DIAS

All India TEST – SERIES CSE – 2024

Organic-II TEST -5

Syllabus -: Rearrangements, Named reaction & Reagents.

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:- AAYUSH SAINI

UPSC Roll no:- 0841801

Mobile Number. [redacted]

Date :- 29-07-24

Dias Roll No.

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	37	36	35	31½				21½

Signature of invigilator

V. Good

161/250

Signature of Examiner

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UPSC/IAS/IFoS Mains Test Series For Chemistry Optional CSE 2024

From 30th June 2024

Schedule of Chemistry Test Series 2024

Sr. No.	Test No.	Topics to be Covered	Date
1	Test 1	Atomic structure, Chemical bonding, Liquid state, Gaseous state, Solid state.	30/06/2024
2	Test 2	Thermodynamics, Phase equilibrium, Electrochemistry, Chemical kinetics.	07/07/2024
3	Test 3	Surface chemistry, Photo chemistry, F-block, Coordination compounds, P-block, Biochemistry.	14/07/2024
4	Test 4	Aromaticity and Reaction mechanism.	21/07/2024
5	Test 5	Rearrangement, Named reaction and Regents.	28/07/2024
6	Test 6	Pericyclic, Photochemistry, Polymer and Spectroscopy.	04/08/2024
7	Test 7	Full Syllabus – (Paper I)	11/08/2024
8	Test 8	Full Syllabus – (Paper II)	18/08/2024
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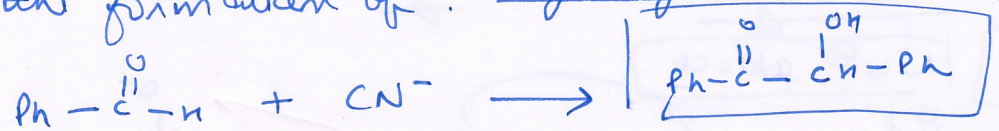
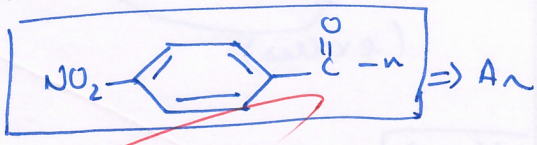
Section- A

1(a) (i) Why p –nitro benzaldehyde does not follow benzoin condensation? Explain. (5)

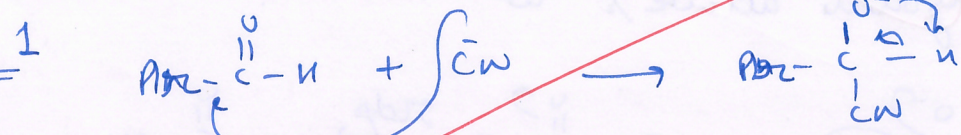
Benzoin condensation is a reaction of benzaldehyde in presence of $-CN^-$ resulting in the formation of α-hydroxy-diphenyl Ketone

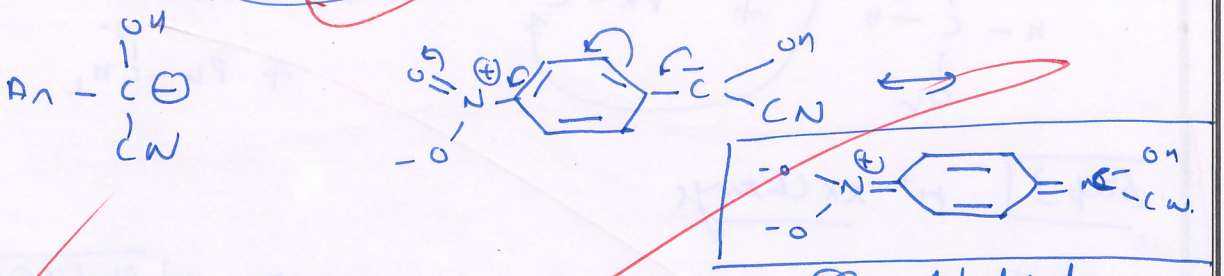


For p-nitro-benzaldehyde



Step 1





(A) Stable form

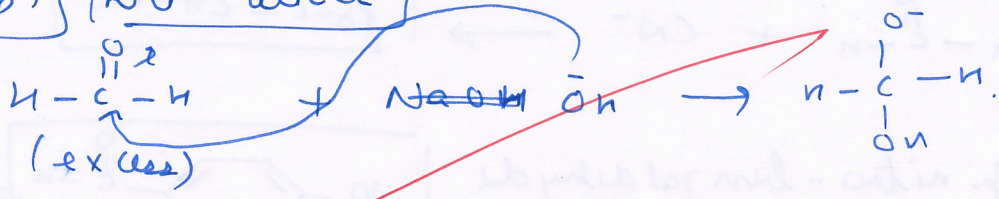
In the stable form [A], the carbanion gets deactivated for further attack (Nucleophilic)

Thus the reaction do not proceeds further.

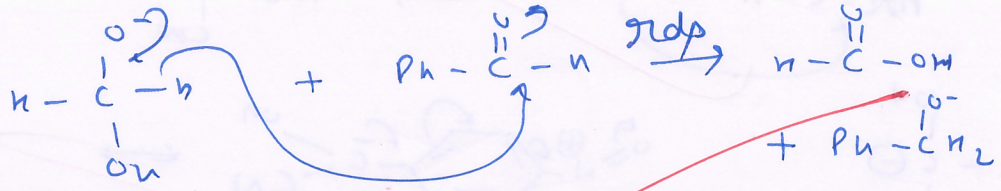
(ii) C_6H_5CHO is refluxed in the presence of NaOH and excess HCHO. Write the major aromatic product. **(5)**

Such reaction is a type of ~~Aldol~~ ~~Condn~~ Cannizzaro reaction, which occurs in non-enolizable carbonyls

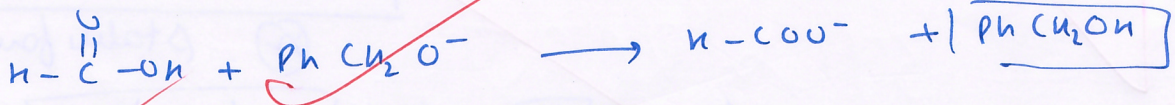
Step 1 $\boxed{Nu^{\ominus} \text{ attack}}$



Step 2 Hydride attacks at Ph–CHO



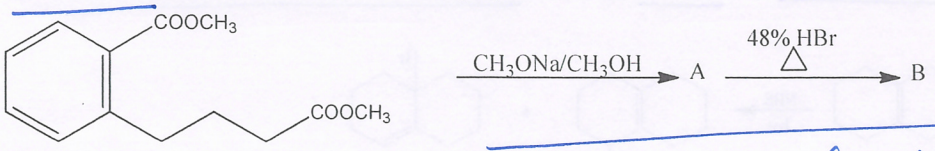
Step 3 H^+ exchange



Major aromatic product would be

$\boxed{PhCH_2OH}$

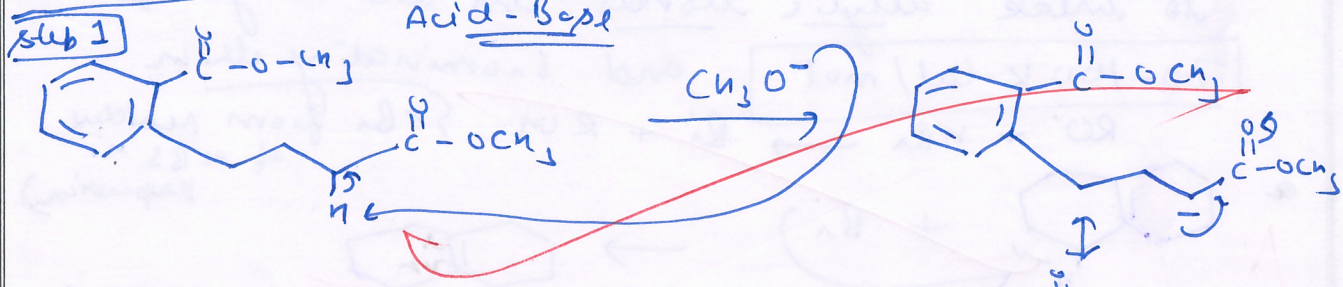
(b) In the following reactions, identify the products A and B. Explain the mechanism of formation of A: **(10)**



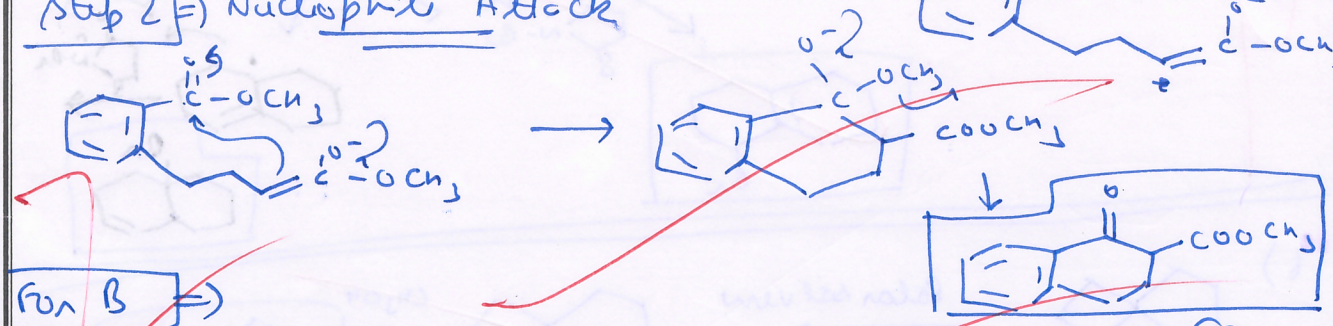
Such reaction is Dieckmann Condensation, helps in preparing rings of various sizes.

Mechanism of (A) formation

Step 1 Acid-Base

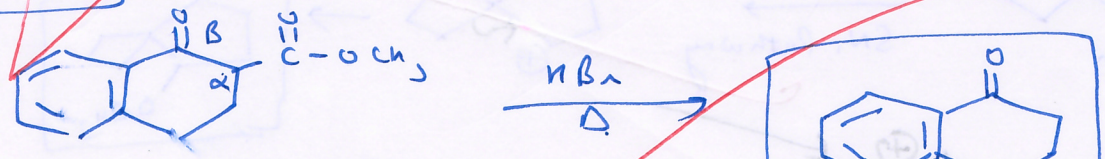


Step 2 ⇒ Nucleophile Attack



(A)

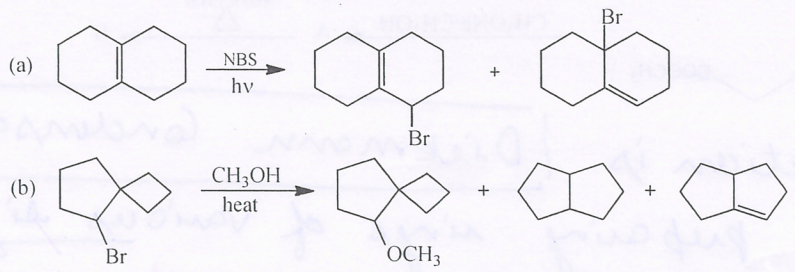
For B ⇒



β-Keto ester

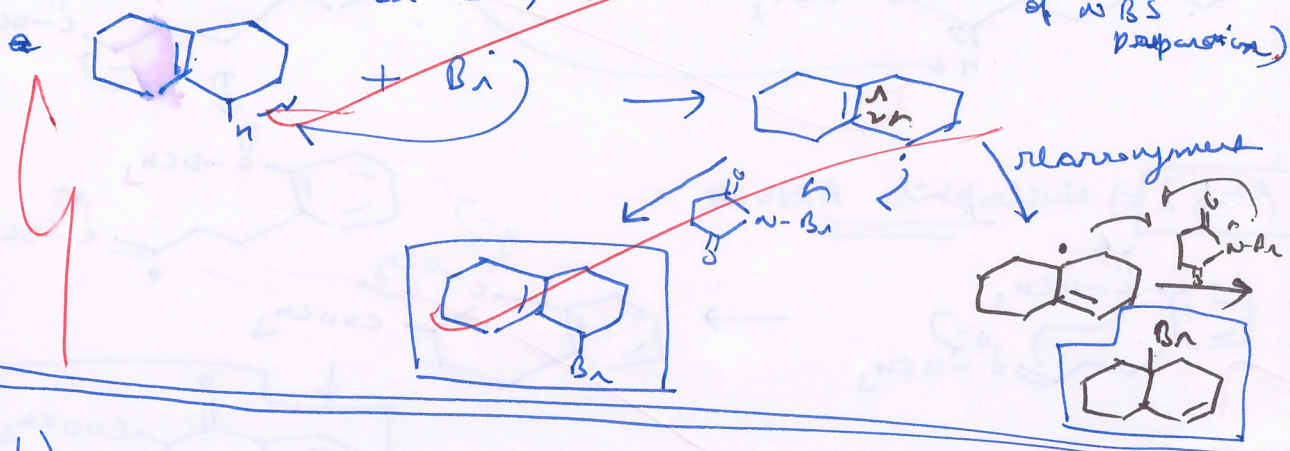
(B)

(c) Propose mechanism to account for the observed products in the following reactions. In some cases more products are formed, but you only need account for the ones shown here. **(10)**

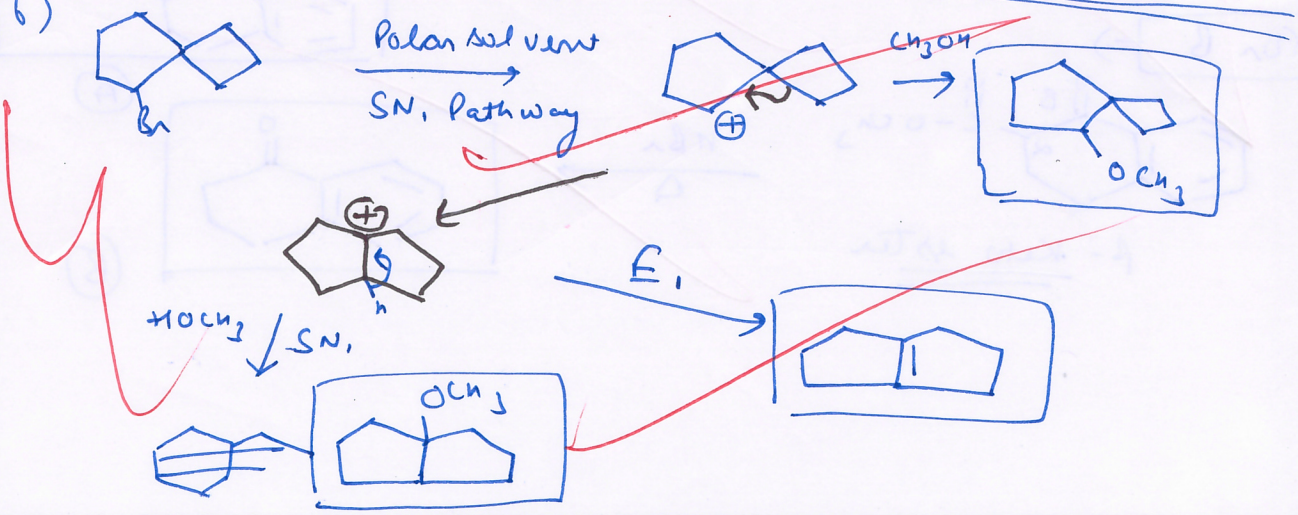


a) NBS is a brominating agent being able to break allylic bonds in the range of 70-100 K-Cal/mol and brominating them

$RO^{\cdot} + HBr \longrightarrow Br^{\cdot} + ROH$ (HBr from residue of NBS preparation)

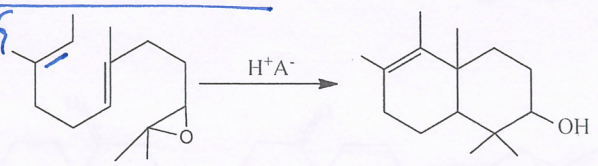


b)

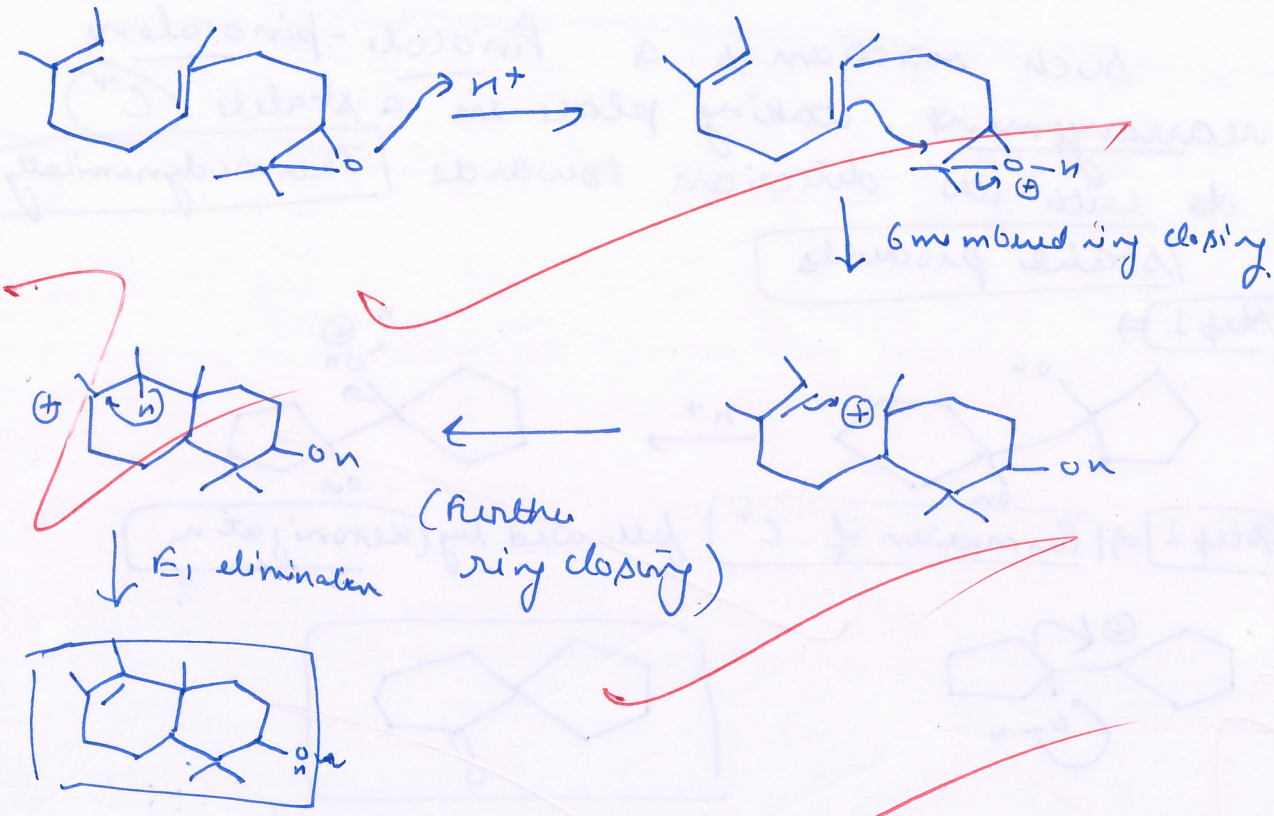


(d) Under the right conditions, following acid – catalyzed double cyclization proceeds in remarkable good yields. Propose a mechanism. Does this reaction resemble a biological process you have seen? **(10)**

missing ??

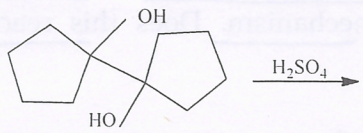


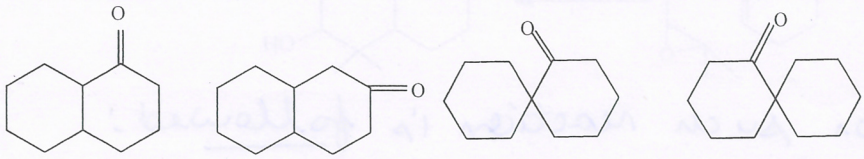
Mechanism for such reaction is followed:



Biological process ⇒ Vitamin formation (cholesterol formation)

(e) What is the product of the following reaction? Justify. **(10)**

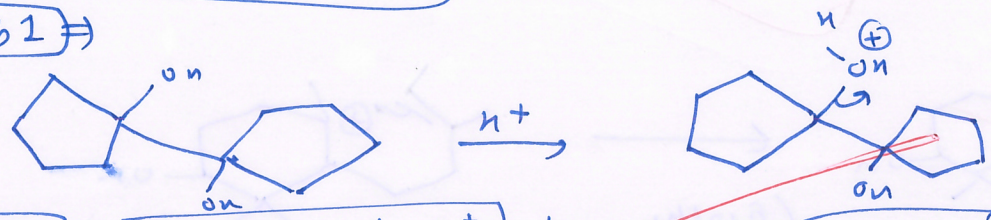




A. B. C. D.

Such reaction is a Pinacol-pinacolone rearrangement taking place in a stable C^+ ~~to~~ with the direction towards Thermodynamically stable products

Step 1 ⇒

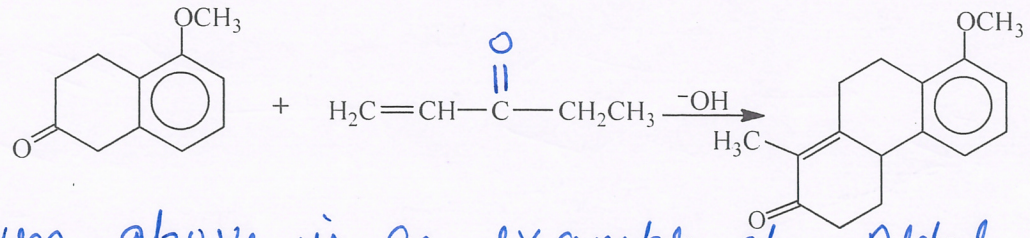


Step 2 ⇒ Formation of C^+ followed by Ketonization

~~One is~~ 5 membered ring is in space formation with 6-membered ring.

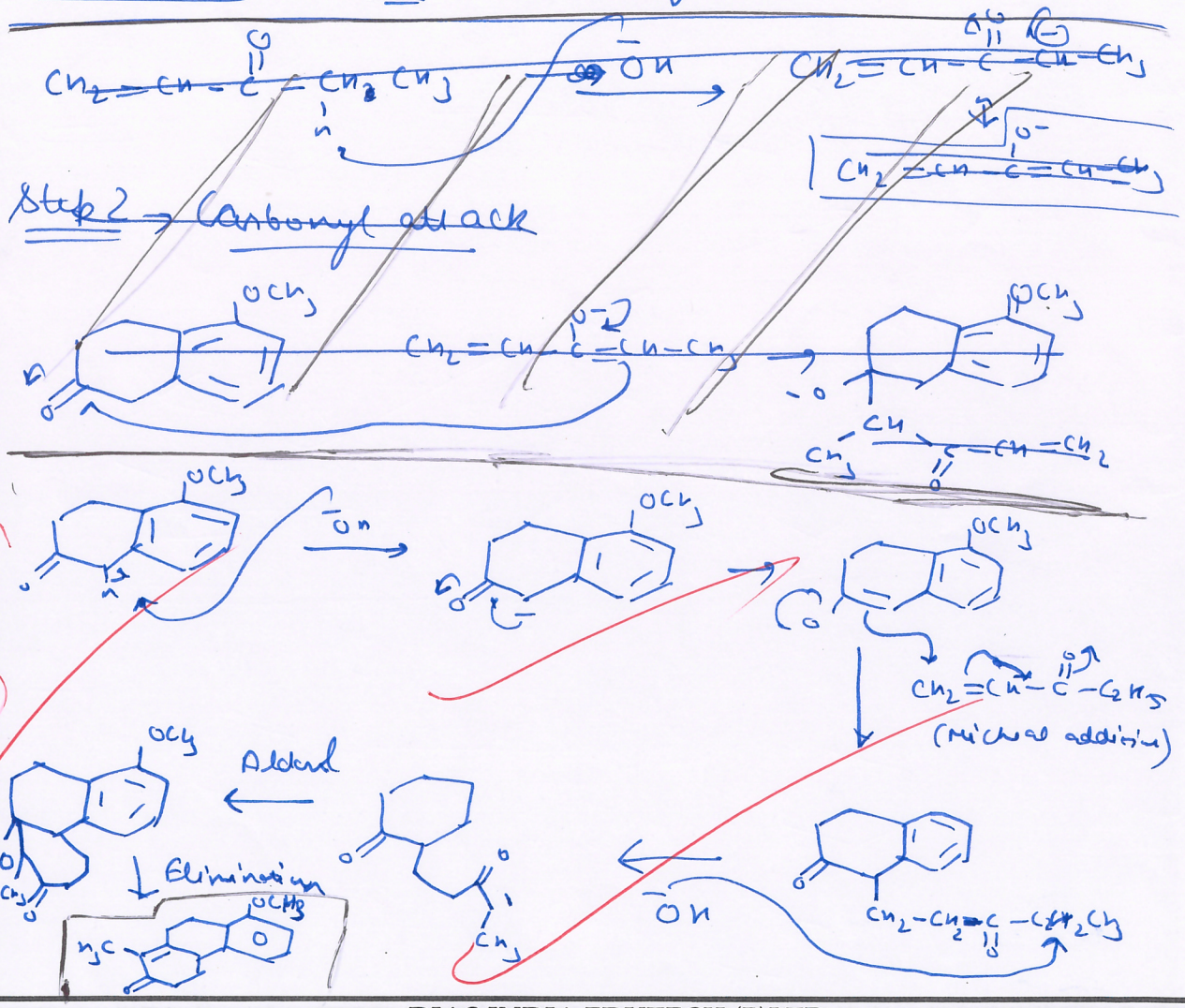
None of the above given matches the final product

3(a). Propose mechanism for the following reactions. **(10)**

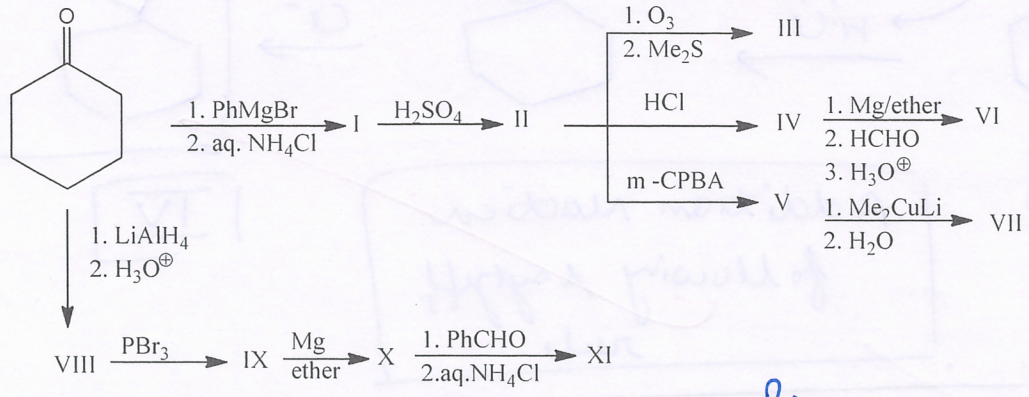


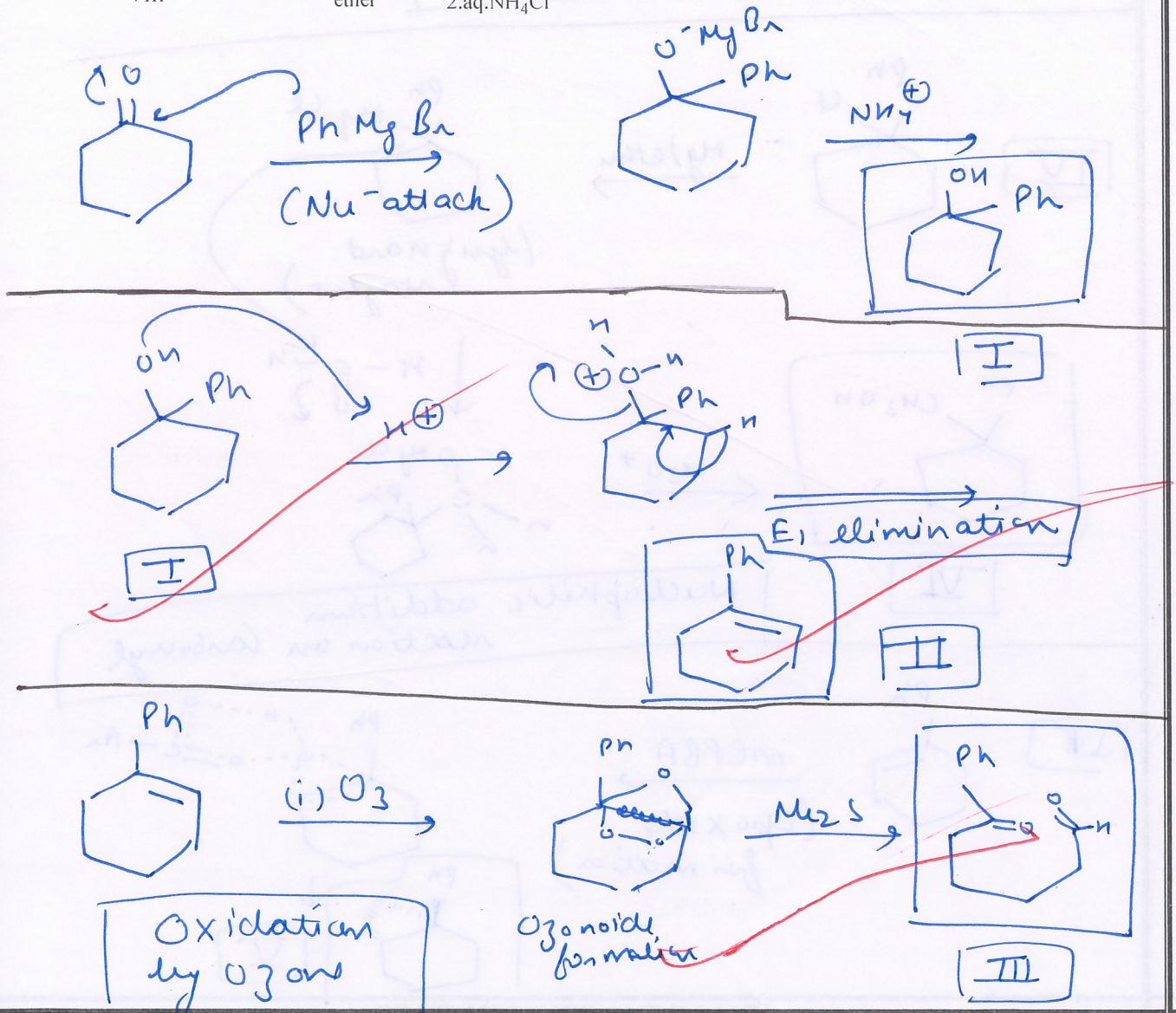
Given above is an example of Aldol condensation followed by heating to get α-β-unsaturated ketone.

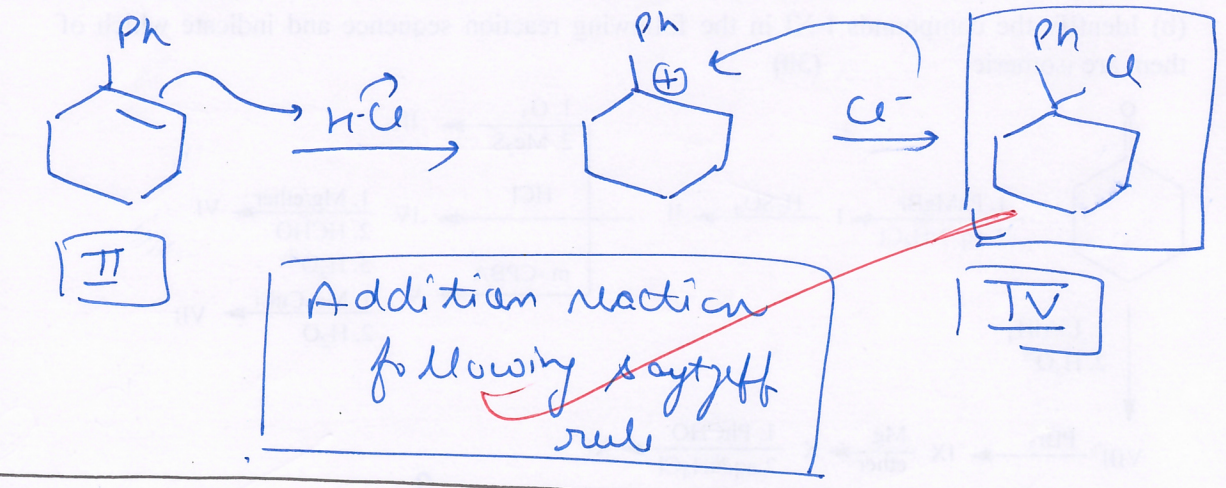
Mechanism ⇒ Step 1 – Enolization

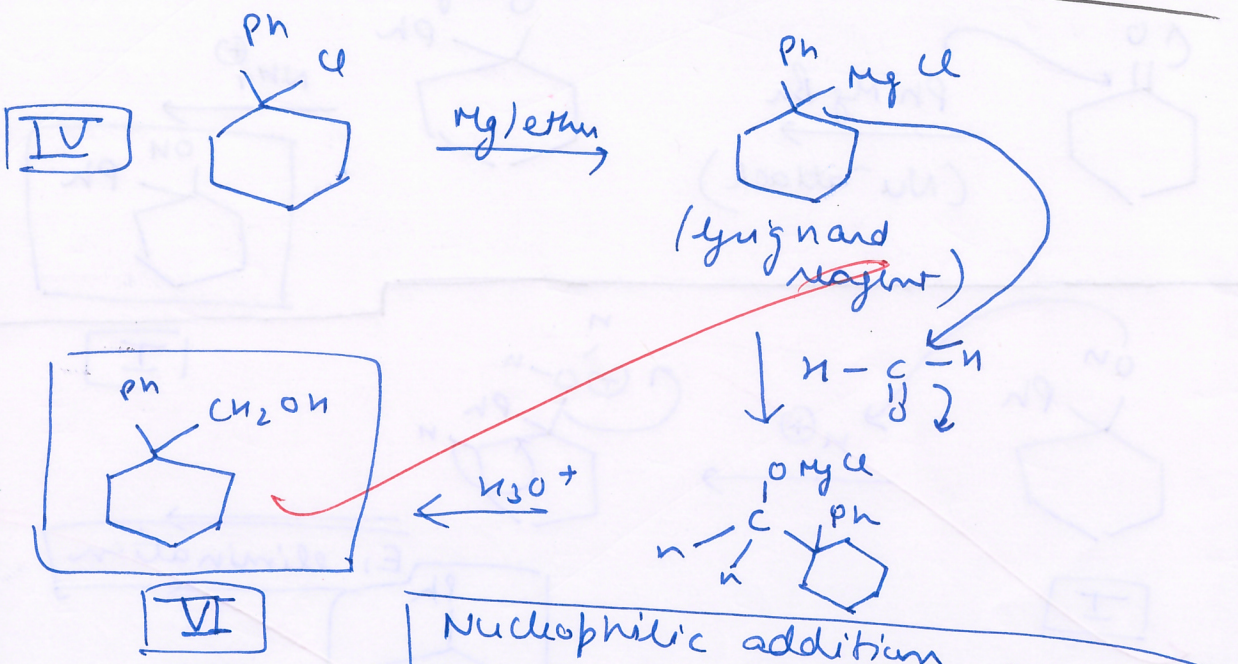


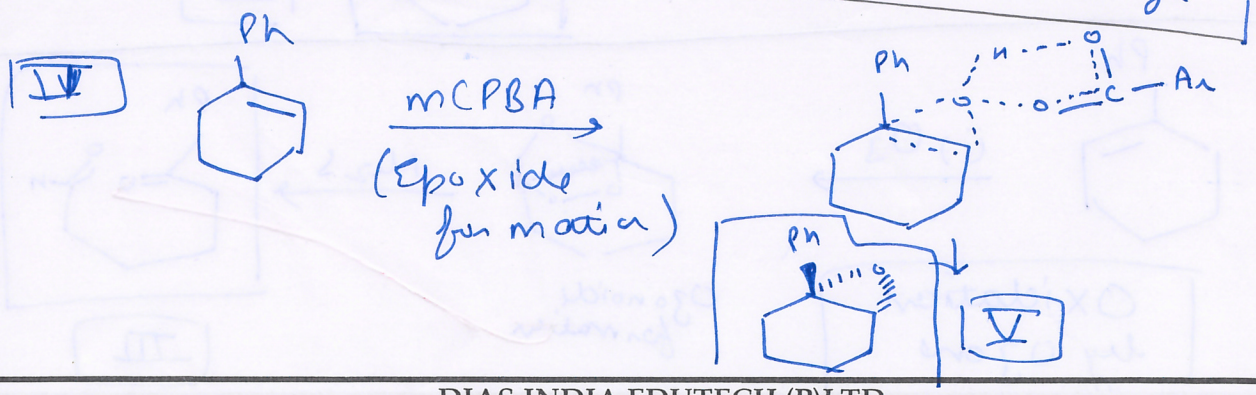
(b) Identify the compounds I-XI in the following reaction sequence and indicate which of them are isomeric: **(30)**

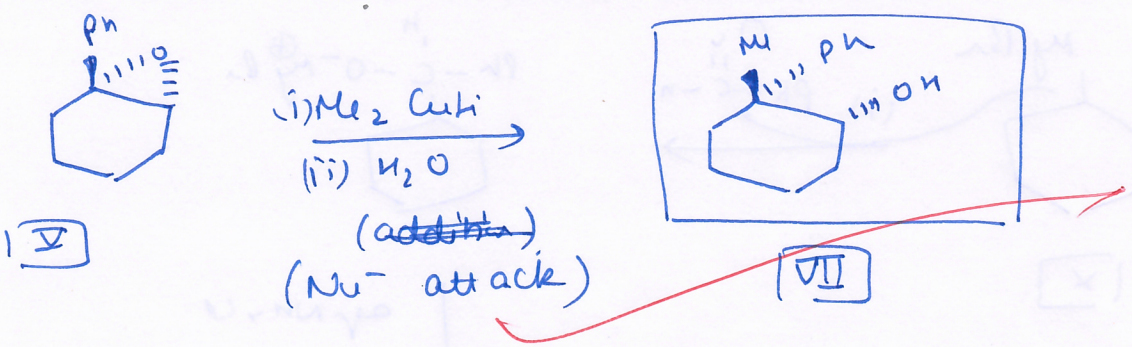


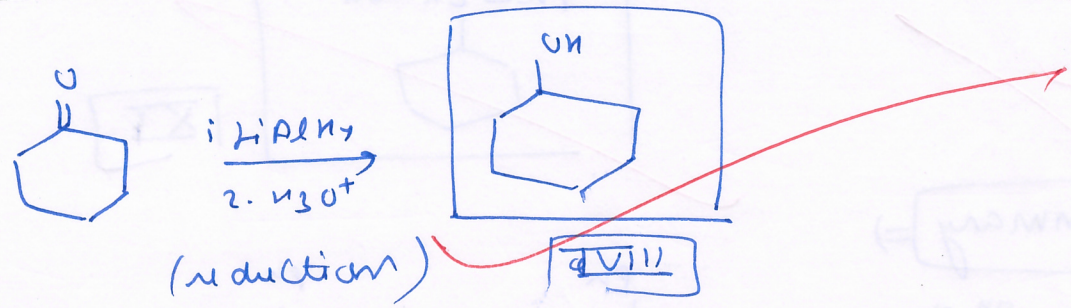


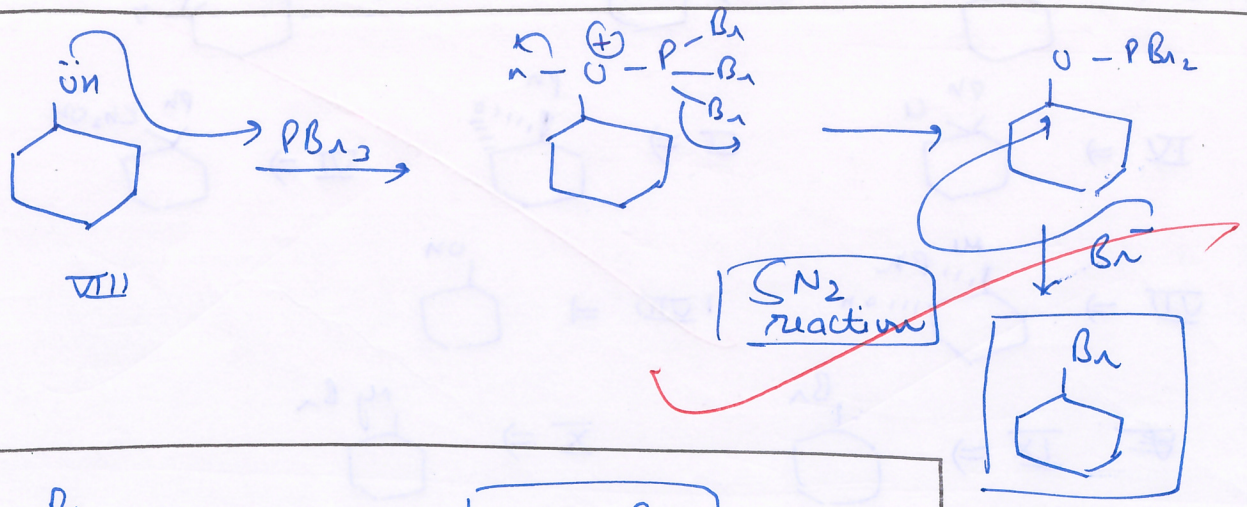

Ph
H-Cl
Ph
Cl⁻
Ph
Cl
II
IV
Addition reaction following Saytzeff rule

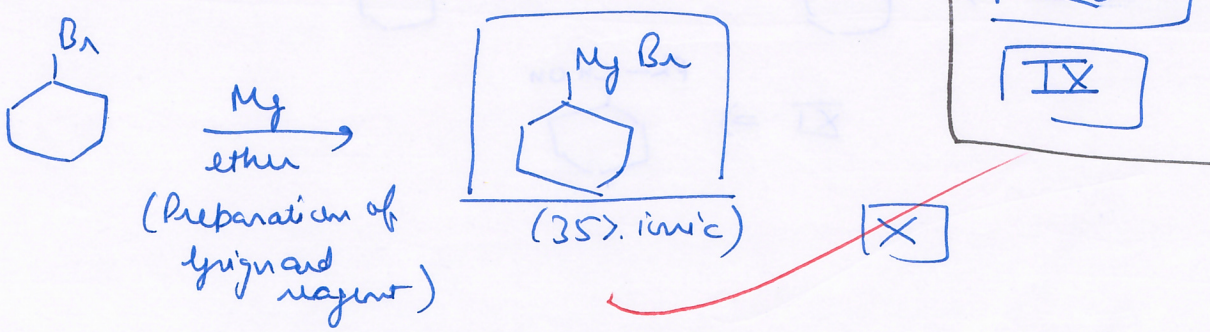

IV
Ph
Cl
Mg/ether
Ph
MgCl
(Grignard reagent)
H-C=O-H
OMgCl
Ph
H
H
H3O+
Ph
CH2OH
VI
Nucleophilic addition reaction on Carbonyl

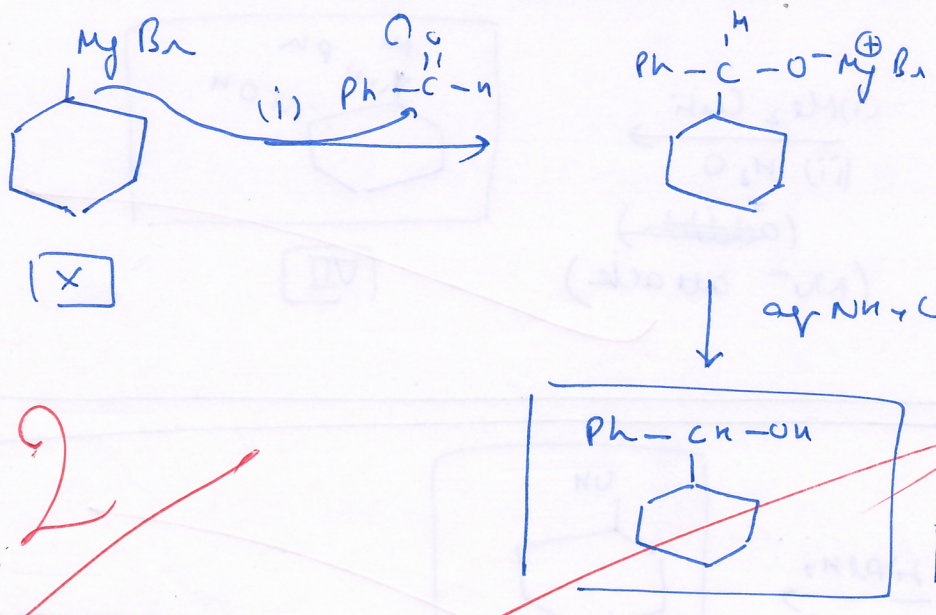

IV
Ph
mCPBA
(Epoxide formation)
Ph
Ph
V


Ph
O
V
(i) Me_2CuLi
(ii) H_2O
(addition)
(Nu^- attack)
Me
Ph
OH
VII


O
i. $LiAlH_4$
2. H_3O^+
(reduction)
OH
VIII

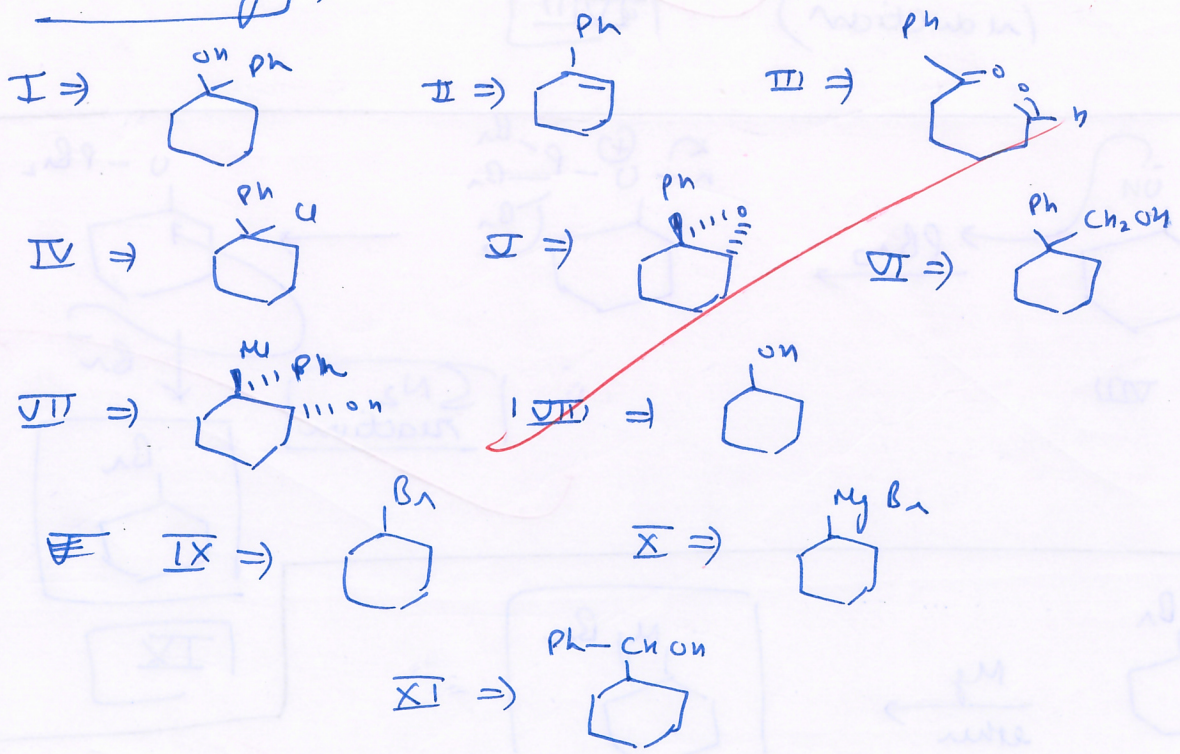

OH
VIII
PBr_3
Br^-
O – P – Br
Br
Br
O – PBr_2
SN_2 reaction
Br^-
Br
IX


Br
Mg
ether
(Preparation of Grignard reagent)
Mg Br
(35% ionic)
X


MgBr
(i)
Ph–C–H
O
H
Ph–C–O⁻ Mg⁺ Br
X
aq NH4Cl
Ph–CH–OH
XI

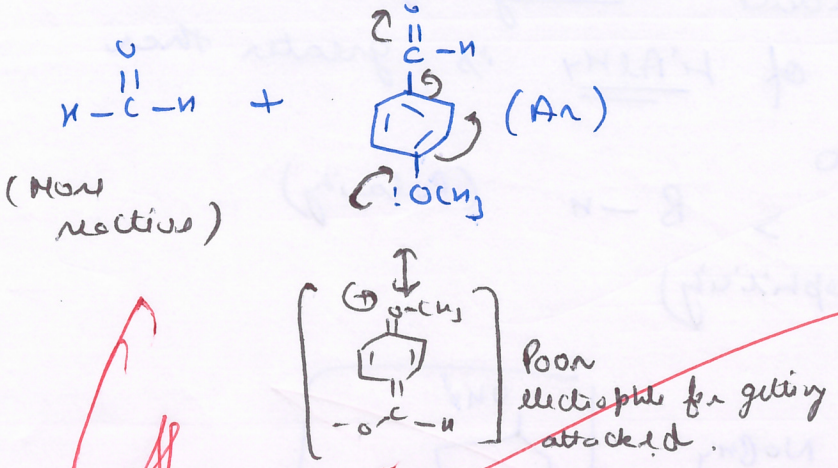
22

Summary ⇒

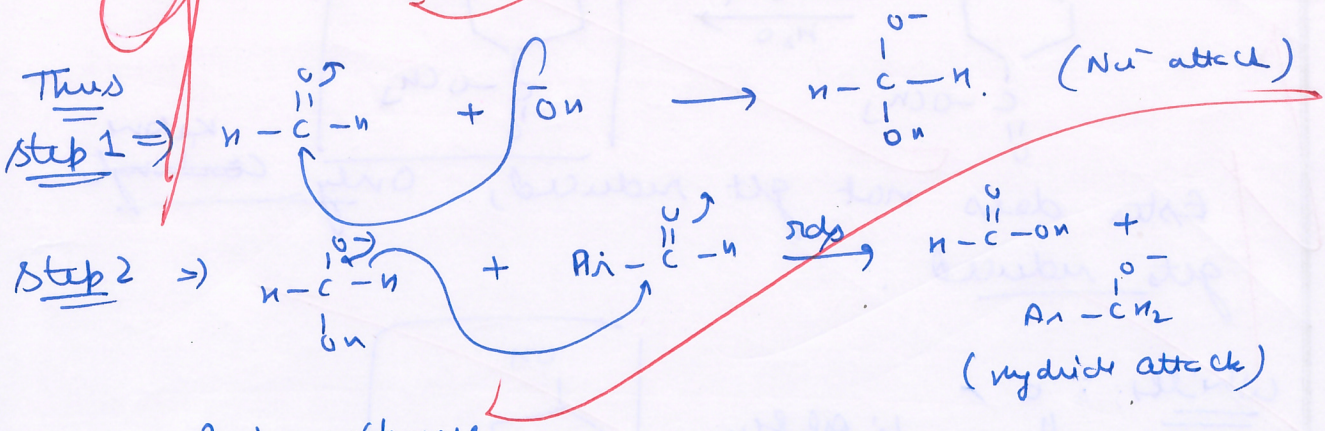

I ⇒
OH Ph
II ⇒
Ph
III ⇒
Ph
IV ⇒
Ph Cl
V ⇒
Ph
VI ⇒
Ph CH2OH
VII ⇒
Mg Ph OH
VIII ⇒
OH
IX ⇒
Br
X ⇒
MgBr
XI ⇒
Ph–CH OH

(c) A mixture of formaldehyde and p-methoxy benzaldehyde is treated with Conc. KOH. Write the products of reaction. (5)

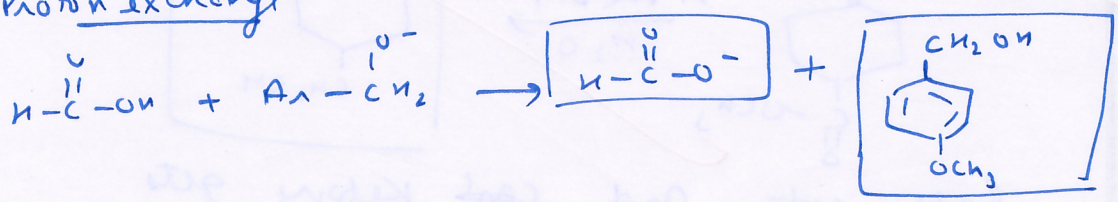
Such reaction is cannizaro reaction, consisting of non-enolizable carbonyls leading to disproportionation reaction.



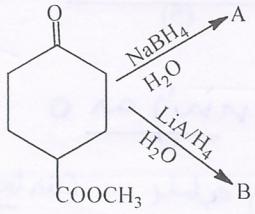
Thus



Step 3 ⇒ Proton exchange



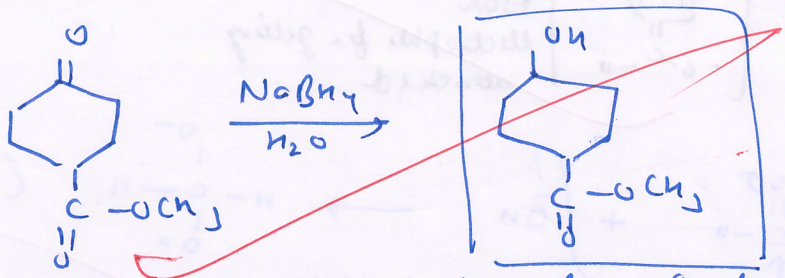
(d) Identity A and B and discuss the selectivity of the reagents **(5)**



NaBH4 and LiAlH4 are two important reagents to reduce carbonyl groups.
Reducing ability of LiAlH4 is greater than NaBH4 due to

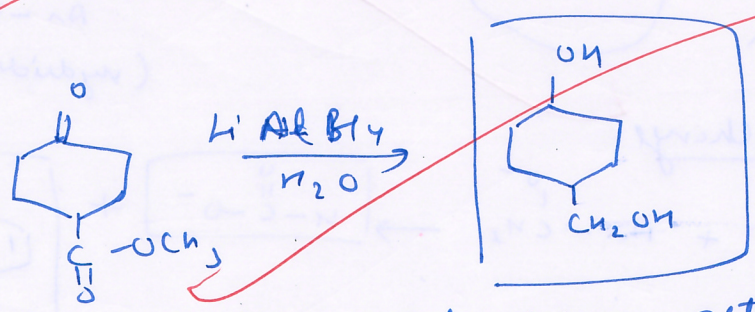
Al — H > B — H (Polarity)
⇓
(More nucleophilicity)

Thus



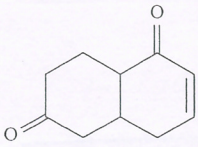
Ester does not get reduced, only ketone carbonyl gets reduced.

While

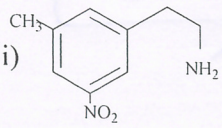


Both ester and ~~cand~~ ketone gets reduced due to higher nucleophilicity of Hydride in LAH.

4(a) Identify the product(x) in the following reaction and write the name of the reaction involved : **(15)**

(i) 

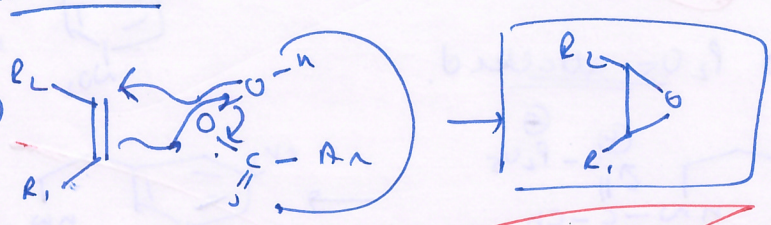
$\xrightarrow{\text{mCPBA}}$ (X)

(ii) 

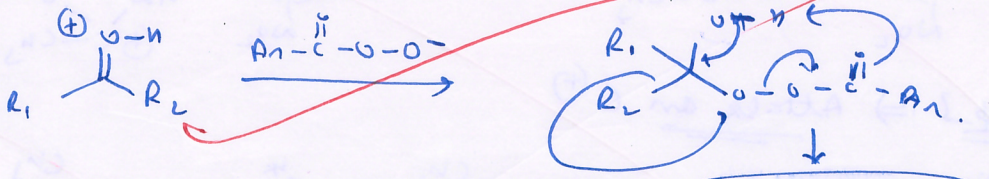
$\xrightarrow[\text{(3) Pd/C, } 100\,^{0}C]{\text{(1) } CH_3COCl,\ \text{(2) } P_2O_5}$ (X)

(i) mCPBA plays two functions, epoxide formation on alkene and Bayer villiger oxidation in carbonyles.

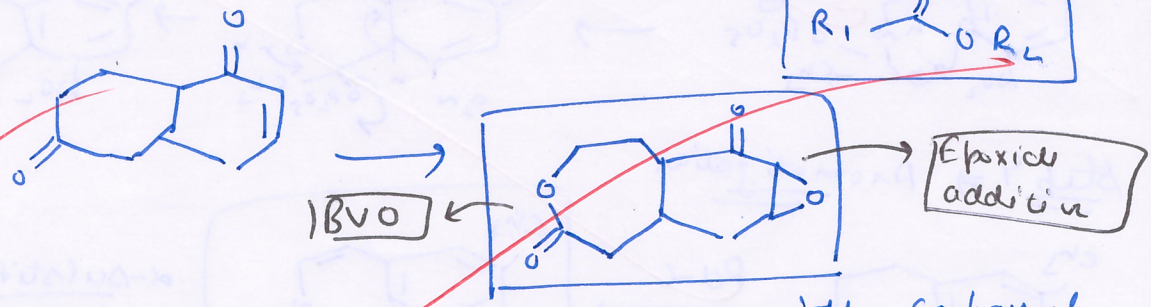
Mechanisms ⇒ (Addition)



BVO ⇒

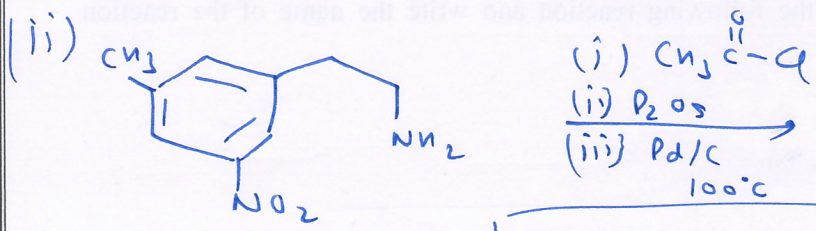


In



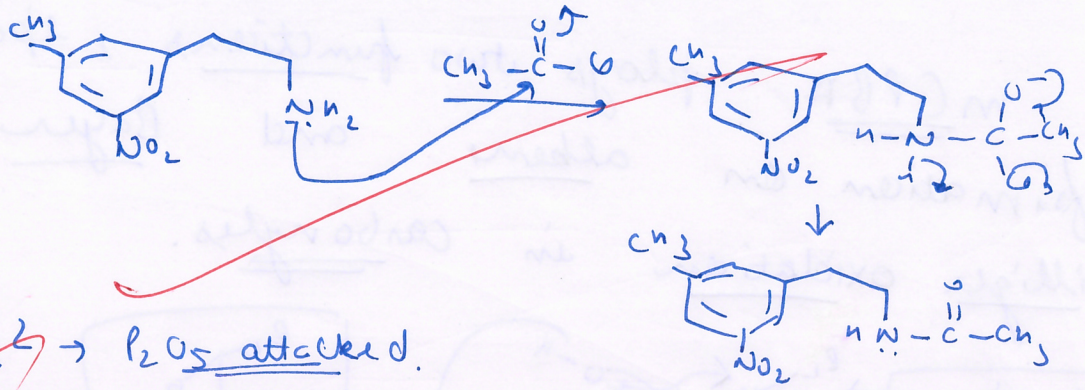
Double bond in conjugation with carbonyl do not undergo BVO rearrangement while other carbonyl do so.

(ii)

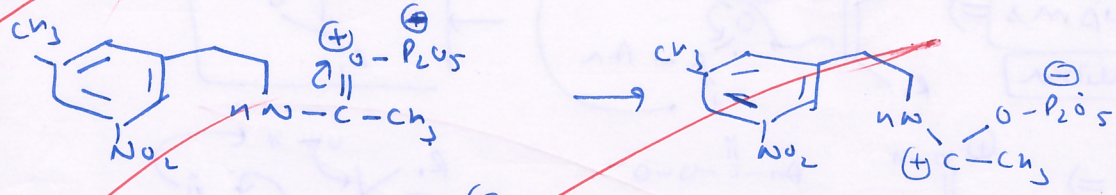


The reaction is **Bischler Napieralski reaction**

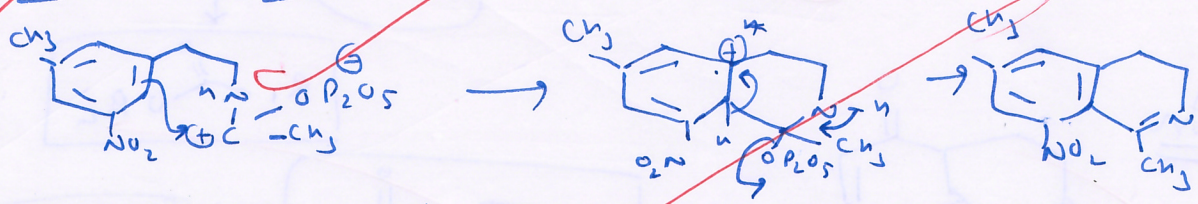
Step 1 : Nucleophile Attack



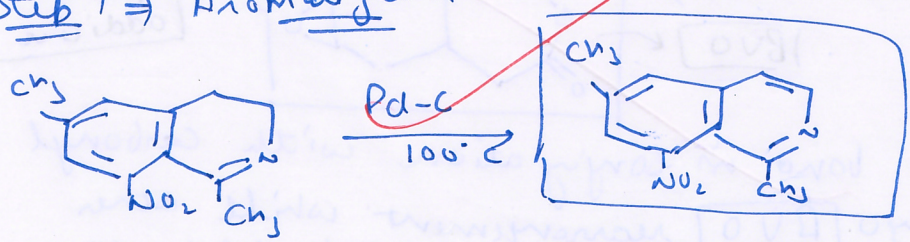
Step 2 → P_2O_5 attacked.



Step 3 ⇒ Attack on $C^{\oplus}$

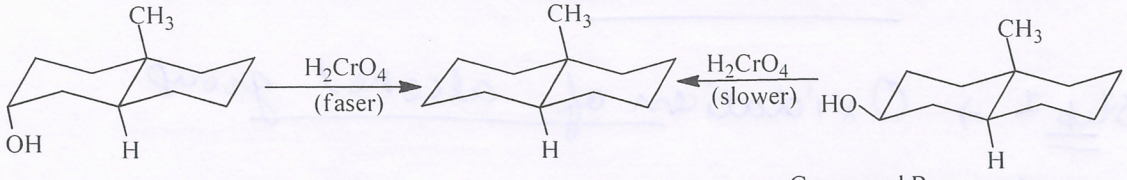


Step 4 ⇒ Aromatization



α-substituted isoquinoline

(b) Chromic acid oxidation of an alcohol occurs in two steps: formation of the chromate ester, followed by an elimination of H^+ and chromium. Which step do you expect to be rate-limiting? Careful kinetic studies have shown that compound A undergoes chromic acid oxidation over 10 times as fast as Compound B. Explain this large difference in rates. (10)

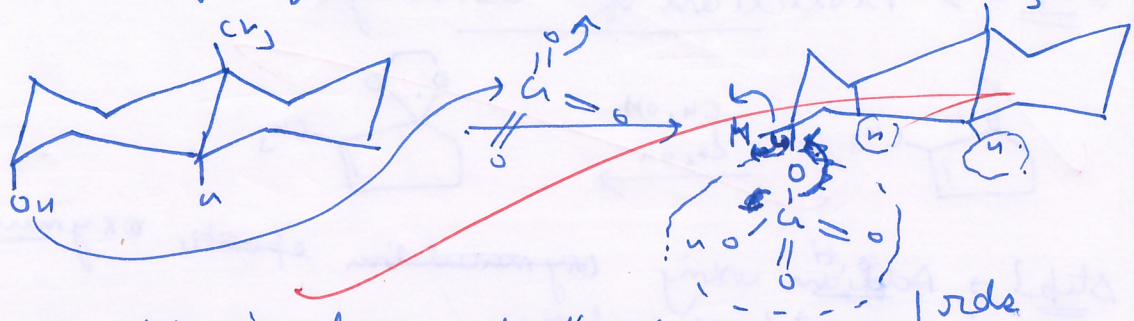


Compound B

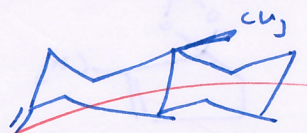
The rate is dependendent on rds step.

The rds step in ~~Chr~~ oxidation by chromic acid is removal of ~~hydride step~~ Hydroxy hydrid

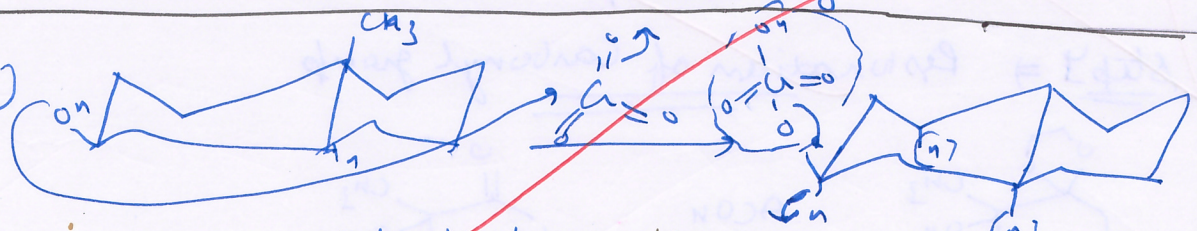
(A)



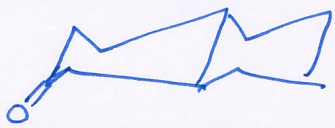
rds step involves reduction (relief) in strain arising due to steric hindrance from axial hydrogens



(B)

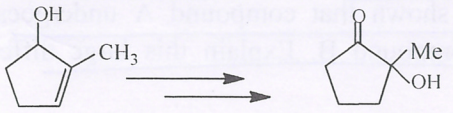


No such relief in strain in rds

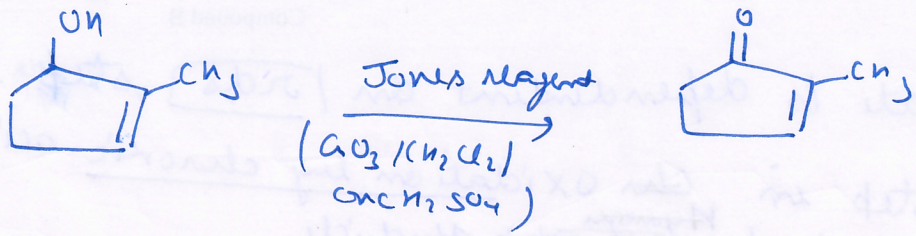


Thus (A) performs oxidation at a faster rate

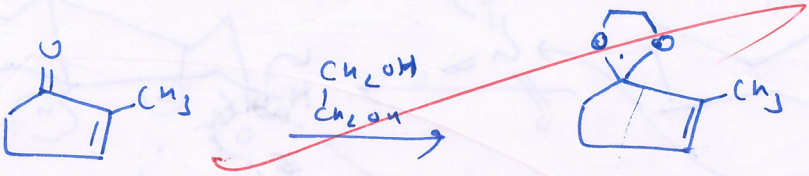
(c) Suggest a syntheses route for the following conversion. **(10)**



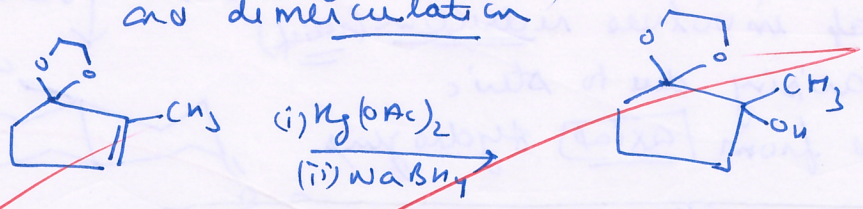
Step 1 ⇒ Oxidation of alcohol group



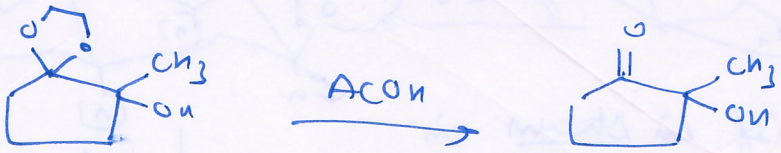
Step 2 ⇒ Protection of Carbonyl



Step 3 → Addition using ~~oxymercuration~~ ~~epoxide~~ oxymercuration and demercuration

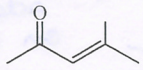
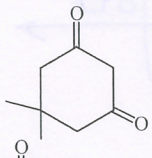


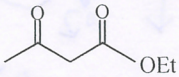
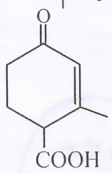
Step 4 ⇒ Restoration of Carbonyl group



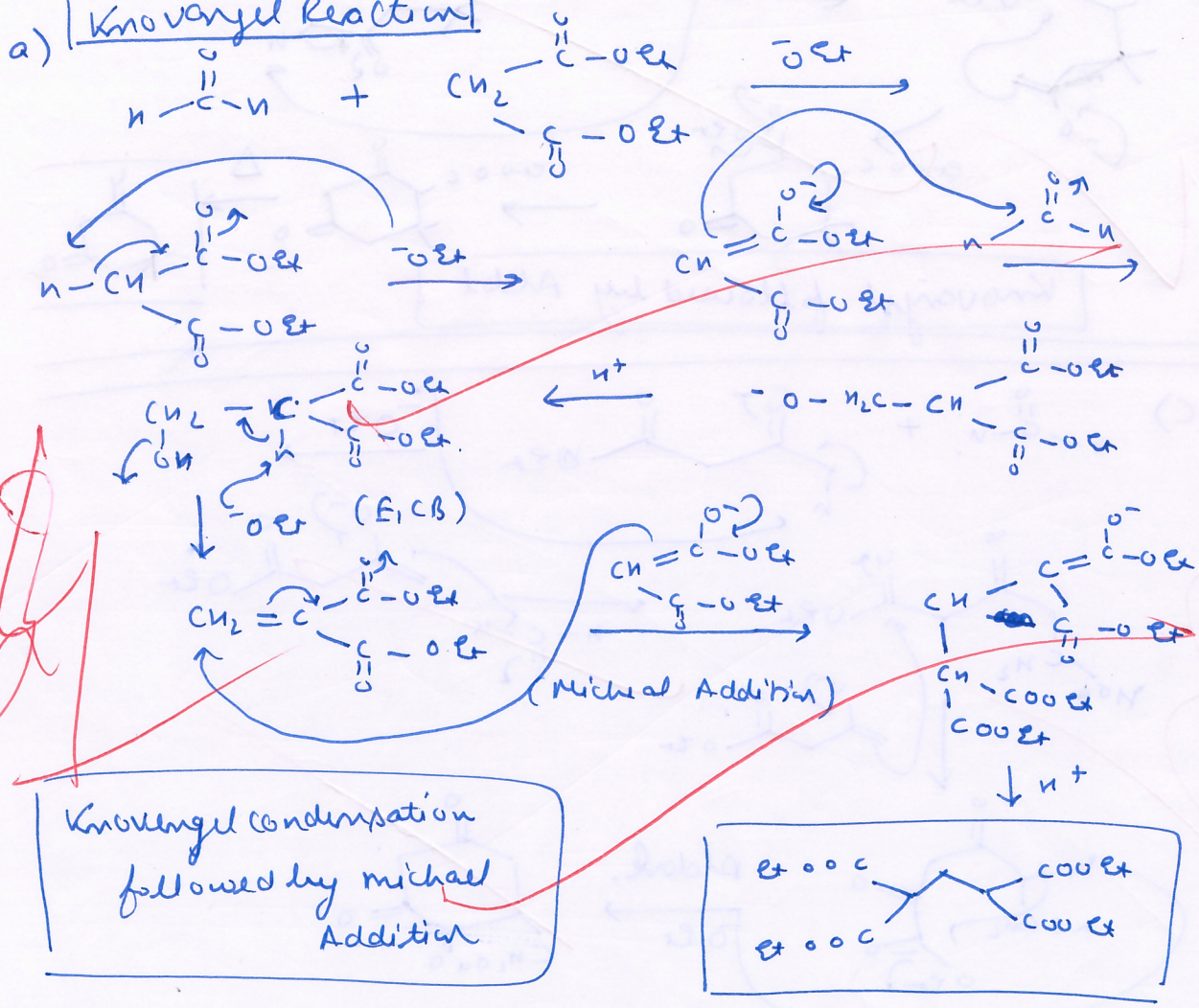
(d) Show reaction sequence (not detailed mechanism) that explain these transformations: **(15)**

(a) $CH_2O + 2CH_2(COOEt)_2 \xrightarrow[(2)\ H^+]{(1)\ NaOEt}$ EtOOC, COOEt, EtOOC, COOEt

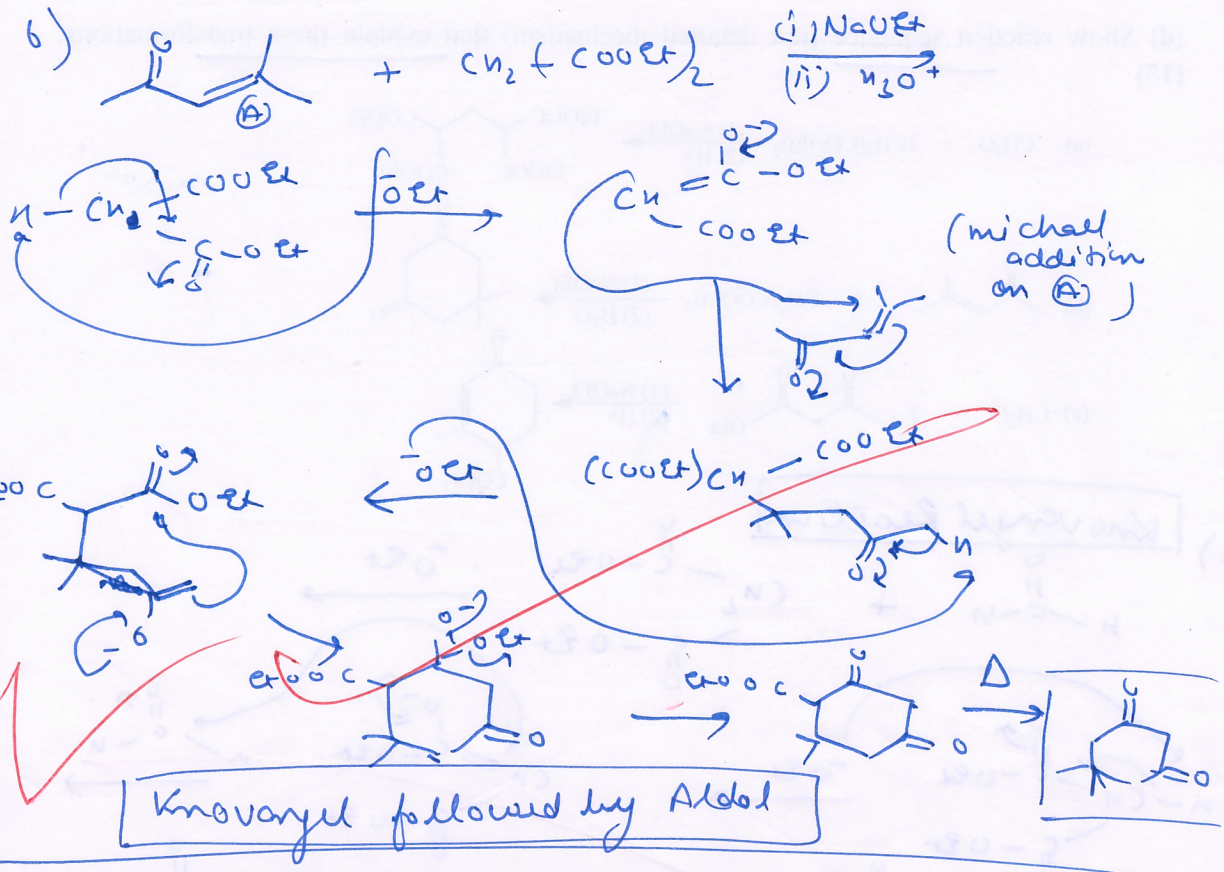
(b)  + $CH_2(COOEt)_2 \xrightarrow[(2)\ H_3O]{(1)\ NaOEt}$ 

(c) CH_2O + 2  $\xrightarrow[(2)\ H^+]{(1)\ NaOEt}$ 

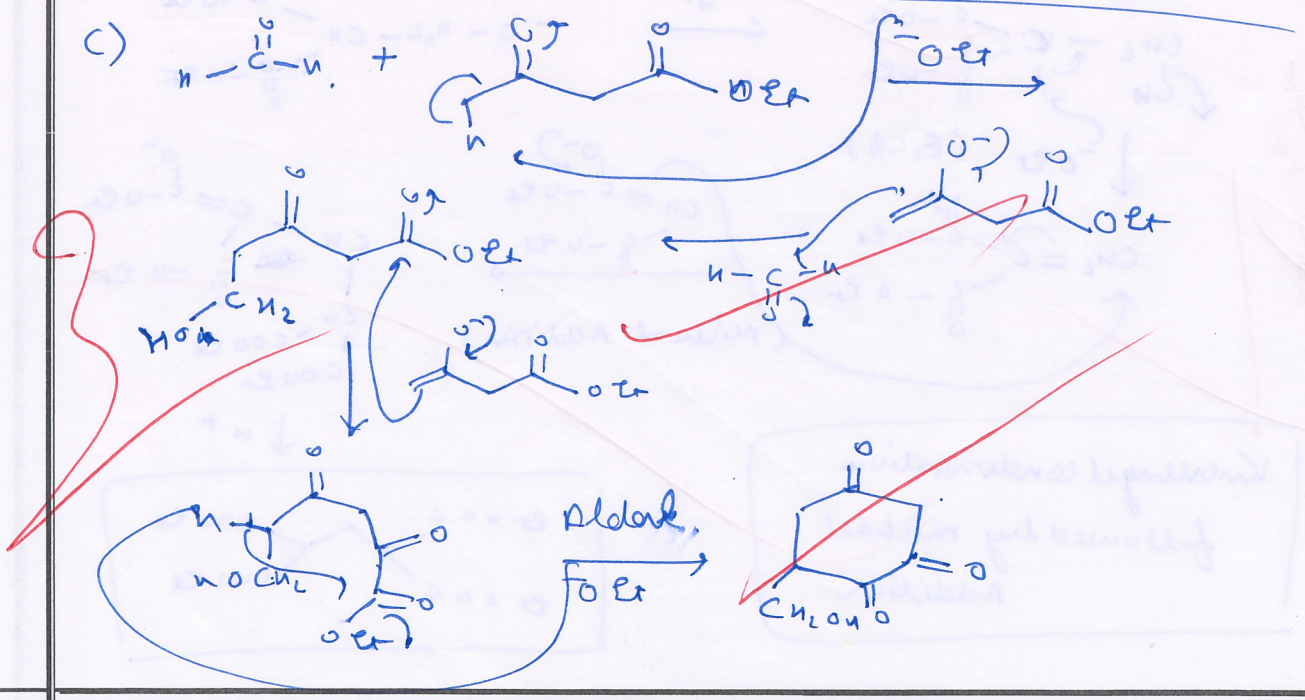
a) Knovangel Reaction



b)

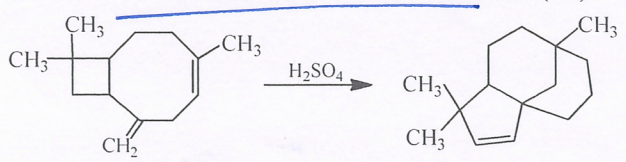

(i) NaOEt
(ii) H3O+
(michael addition on A)
Knovagel followed by Aldol

c)

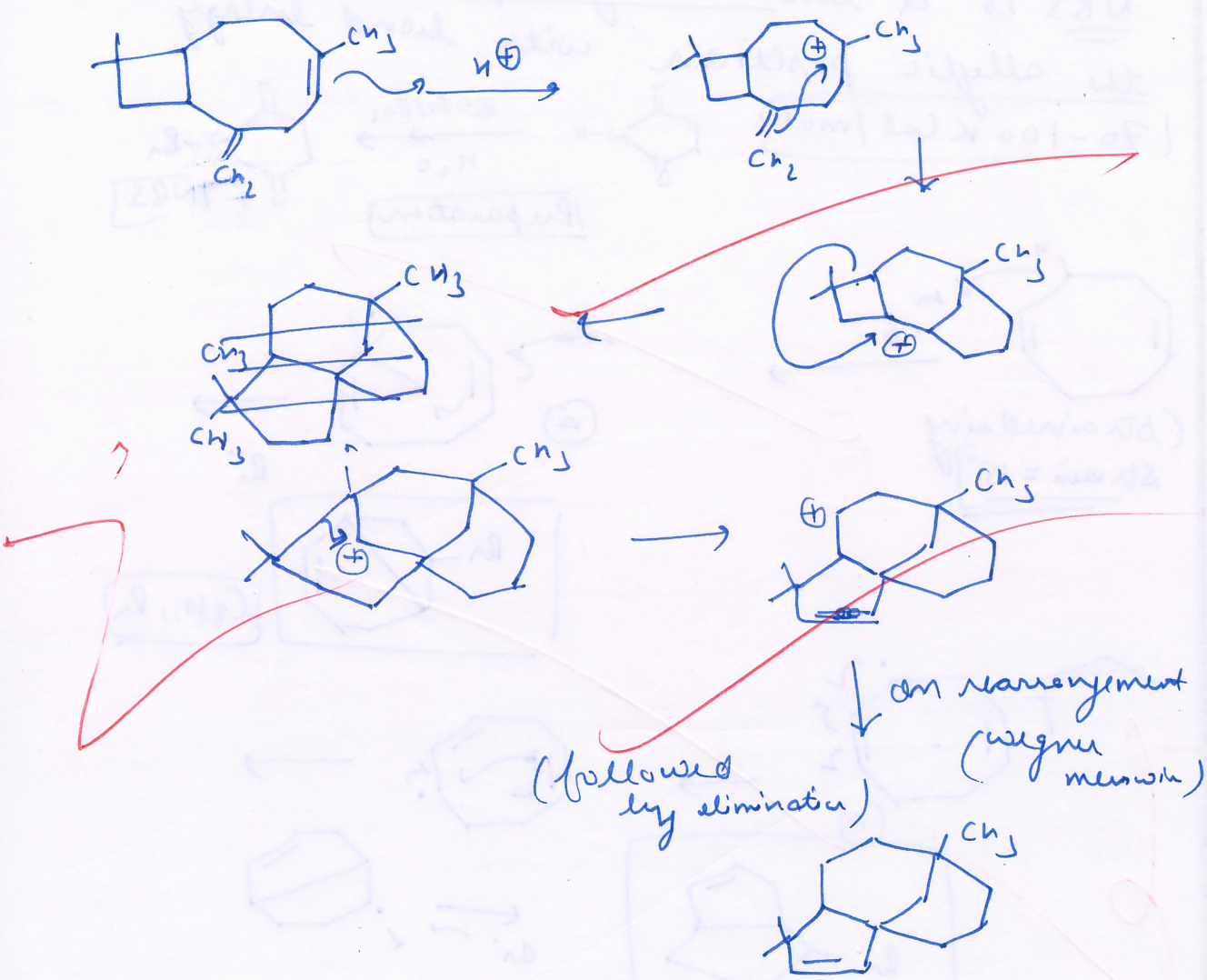

Aldol.

Section- B

5(a) The oil caryophyllene is a natural constituent of cloves. On treatment with sulfuric acid. It isomerizes to a substance called clovene. (10)



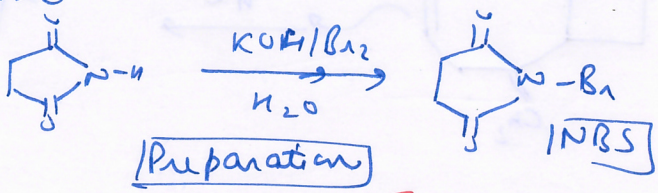
Caryophyllene Clovene **(10)**



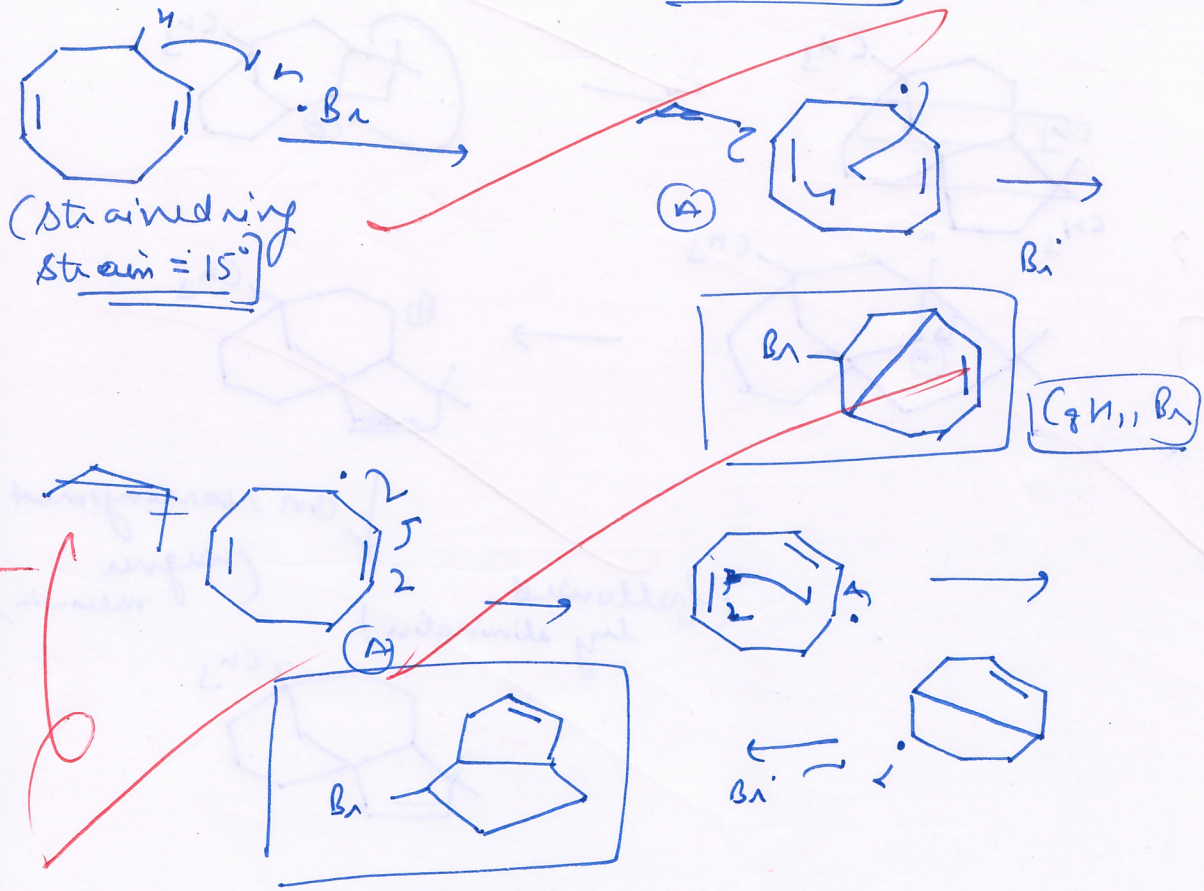
(b) Bromination of 1,5-cyclooctadiene with N-Bromo succinimide (NBS) gives a mixture of two constitutional isomers of $C_8H_{11}Br$. Suggest reasonable structures for these two isomers. **(10)**

1,5-Cyclooctadiene

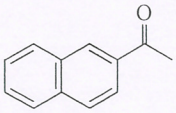
NBS is a brominating agent that brominates the allylic position with bond energy 70-100 KCal/mol



Preparation

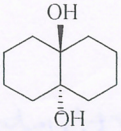


(c) Identify the major product (X) formed in the following reactions: **(10)**

(i) 

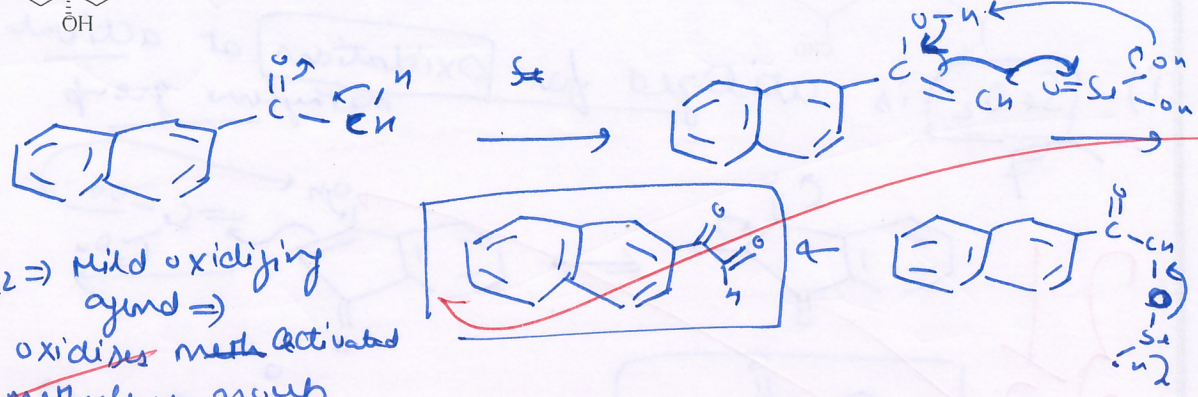
$\xrightarrow{SeO_2}$ (X)

(ii) 
$\xrightarrow[\text{2) hv/heat}]{\text{1) NBS}}$ (X)

(iii) 

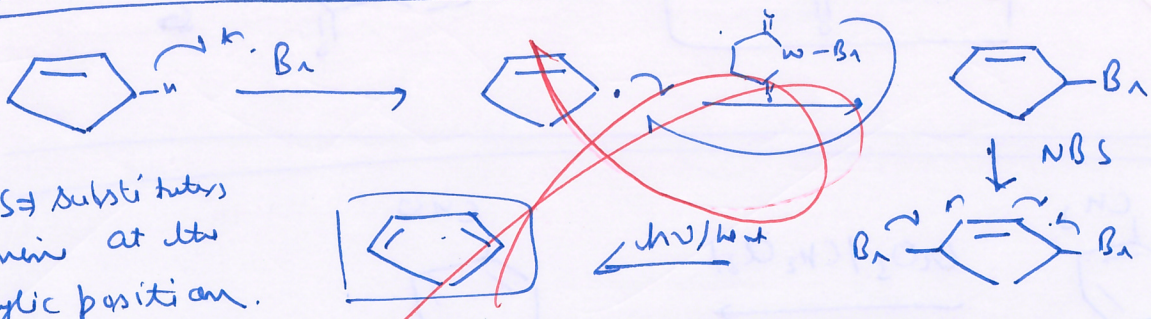
$\xrightarrow{Pb(OAc)_4}$ (X)

(i)



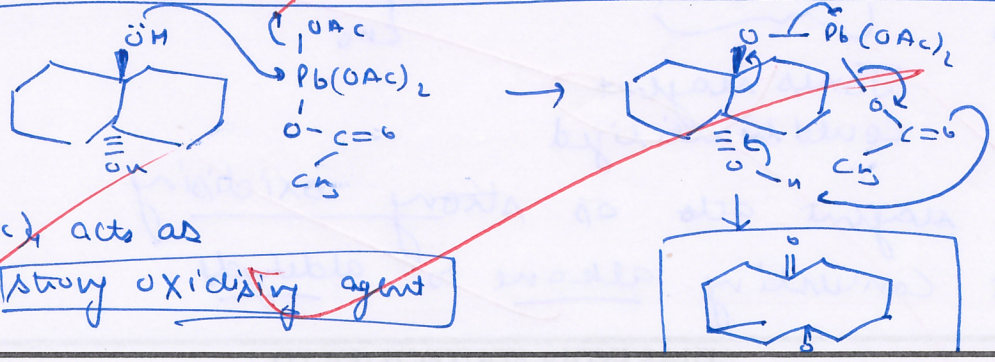
$SeO_2 \Rightarrow$ Mild oxidizing agent $\Rightarrow$ oxidises ~~meth~~ activated methylene group.

(ii)



NBS $\Rightarrow$ substitutes Bromine at the allylic position.

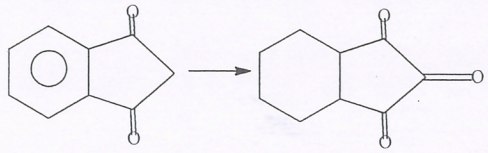
(iii)



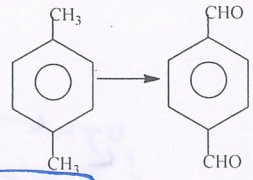
$Pb(OAc)_4$ acts as $\boxed{\text{strong oxidizing agent}}$

(d) Write the reagents required for the following conversions. **(10)**

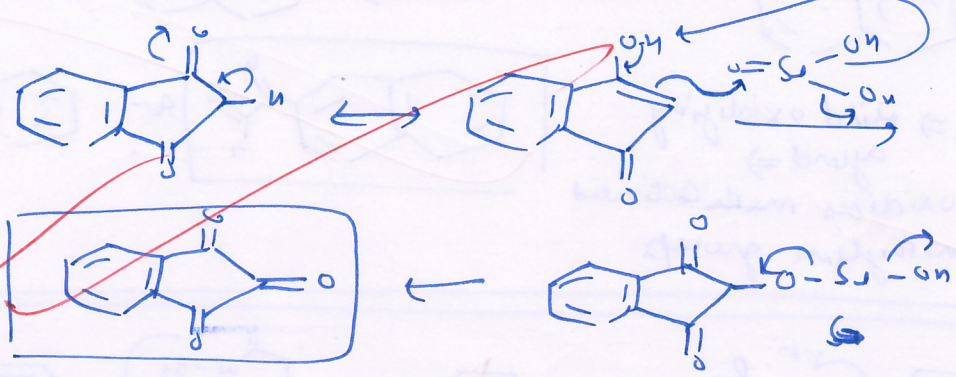
i)



ii)

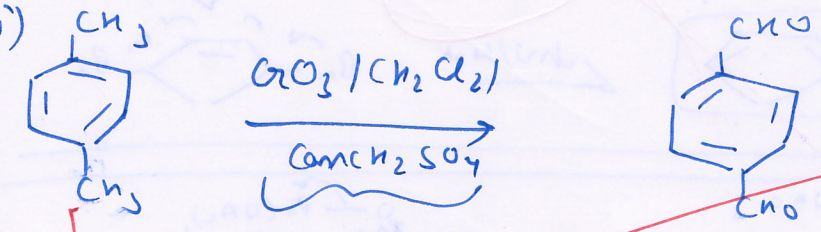


i) SeO_2 is utilized for oxidation at activated methylene group



3½

ii)

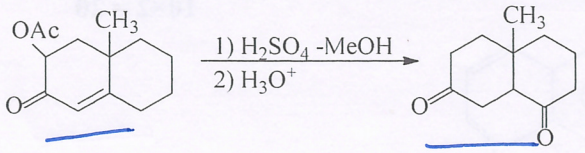


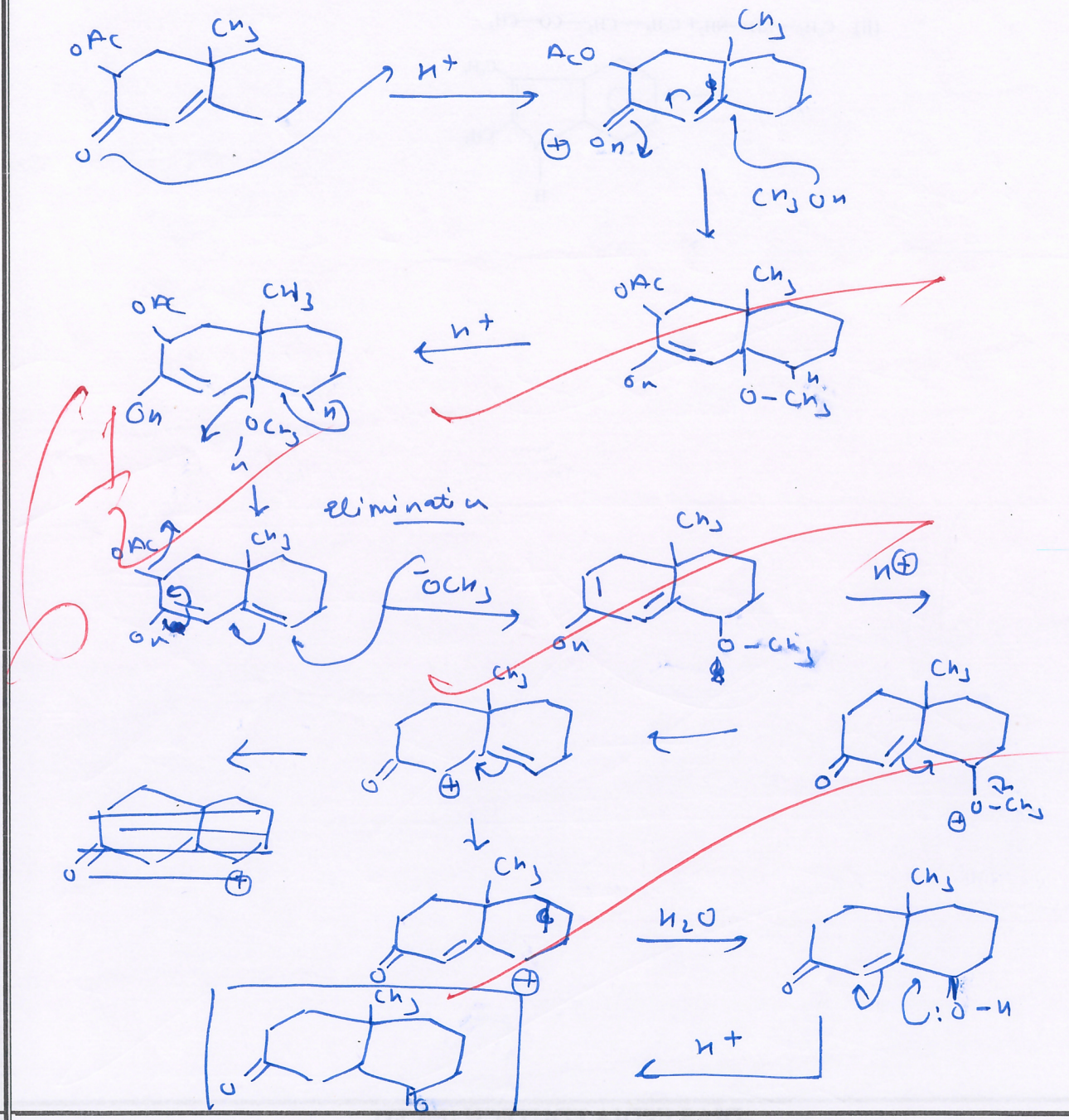
Jones reagent could be utilized

Jones reagent acts as strong oxidising agent converting alkene to aldehyde

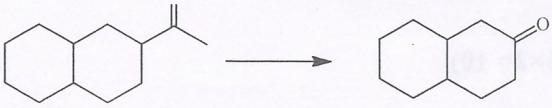
2½

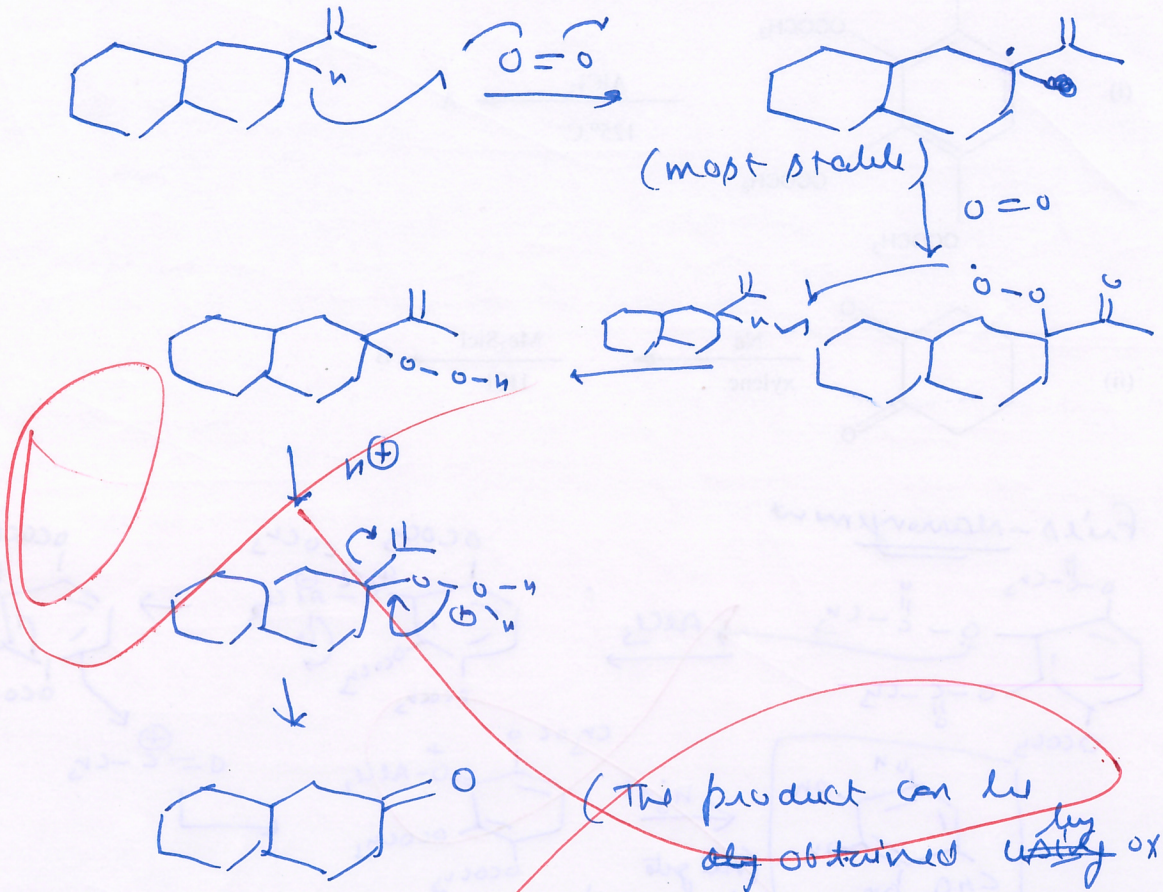
(e) Write down mechanism for below conversion. **(10)**





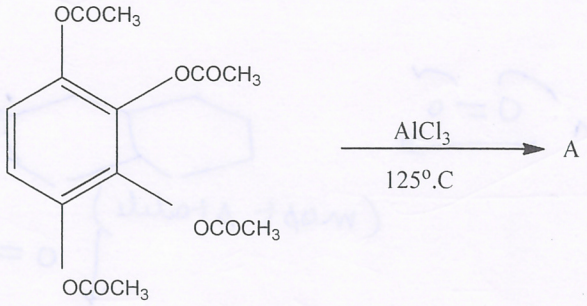
8(a) Suggest a suitable methodology for the following transformation. **(10)**

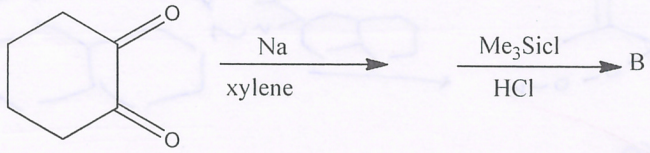




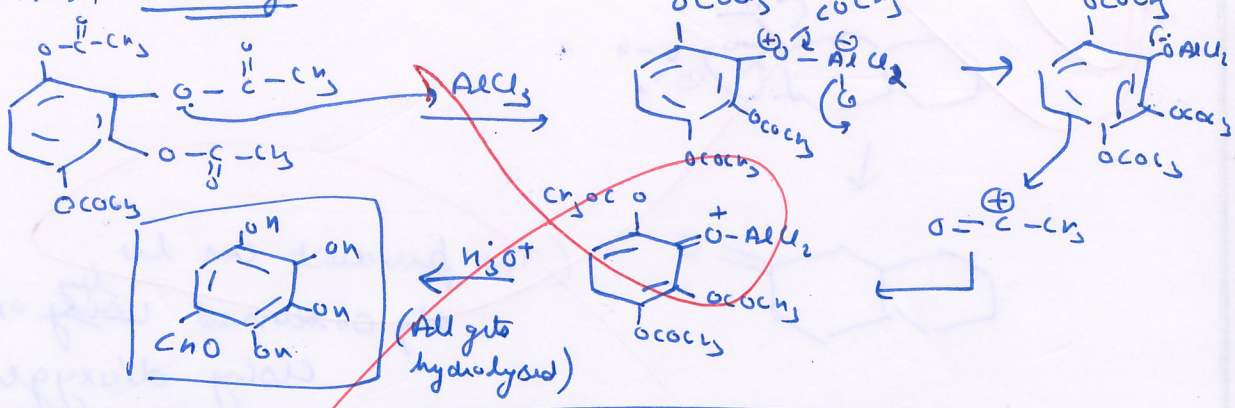
(The product can be ~~only~~ obtained ~~using~~ by oxidation using dioxygen and acid)

(b) Write down product give mechanism. **(5×2= 10)**

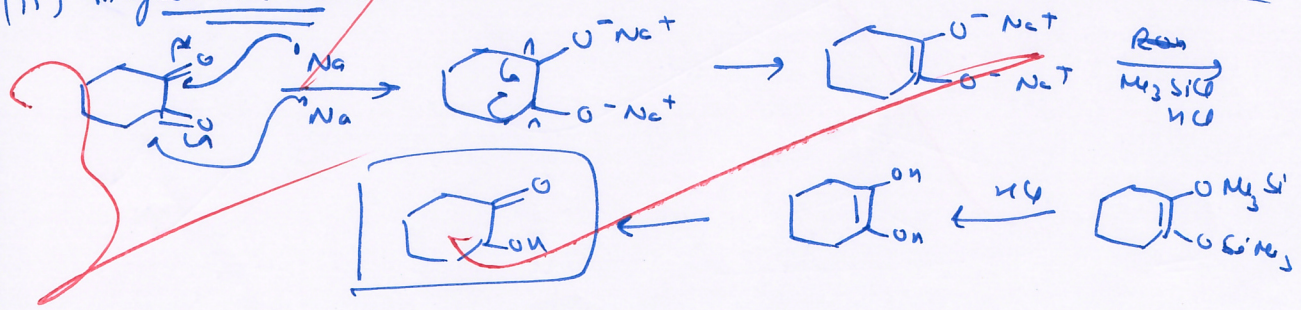
(i) 

(ii) 

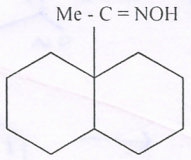
(i) Fries-rearrangement



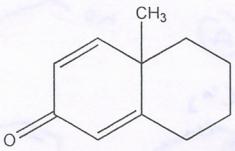
(ii) Acyloin Reaction



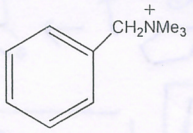
(c) Identify the compounds and write the name of reaction involved. **(20)**

(i) 

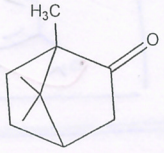
$\xrightarrow[H_2SO_4]{Conc}$ A + B + C

(ii) 

$\xrightarrow[H_2SO_4]{Conc}$ A + B

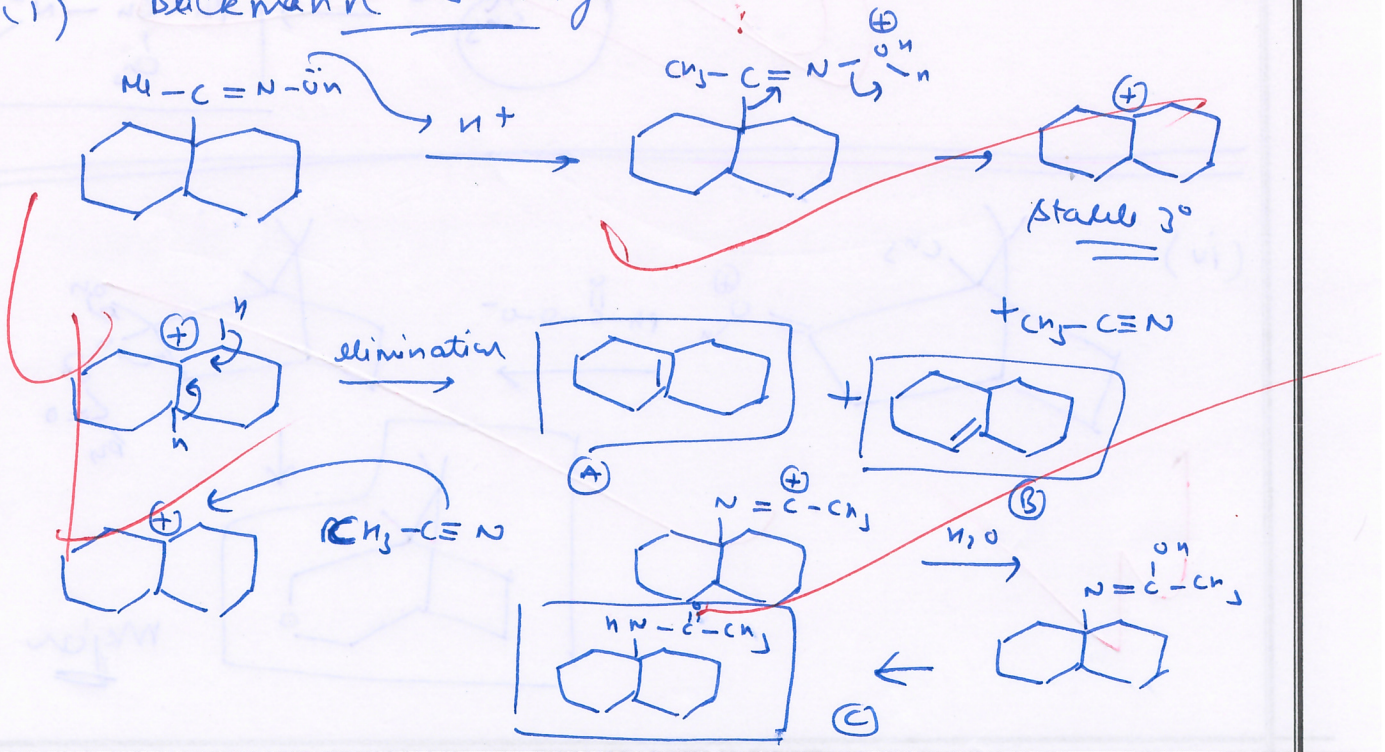
(iii) 

$\xrightarrow{OH^{\ominus}}$ A

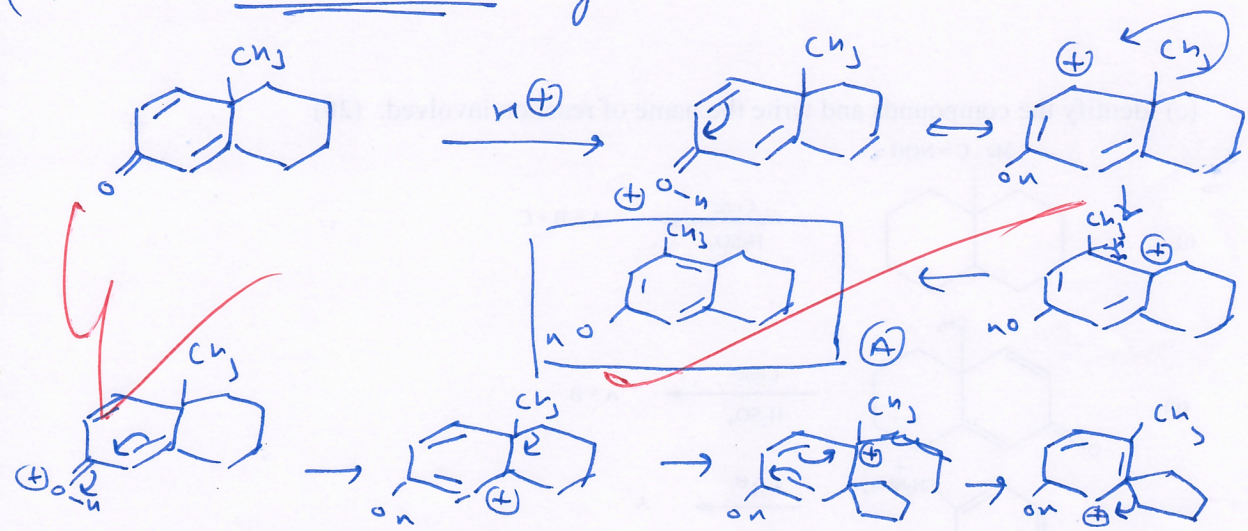
(iv) 

$\xrightarrow{PBA}$ A (Major)

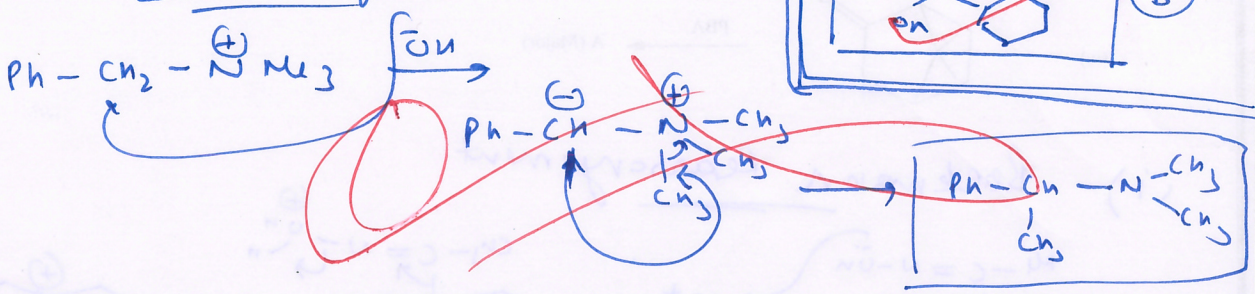
(i) Beckmann Rearrangement



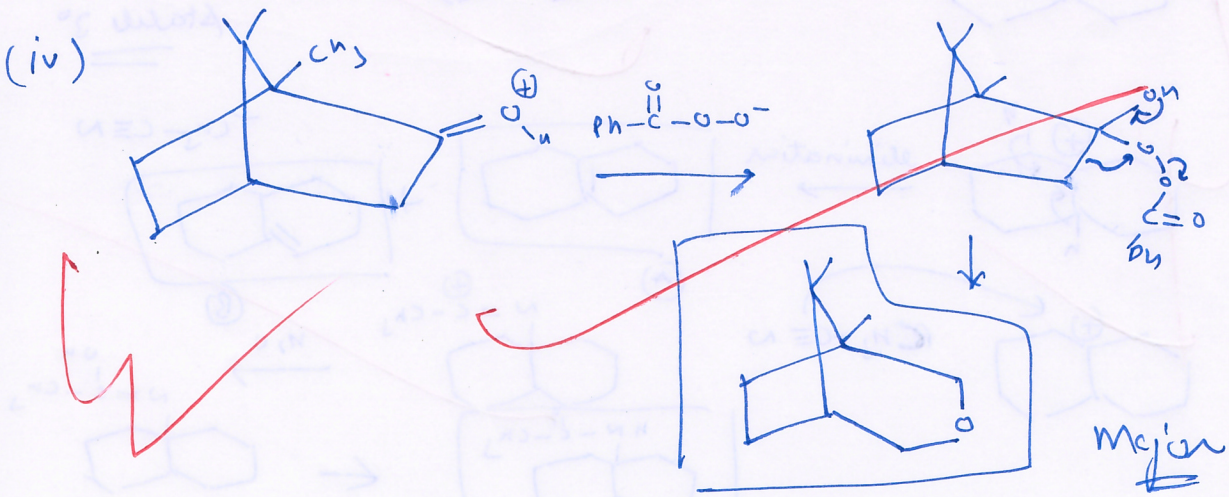
(ii) Dienone-Phenol rearrangement



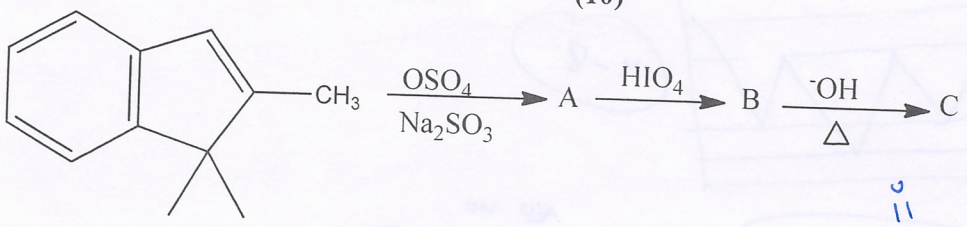
(iii) Stevens Rearrangement

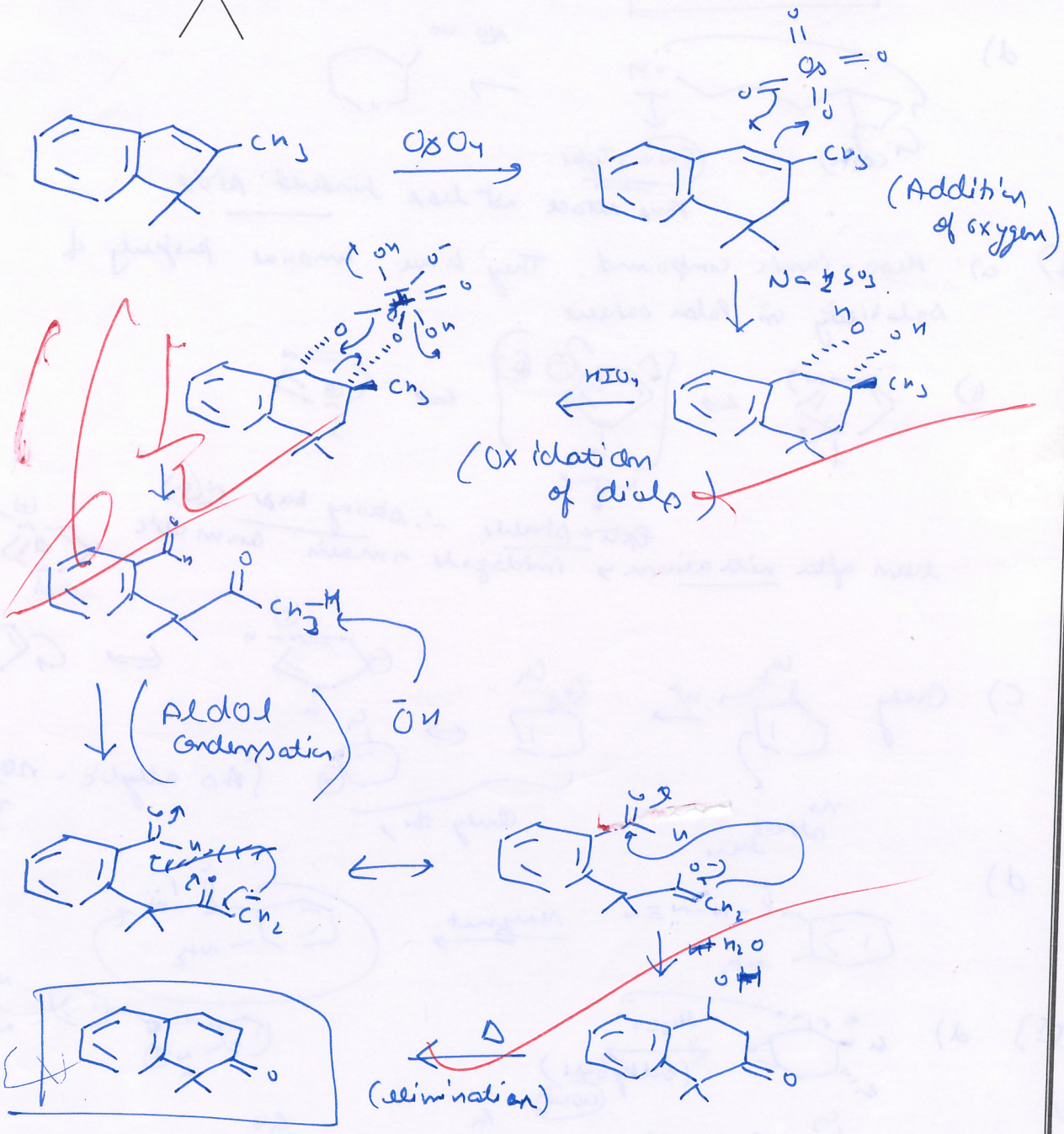


(iv)



(d) Complete the sequence of reaction. **(10)**

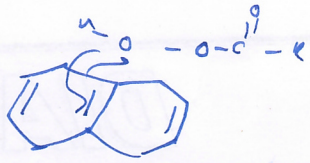




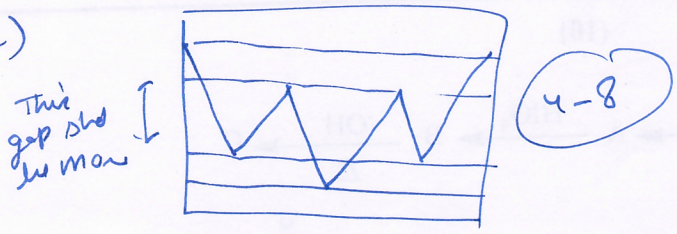
(Test 4)

I)

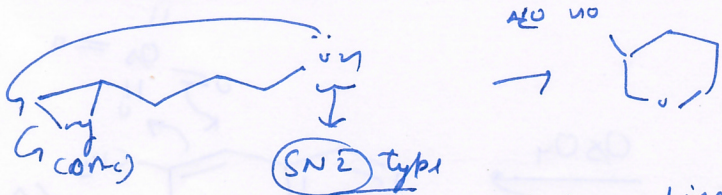
a) Attack above the plane



c)



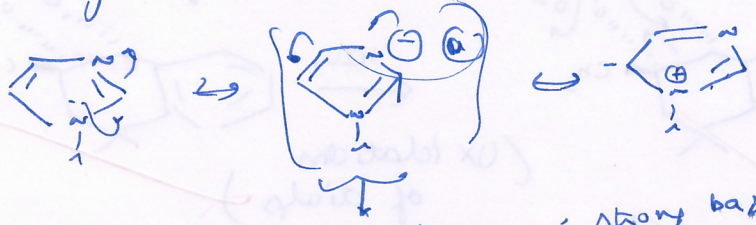
d)



thus attack at less hindered side

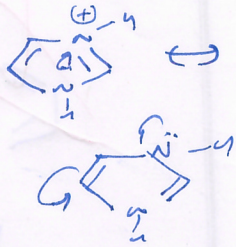
II) a) Meso-ionic compound. They have unusual property of solubility in polar solvent

b)

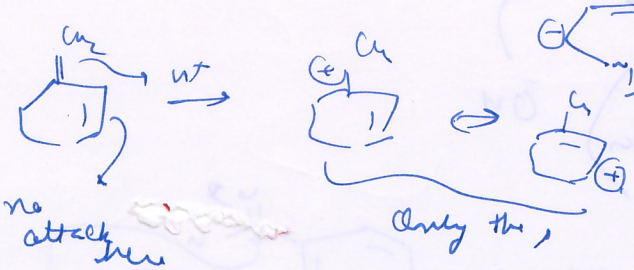


Extra stable ∴ strong base N(a) aromatic

even after nitration → indole remains



c) Only

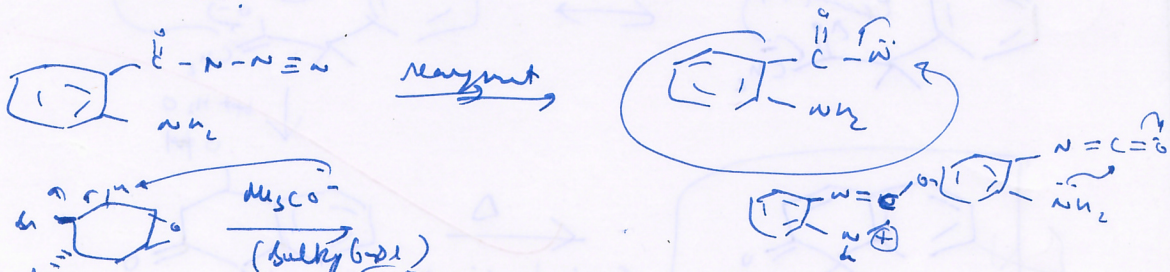


no attack here.

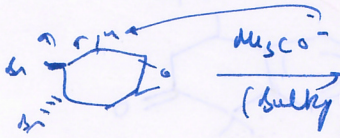
Only this

(As allylic - no carbon rearrangement)

d)



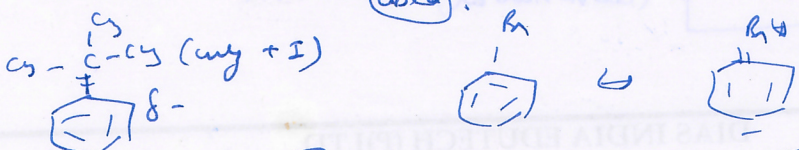
III) d)



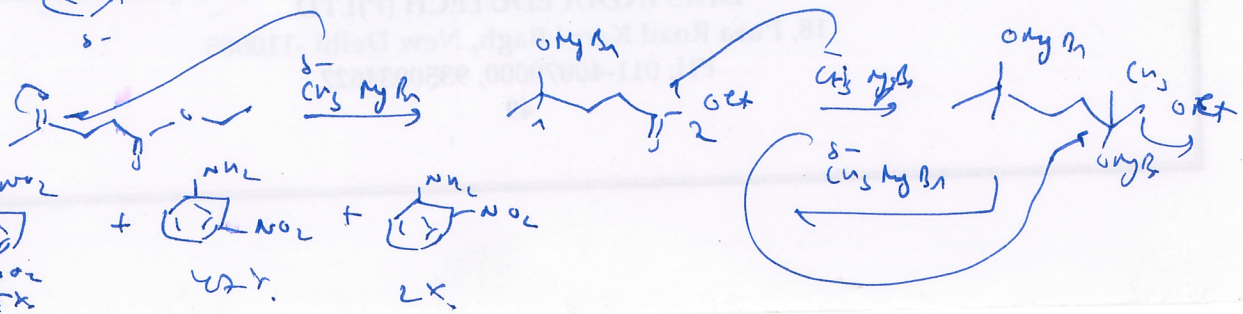
(bulky base) (cold)

IV)

a) ⇒



b)



c)