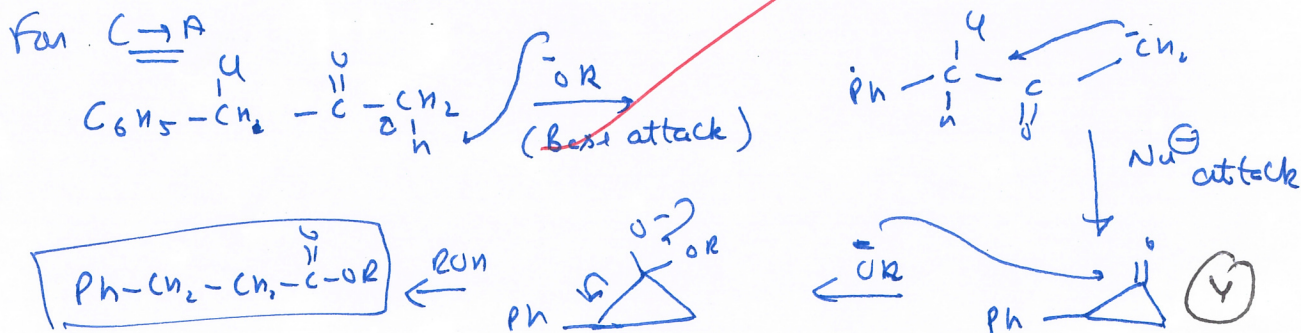
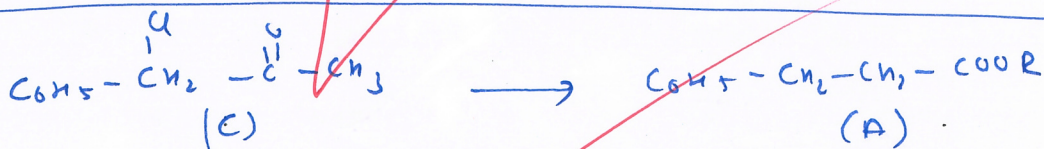
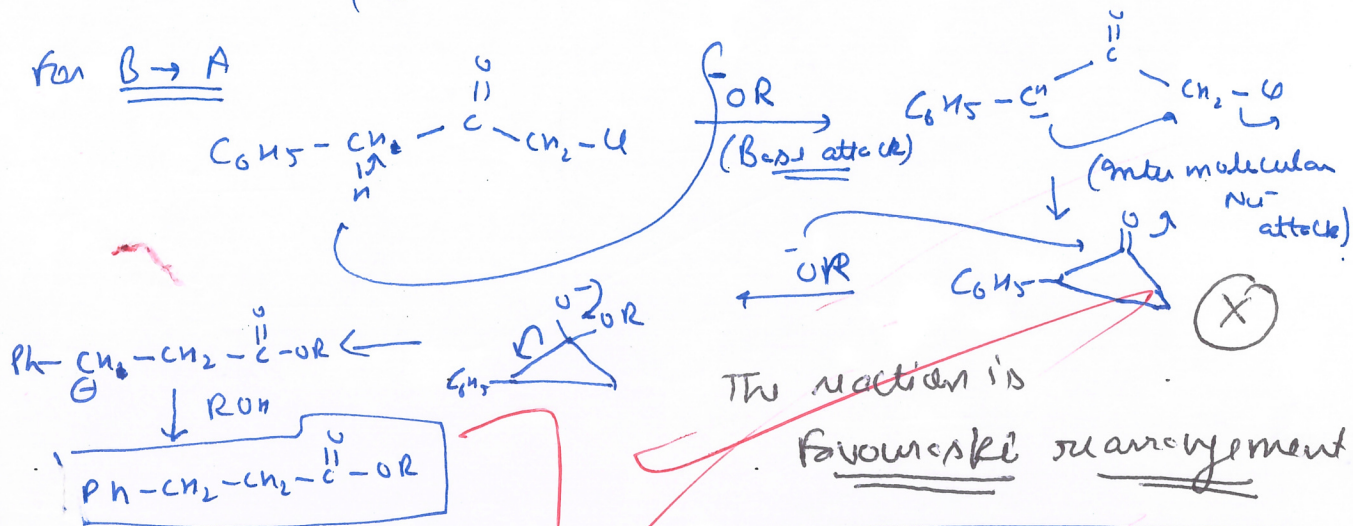
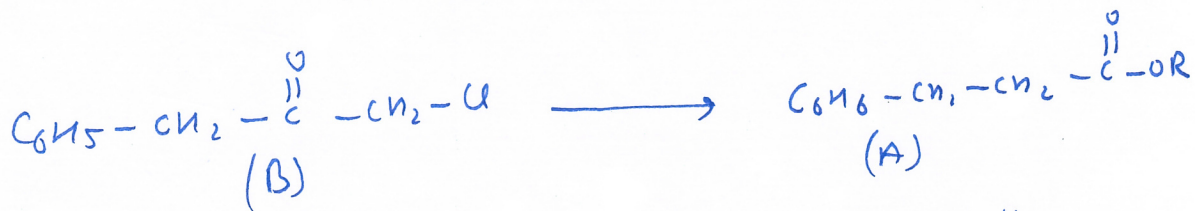
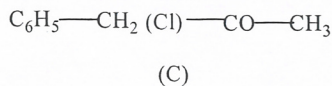
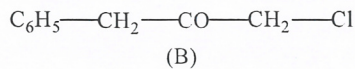
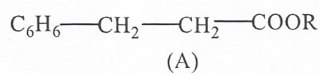
Benzene



for both
 $\Delta_{\text{ASE}} > 80 \text{ KJ/mole}$
Thus, can't be used
as dienes

DIAS

(e) The compound (A) shown below can be synthesized from (B) as well as (C) using alkoxide. Name the reaction and propose the mechanisms. (10)



Since both reactions have common intermediates X and Y , products are same.