

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:- NAVNEET MISHRA

UPSC Roll no:- [REDACTED]

Mobile Number. [REDACTED]

Date :- 18 Aug 2024

Dias Roll No.

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	33½	34	36	x	26	—	—	30

Signature of invigilator

159½
Signature of
Examiner

India's No.1 Institute for Science Optionals

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
9	Test 9	Full Syllabus – (Paper I)	25/08/2024
10	Test 10	Full Syllabus - (Paper II)	01/09/2024

Note: Online / Offline Admission open.

Features of DIAS Chemistry optional Mains Test Series 2024:

- ✓ Tentative Time 12:00 PM to 03:00 PM
- ✓ Discussions on Every SUNDAY at 10:00 AM
- ✓ 10 Tests, including 6 Sectional and 4 Full Syllabus tests.
- ✓ Idea is to cover the entire subject in its length by 10 Sectional Tests.
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- ✓ Detailed analysis and answer checking with proper comments by **Dr. R.K. Singh Sir**.
- ✓ Discussion classes are designed in such a way that they can provide value addition on the other related topics.
- ✓ Copy evaluation and feedback system is designed to provide relevant insights and feedback to each candidate as per his/her performance.
- ✓ Many Questions of Civil Services Examinations 2017,2018,2019,2020,2021 Chemistry Optional Mains with DIAS Test Series
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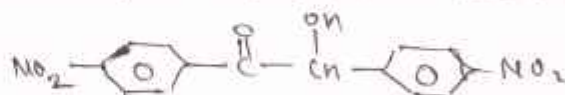
Section- A

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

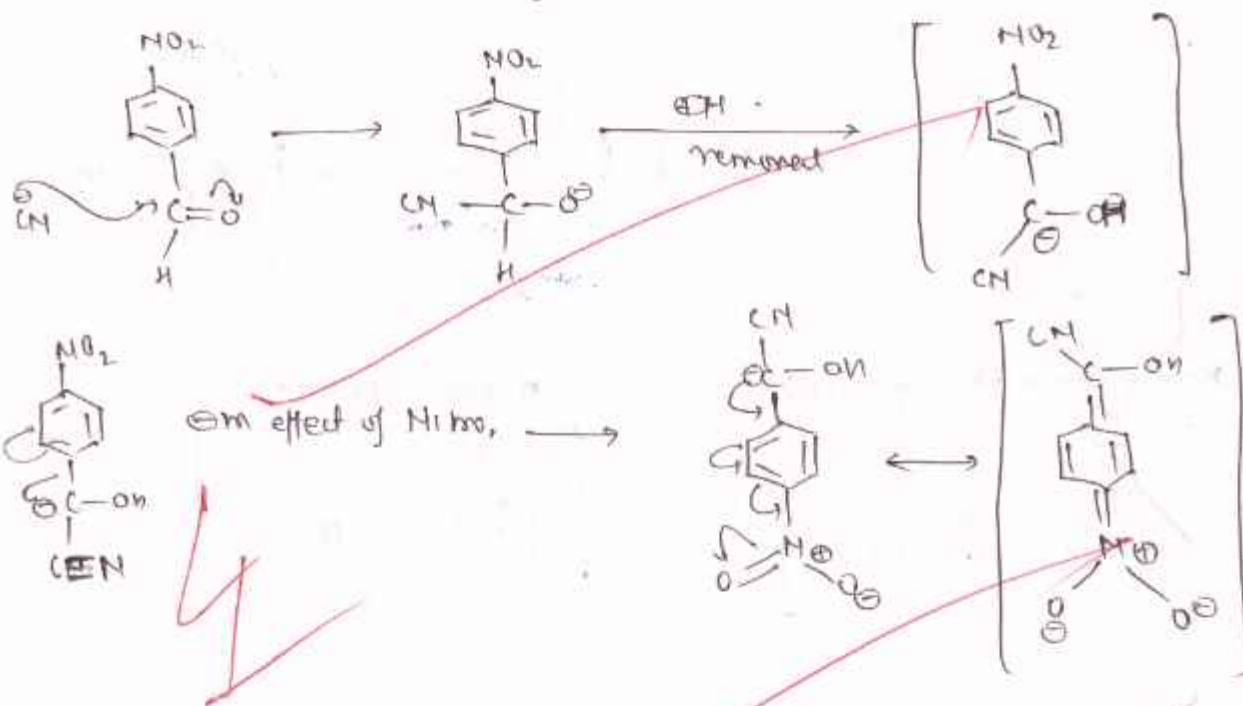
p-nitro benzaldehyde,



For benzoin condensation reaction,



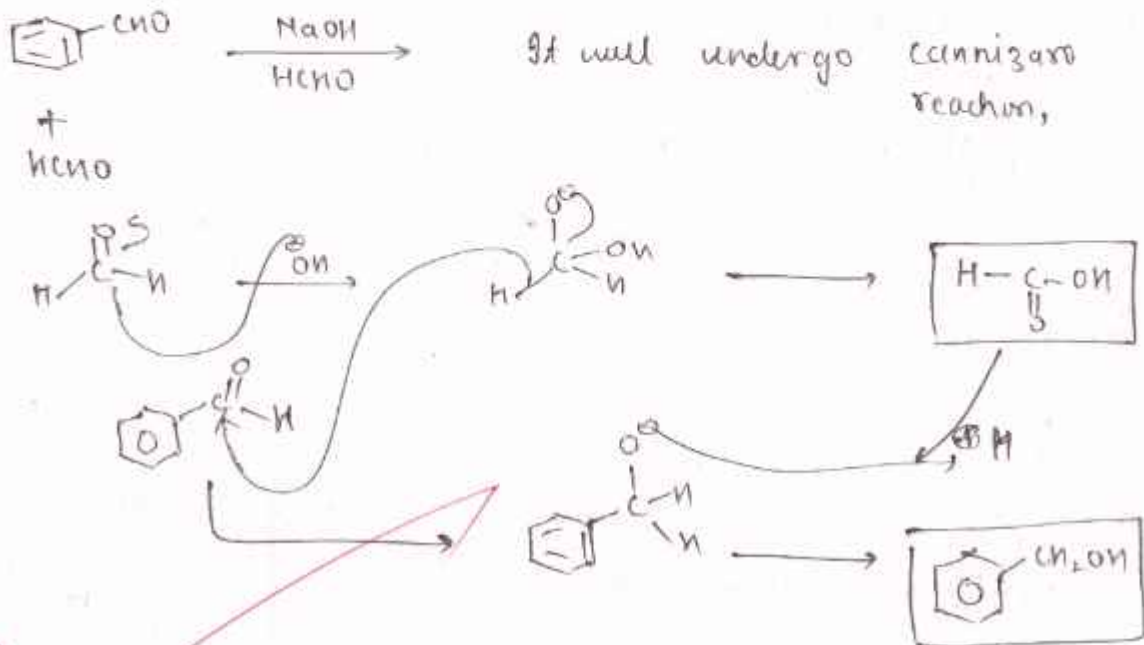
\ominus CN attacks on carbonyl carbon,



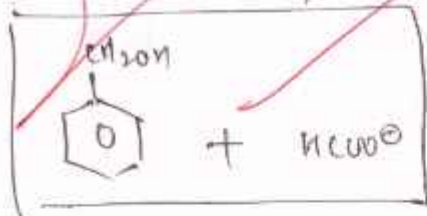
It means, the negative charge ~~is~~ resonates with Nitro group and do not remain with \ominus which is why do not perform benzoin condensation.

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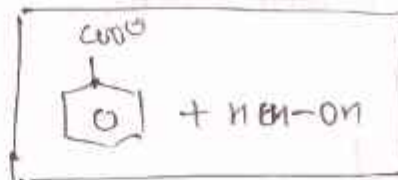
(ii) C_6H_5CHO is refluxed in the presence of NaOH and excess HCHO. Write the major aromatic product. (5)



major aromatic product,



minor product

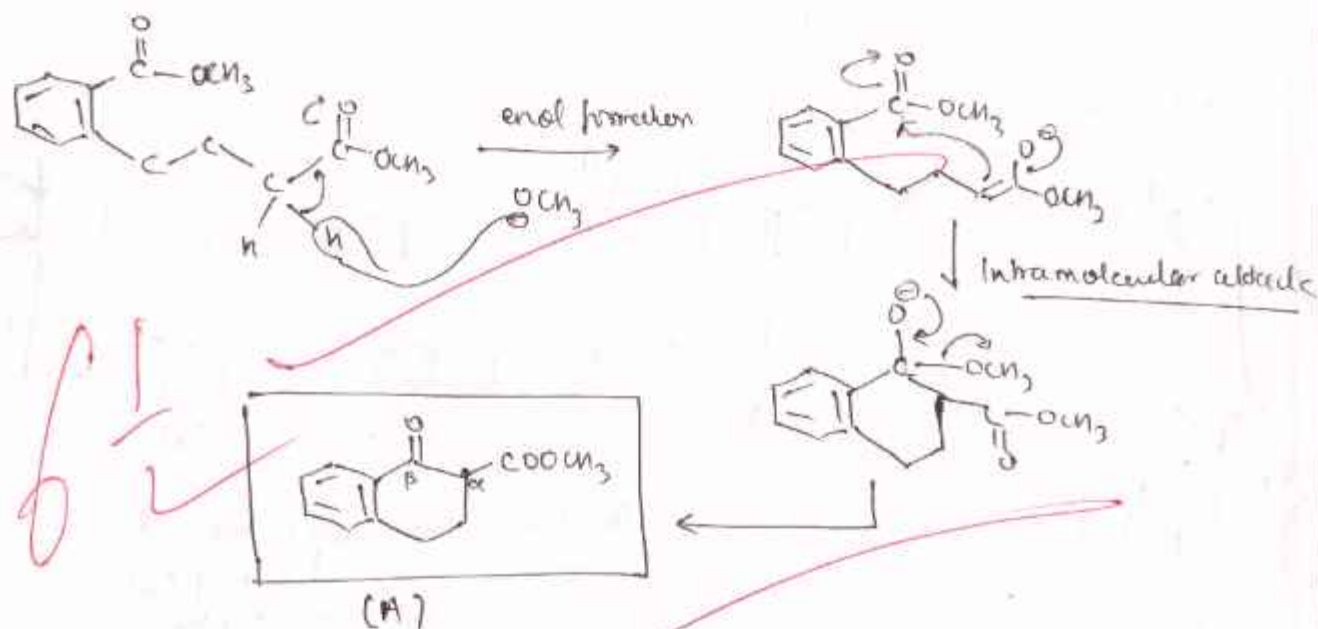


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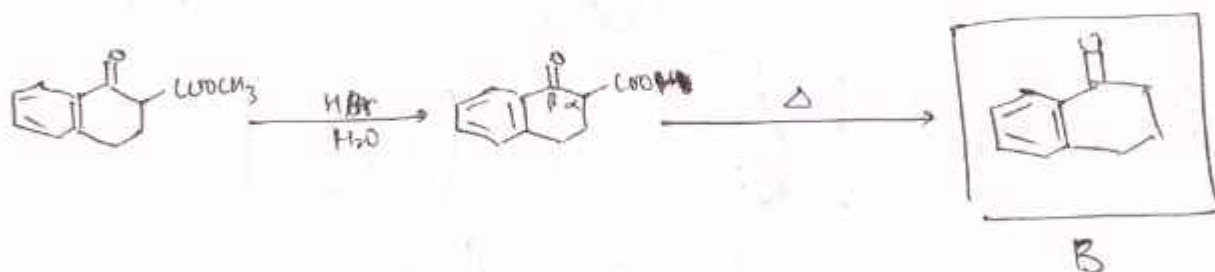
(b) In the following reactions, identify the products A and B. Explain the mechanism of formation of A: (10)



It will undergo via intramolecular - claisen condensation, which is dieckmann synthesis mechanism

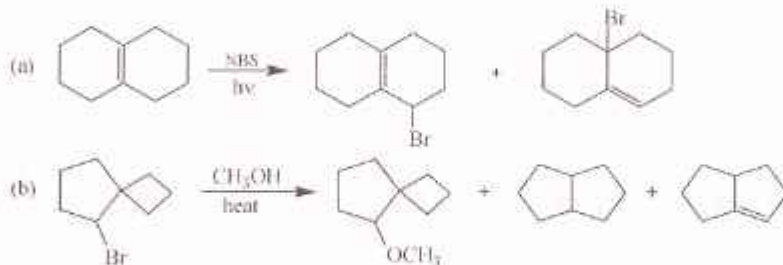


When we add HBr/ Δ \rightarrow β -keto ester will form \rightarrow β -keto acid
 CO_2 release \leftarrow after heating \leftarrow

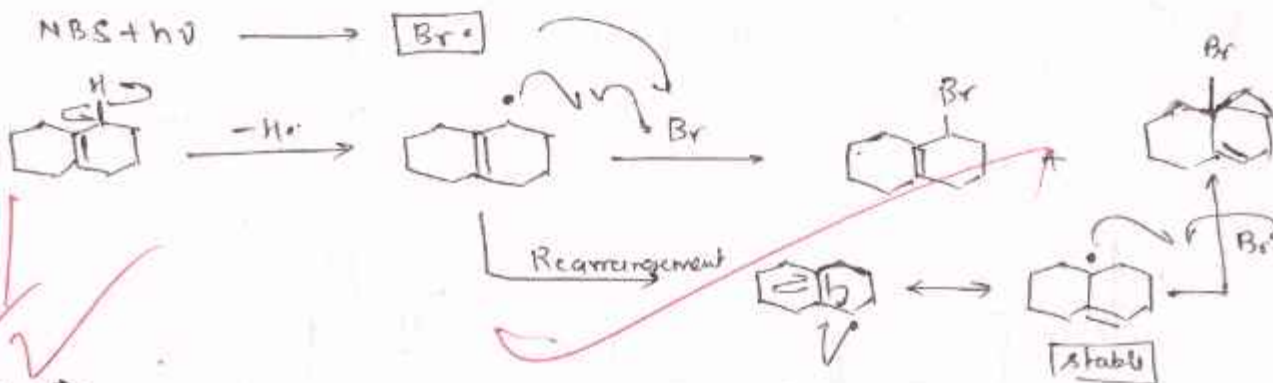


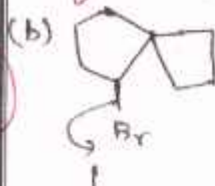
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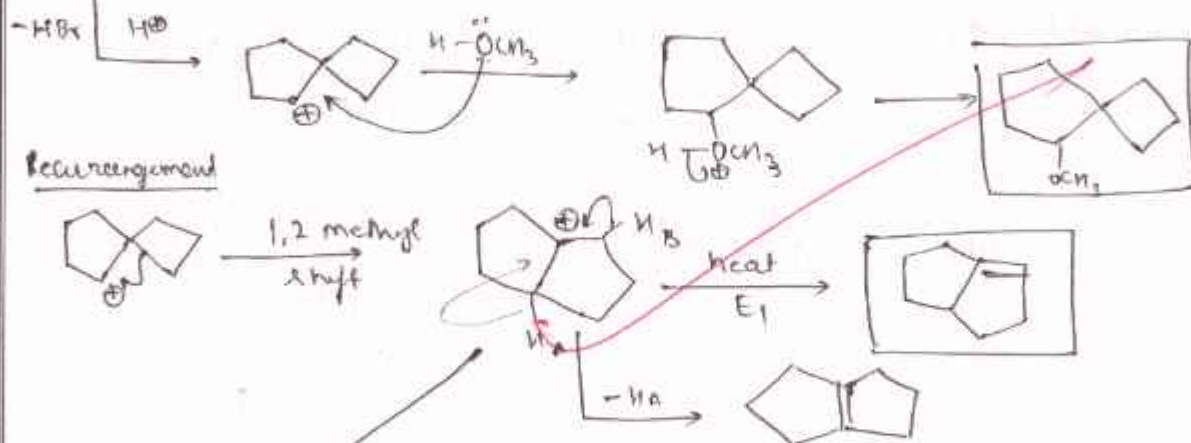
(c) Propose mechanism to account for the observed products in the following reactions. In some cases more products are formed, but you only need account for the ones shown here. (10)



(a) $NBS + h\nu \longrightarrow$ Bromination at allylic carbon via Radical mechanism



(b)  $\xrightarrow{CH_3OH / heat}$ Polar protic solvent \longrightarrow E_1 / S_N1 carbocation formation.



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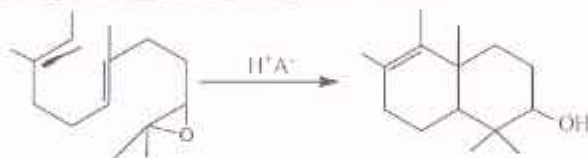
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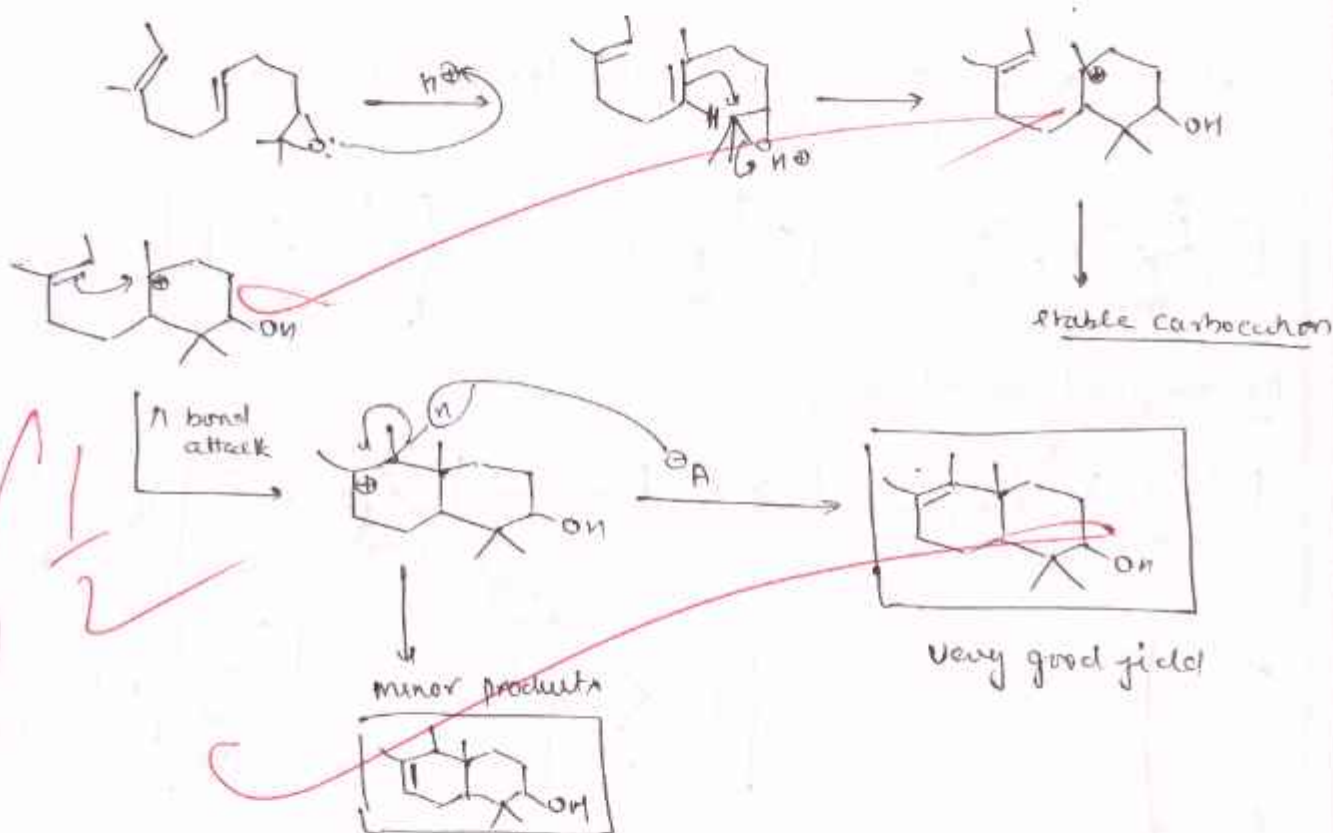
$\xrightarrow{H^+}$ Removal after double bond formation.

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(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)



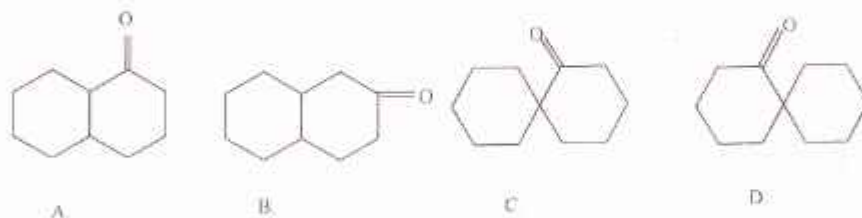
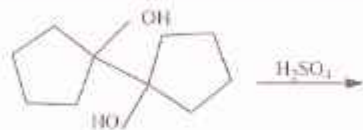
H^+ addition on epoxide,



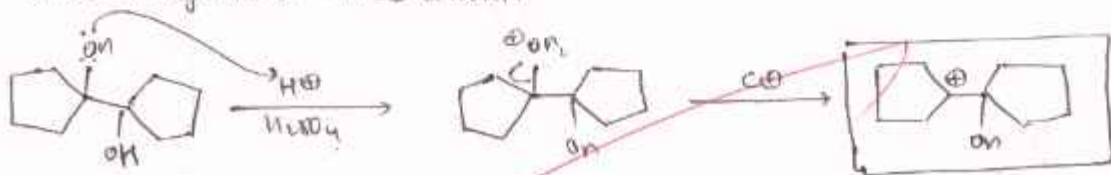
This reaction is similar to cholesterol formation

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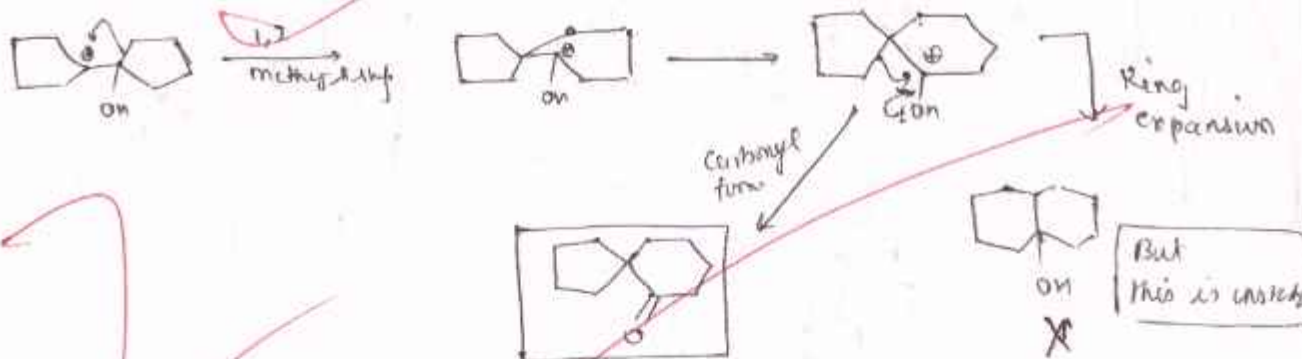
(e) What is the product of the following reaction? Justify. (10)



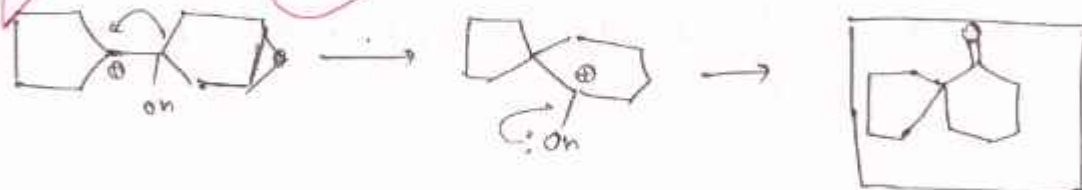
This reaction has $OH \rightarrow$ proceed via pinacol and pinacolone rearrangement mechanism



Rearrangement will take place



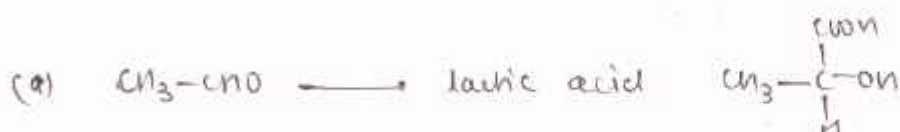
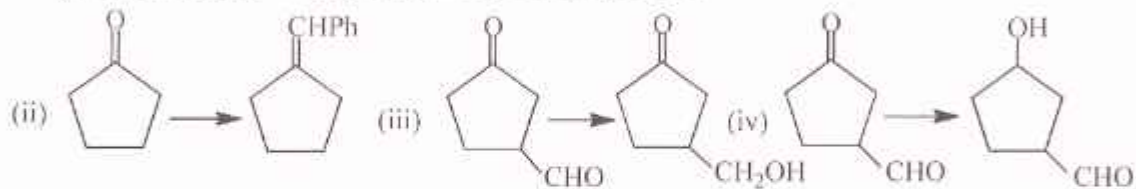
is only product,



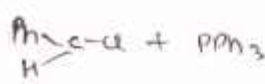
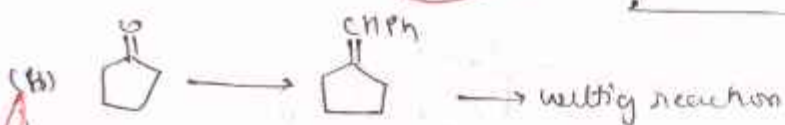
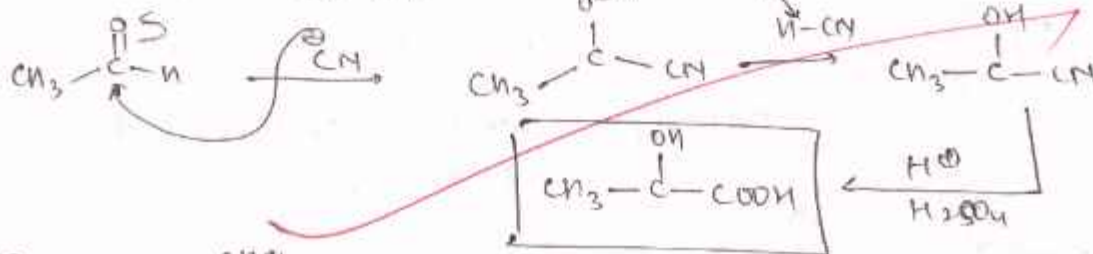
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2(a) Show how you would accomplish the following synthesis efficiently and in good yield. You may use any necessary reagents. (10)

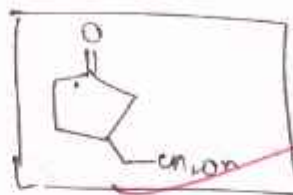
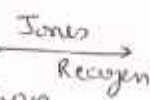
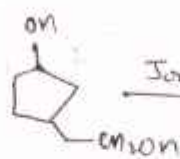
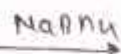
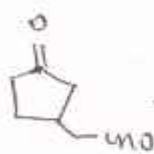
(i) Acetaldehyde \rightarrow lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$



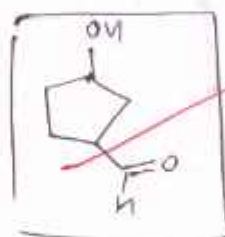
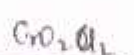
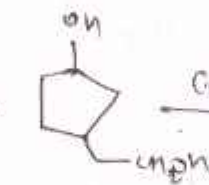
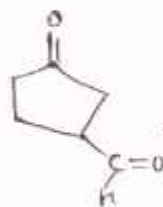
Use KCN as Alu^\ominus or KCN



(iii)



(iv)



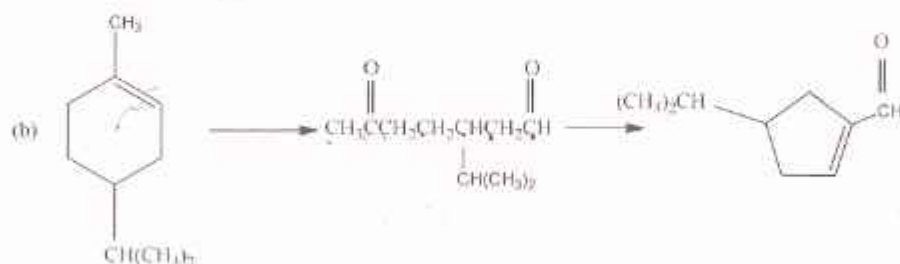
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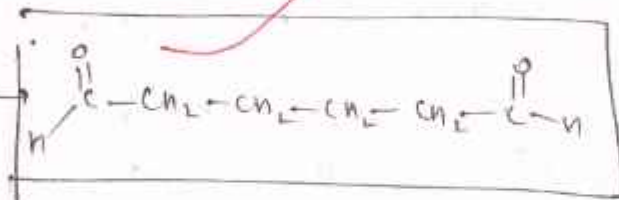
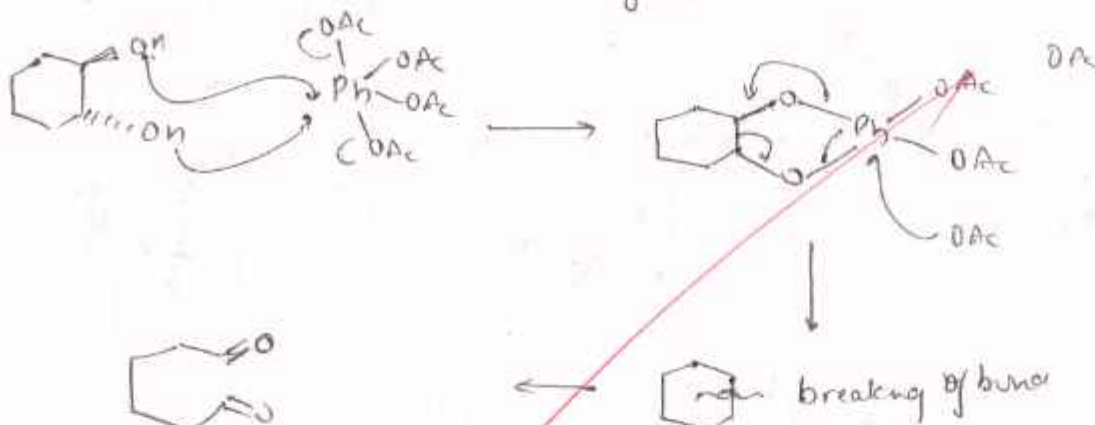
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(b). Identify the reagents appropriate for each step in the following syntheses. (20)



We will use LTA

$\text{Pb}(\text{OAc})_4 \rightarrow$ oxidises cis/trans both system



for next part \rightarrow It is a aldol mechanism

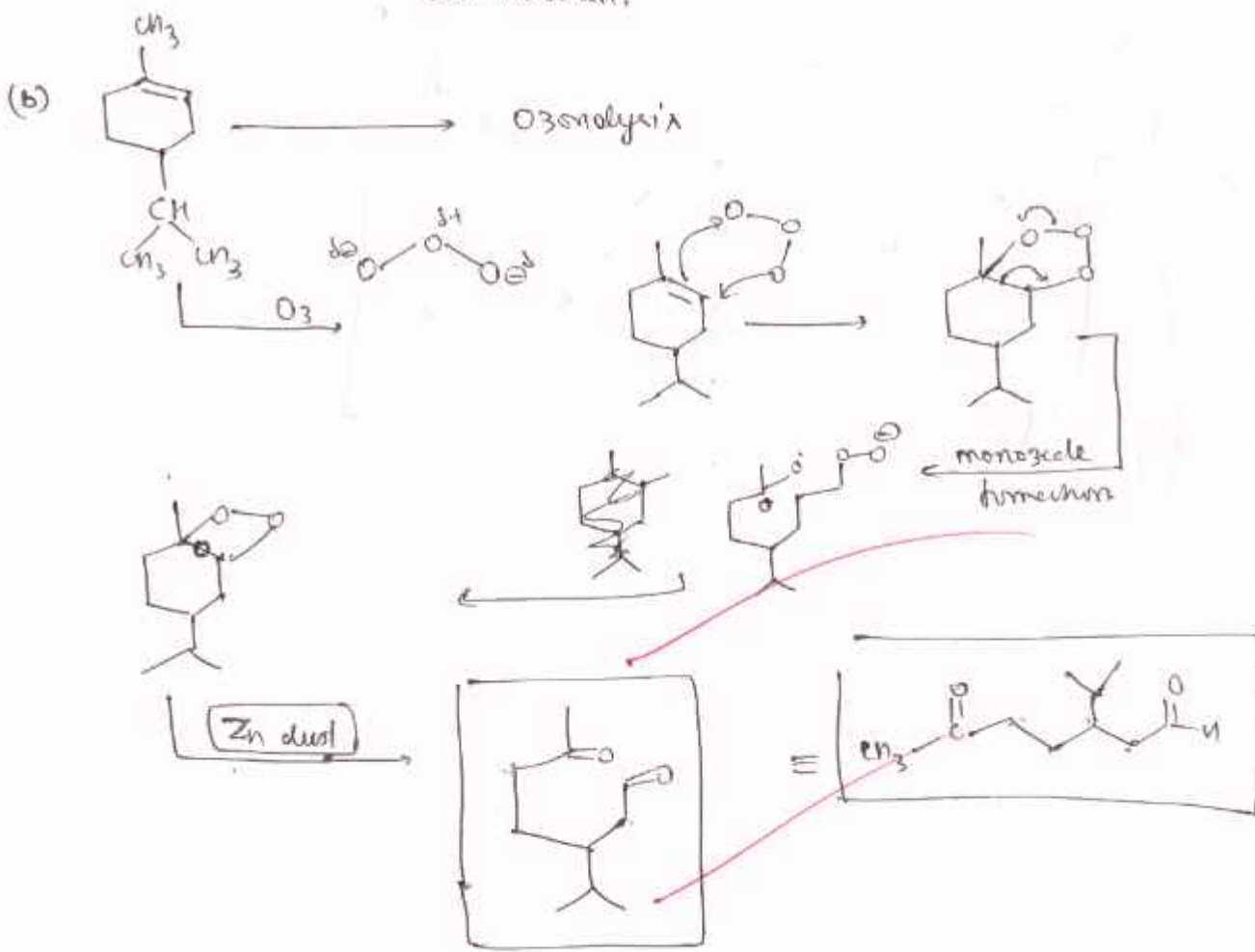
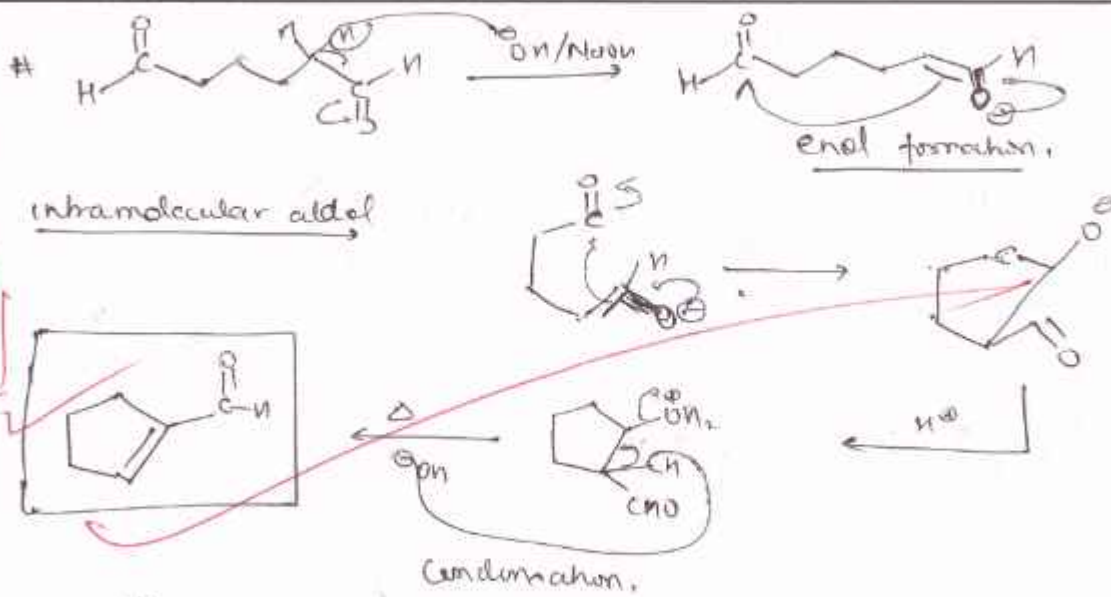
we need $\boxed{\text{OH}^-/\text{NaOH}}$

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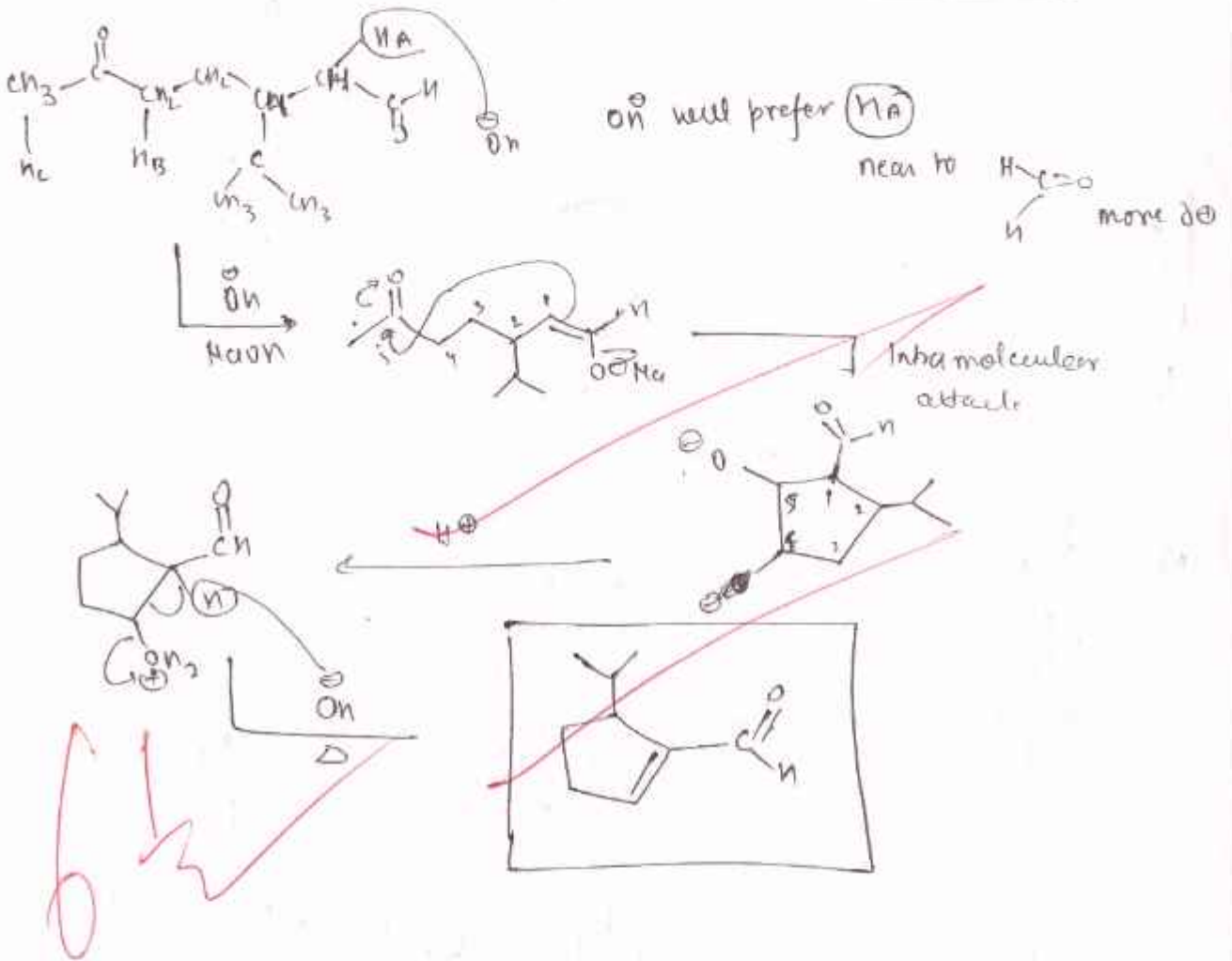
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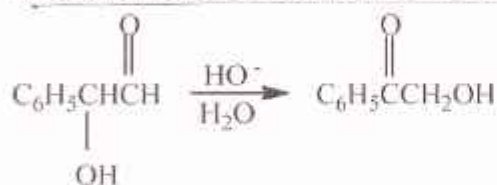
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Next reaction will take place via Aldol condensation



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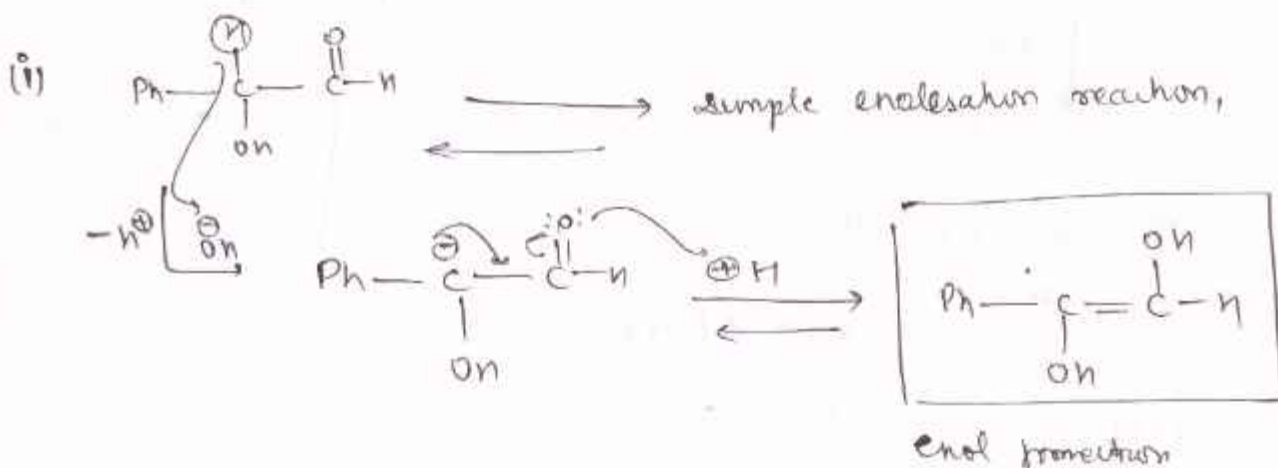
(c)(i) For a long time attempts to prepare compound A were thwarted by its ready isomerization to compound B. The isomerization is efficiently catalyzed by traces of base. Write a reasonable mechanism for this isomerization. (20)



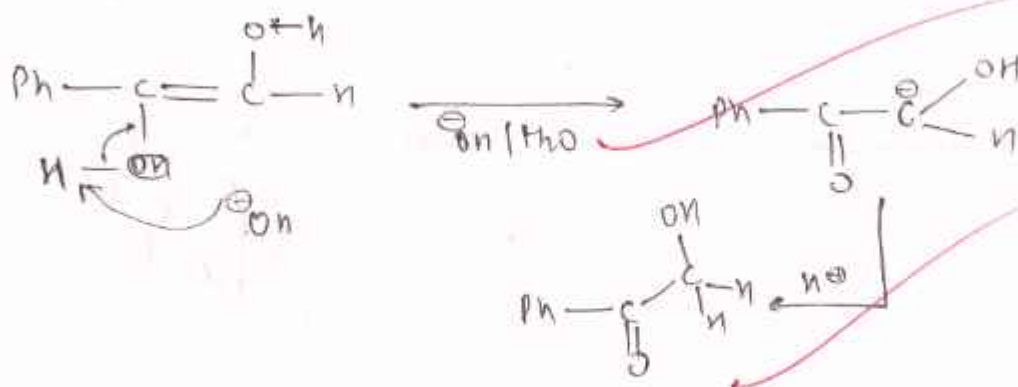
Compound A

Compound B

(ii) Another attempt to prepare compound A by hydrolysis of its diethyl acetal gave only the 1,4-dioxane derivative C. How was compound C formed?



This enol

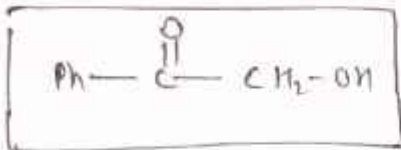


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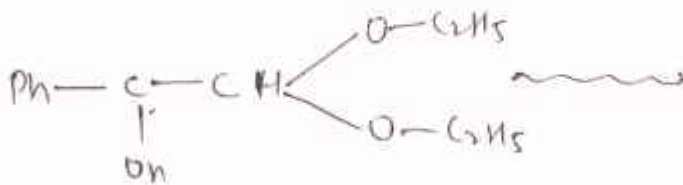
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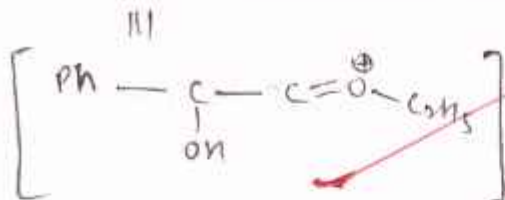
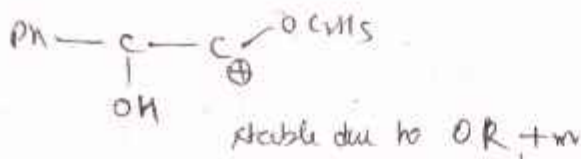
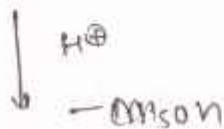
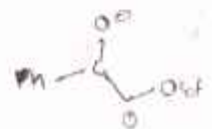
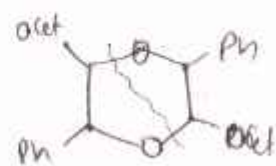


enolization isomerization is a reversible reaction

(ii)



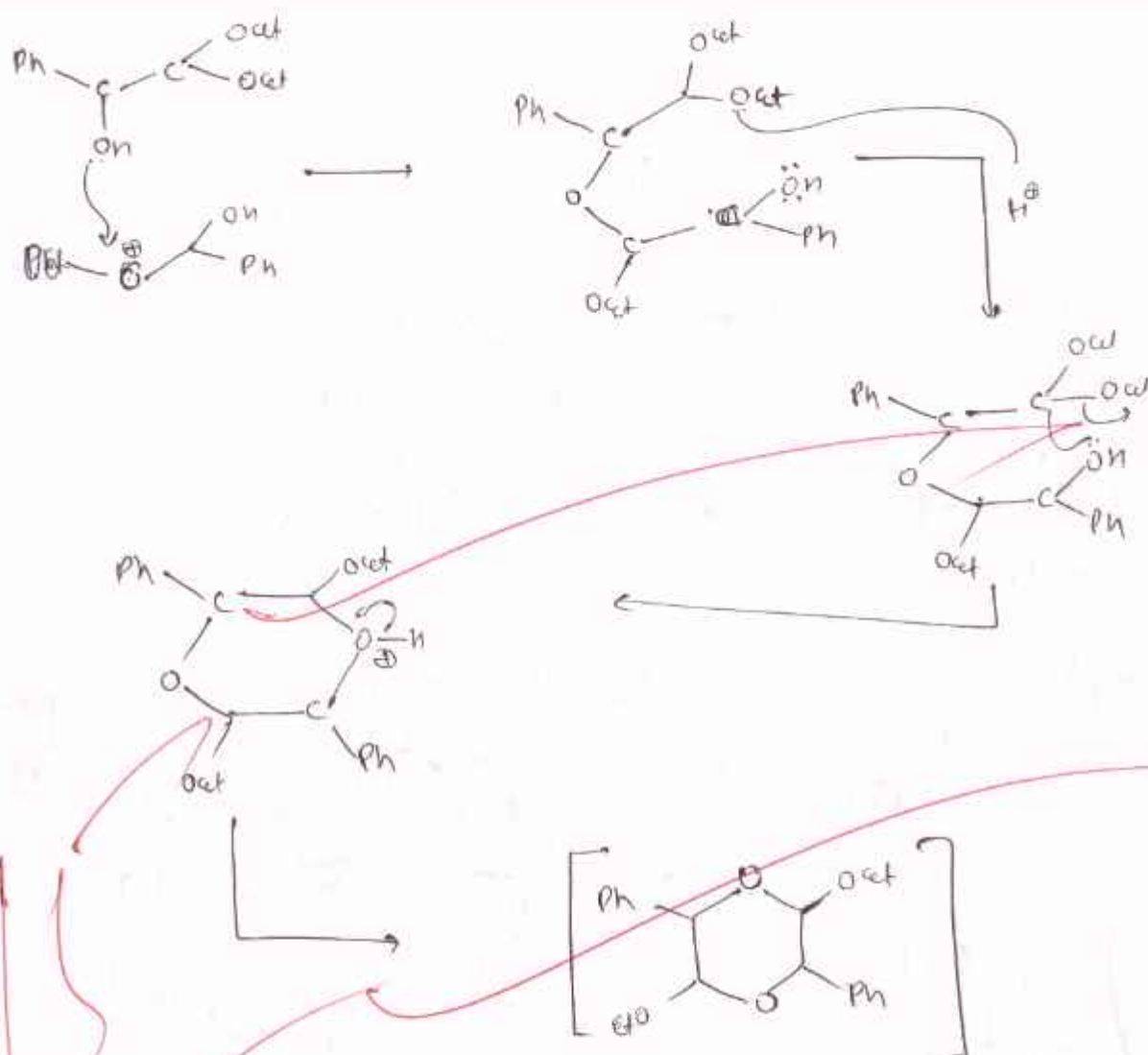
1, 4 dicarbonyl



two molecules of this will undergo ring formation,

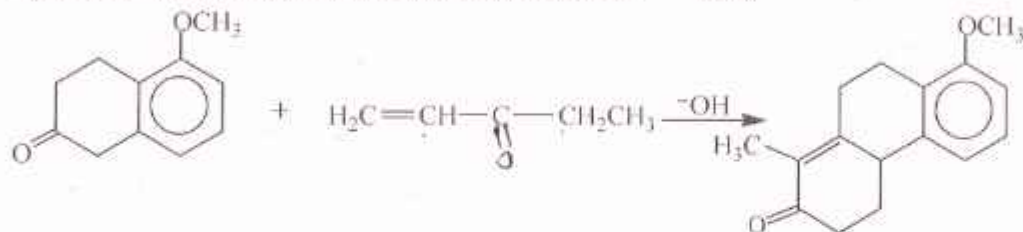
Shankar

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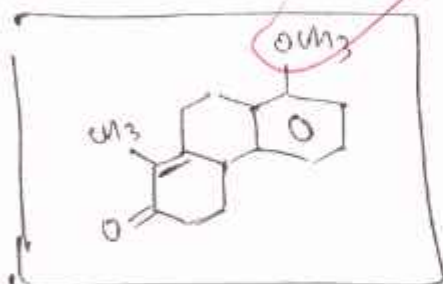
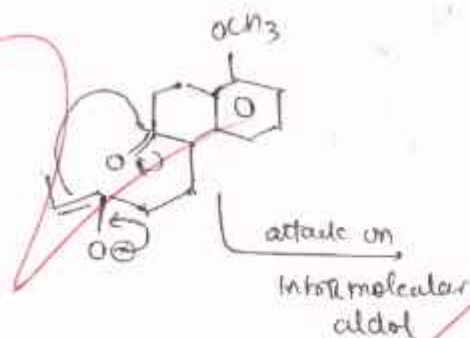
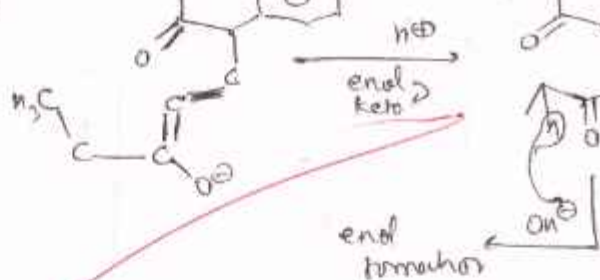
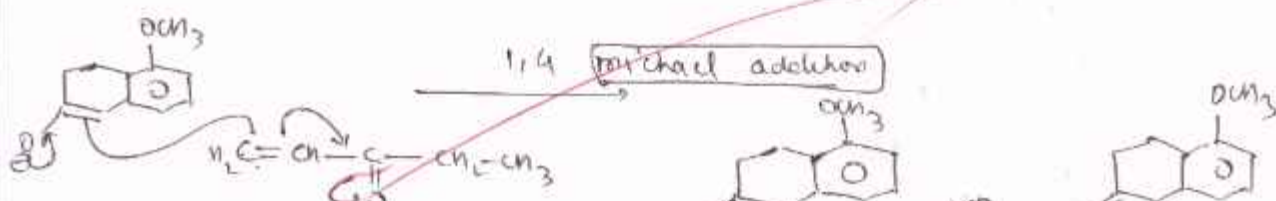
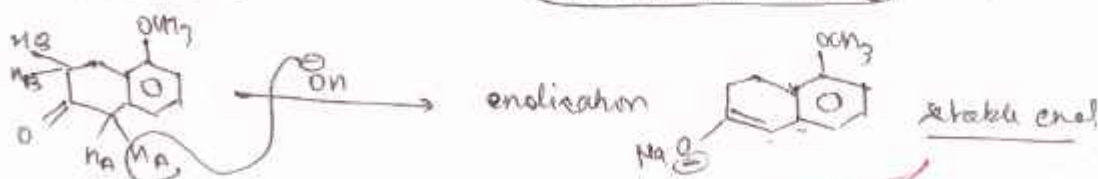
3(a). Propose mechanism for the following reactions. (10)



Now, this reaction will proceed via aldol condensation

mechanism

$H_A > H_B$ in acidity



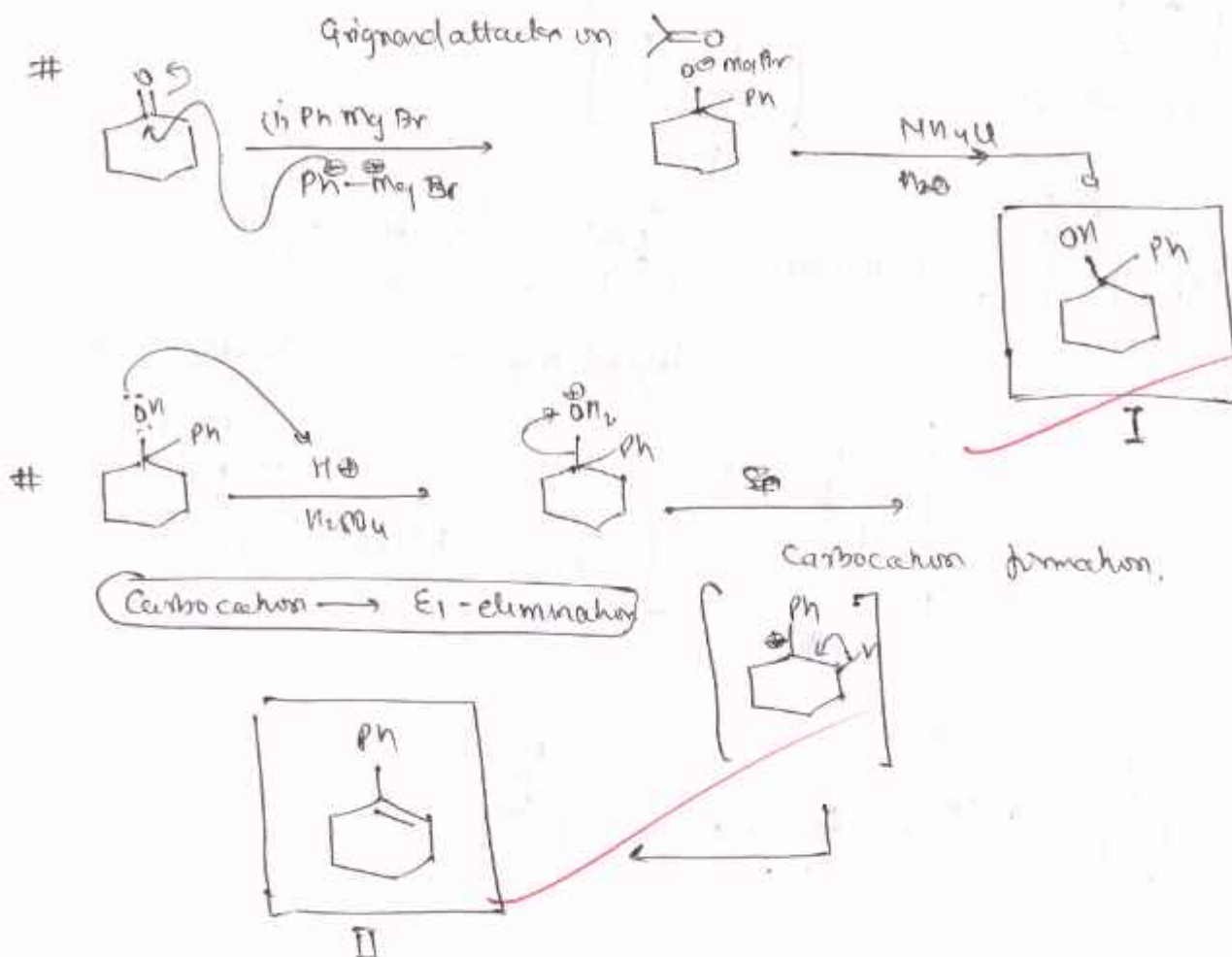
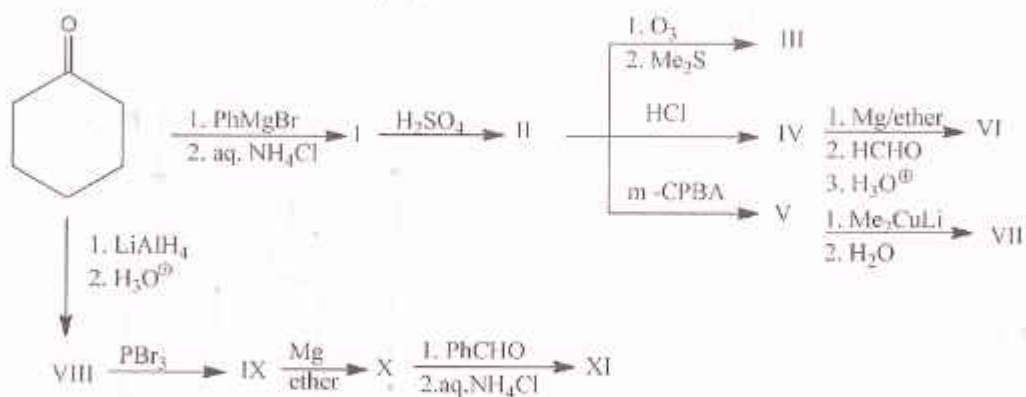
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(b) Identify the compounds I-XI in the following reaction sequence and indicate which of them are isomeric: (30)

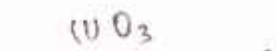
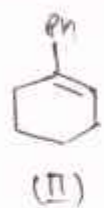


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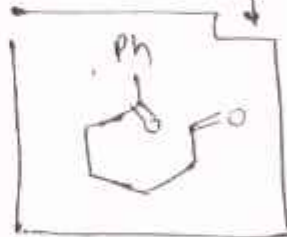
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Ozonolysis.

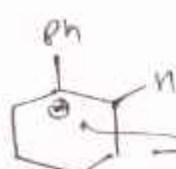


Me, S

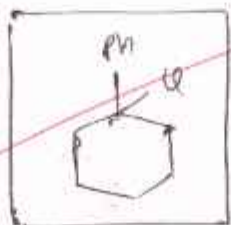


(III)

\downarrow H₂ addition



stable (\oplus)



(IV)

(V)



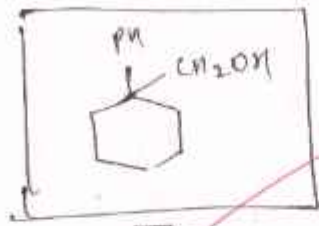
$\xrightarrow{(i) Mg/Ether}$



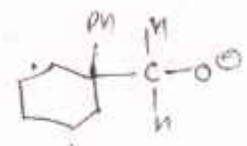
Grignard preparation



$\hookrightarrow Nu^\ominus$ attacks.



(VI)



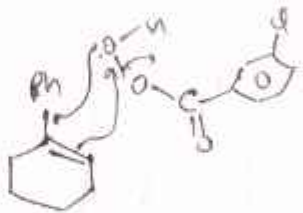
H^+/H_2O

(ii)



$\xrightarrow{m-CPBA}$

epoxidation
oxidation
reaction



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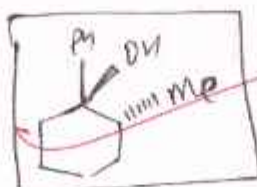
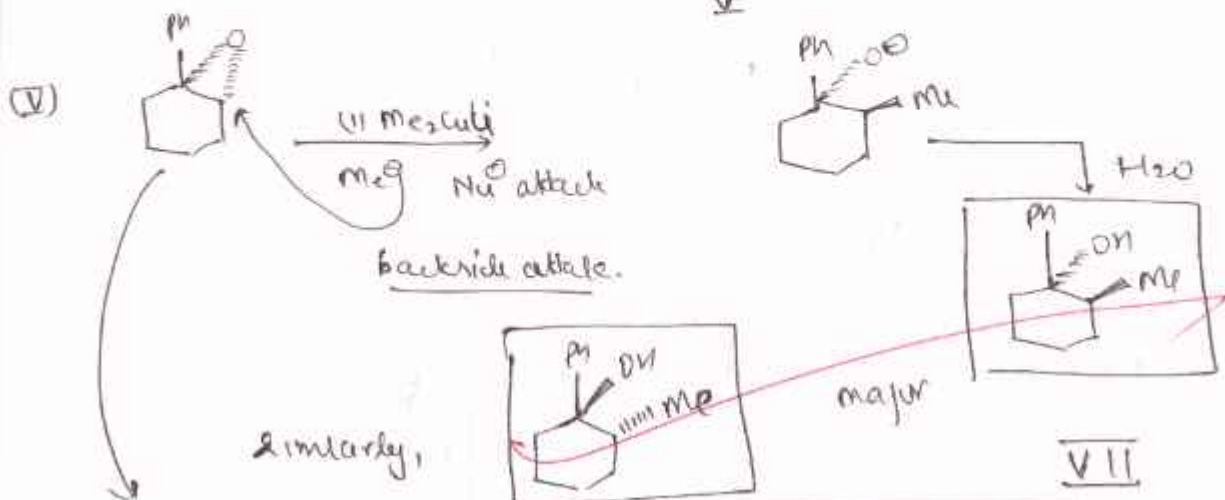
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same side attack

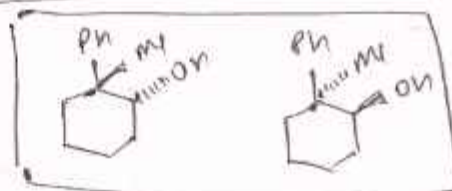


V

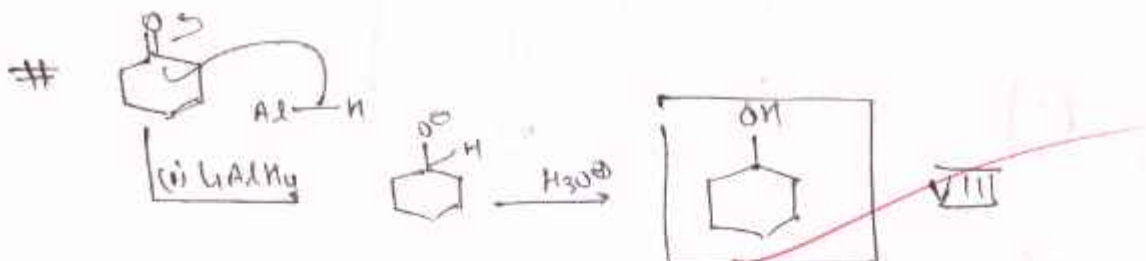


major

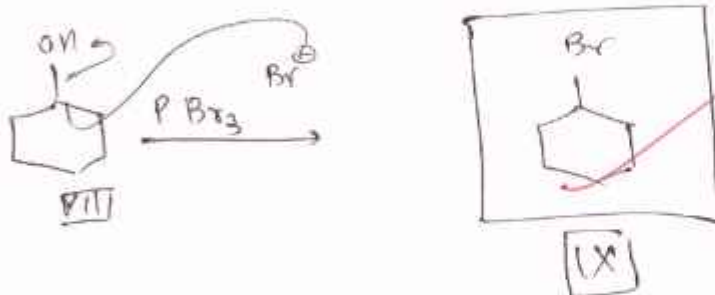
VII



minor



VIII



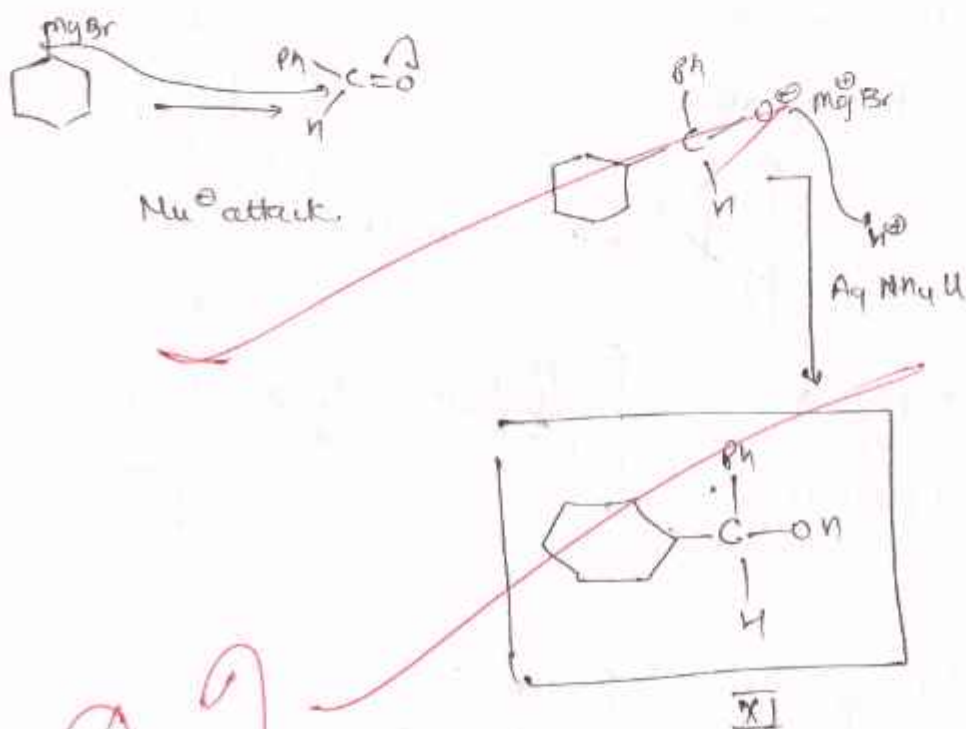
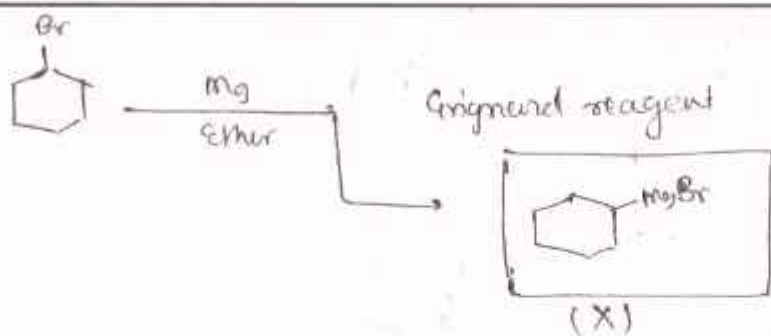
IX

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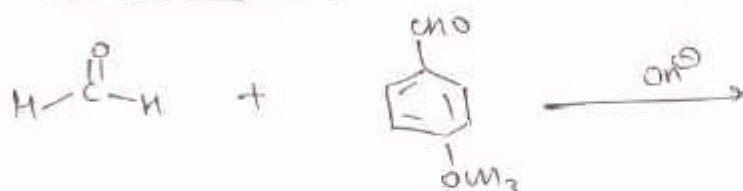
DIAS



22

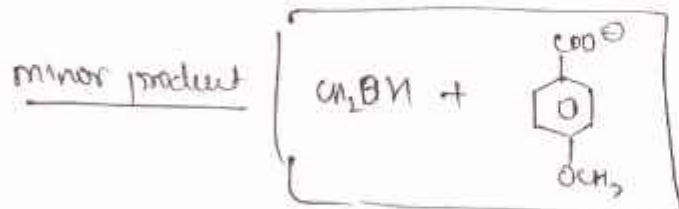
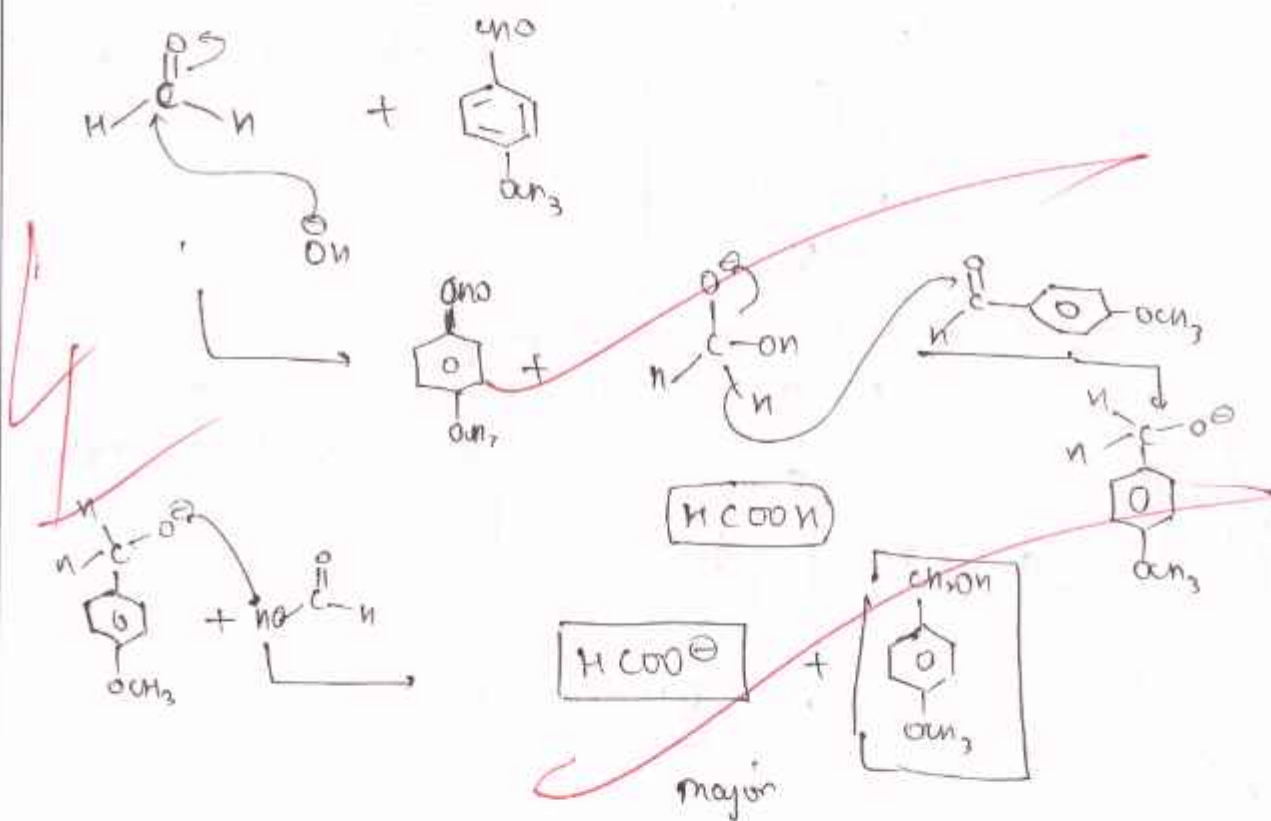
DIAS

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



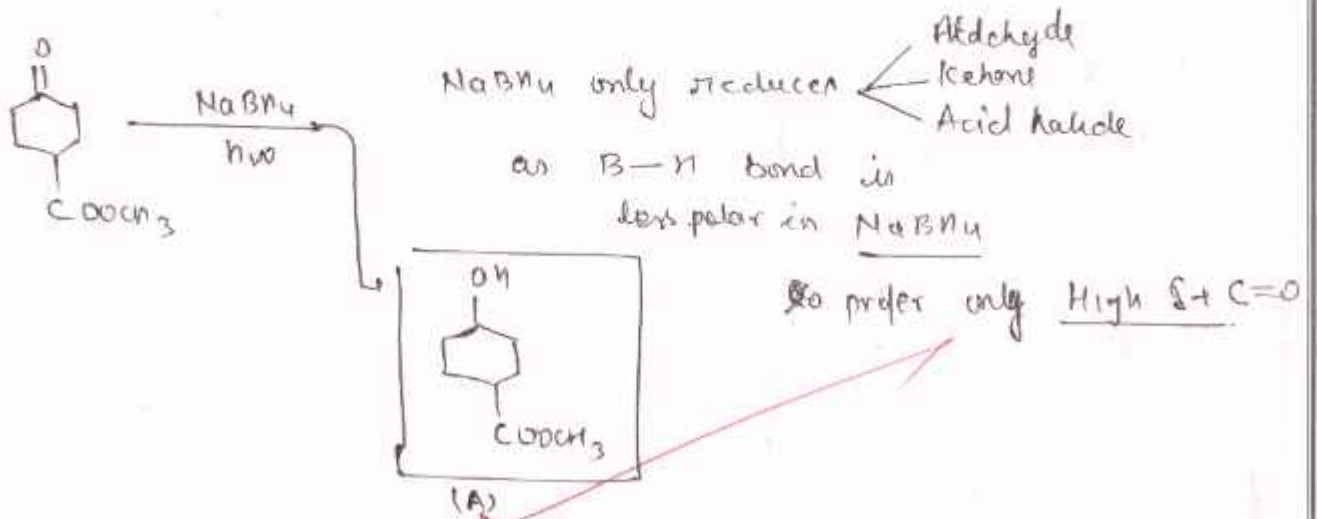
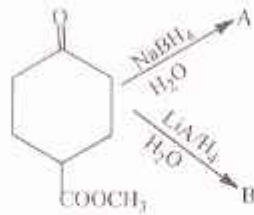
⇒ No α -hydrogen is present

∴ It will undergo Cannizzaro reaction

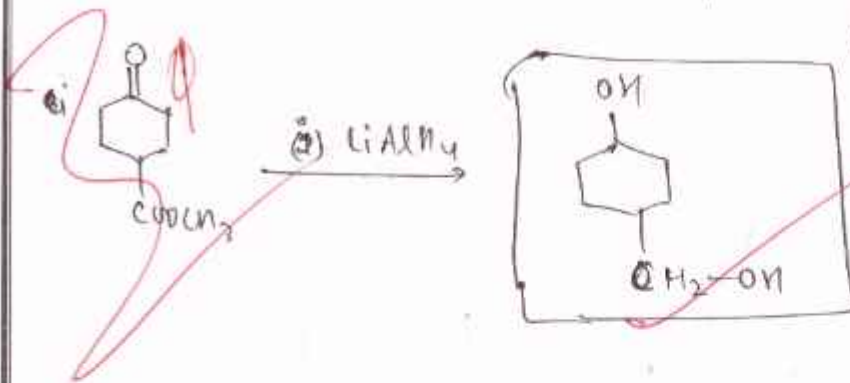


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(d) Identity A and B and discuss the selectivity of the reagents (5)

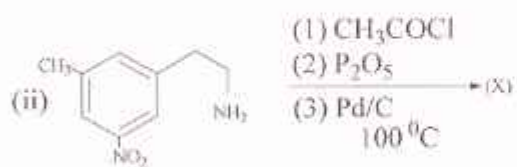
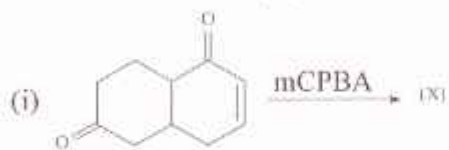


$\text{LiAlH}_4 \rightarrow$ it reduces almost all groups
 Al-H more polar \rightarrow able to penetrate \oplus C=O of all carbonyl



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

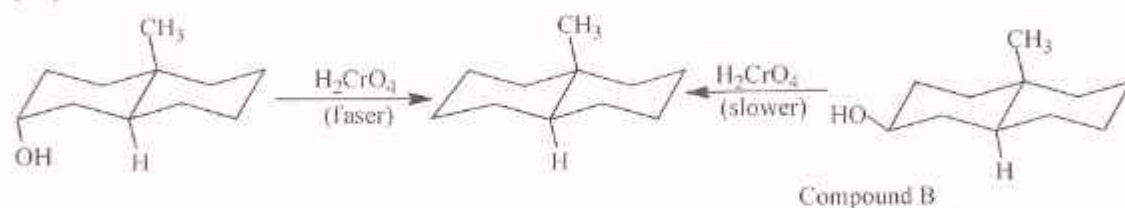


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(b) Chromic acid oxidation of an alcohol occurs in two steps: formation of the chromate ester, followed by an elimination of H^+ and chromium. Which step do you expect to be rate-limiting? Careful kinetic studies have shown that compound A undergoes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



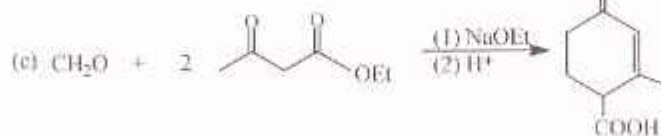
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(c) Suggest a synthesis route for the following conversion. (10)



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



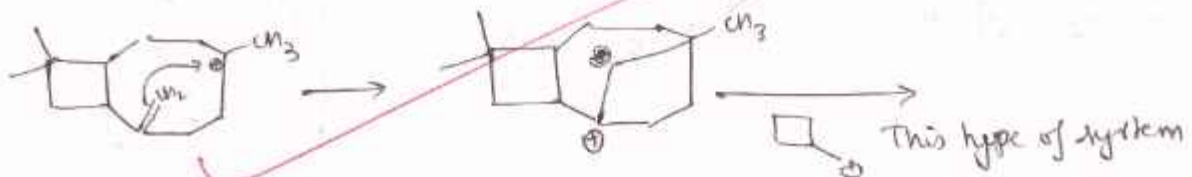
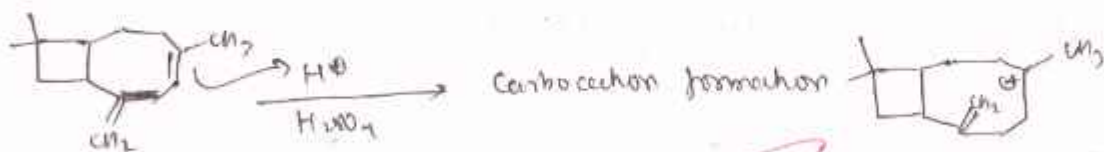
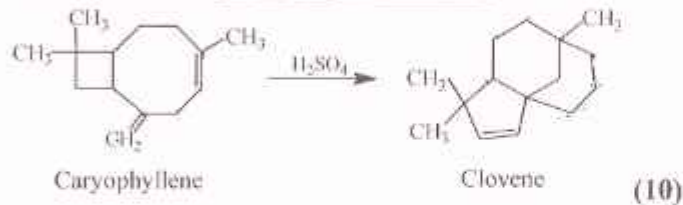
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Section- B

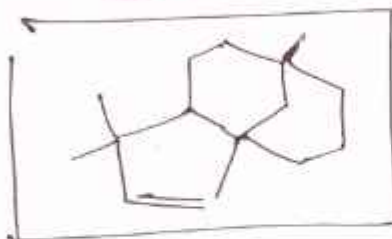
5(a) The oil caryophyllene is a natural constituent of cloves. On treatment with sulfuric acid, it isomerizes to a substance called clovene. (10)



Ring expansion,



Carbocation deprotonation, deprotonation



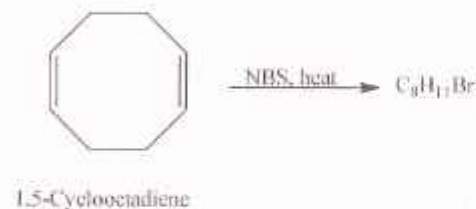
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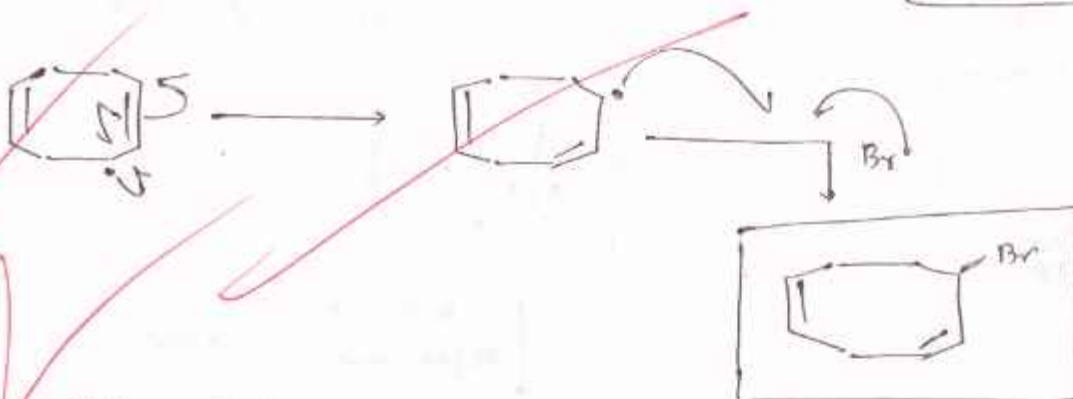
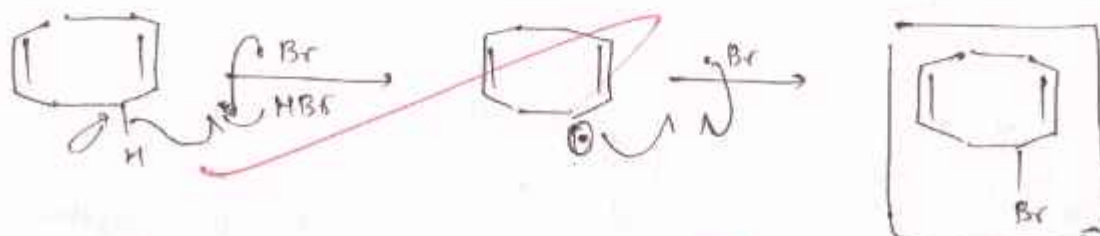
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(b) Bromination of 1,5-cyclooctadiene with N-Bromo succinimide (NBS) gives a mixture of two constitutional isomers of $C_8H_{11}Br$. Suggest reasonable structures for these two isomers. (10)



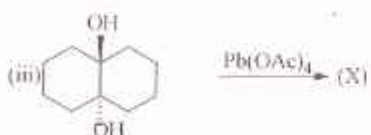
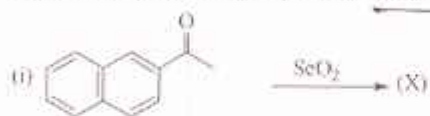
Now, NBS \longrightarrow addition of $Br\cdot$ at allylic position,



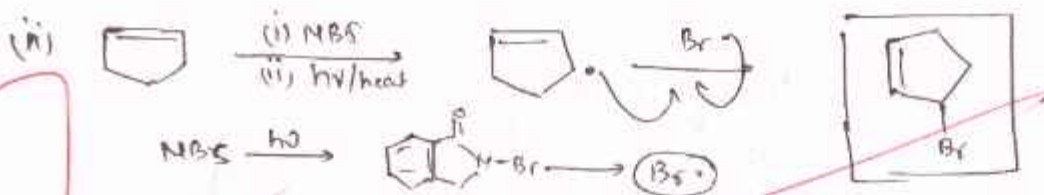
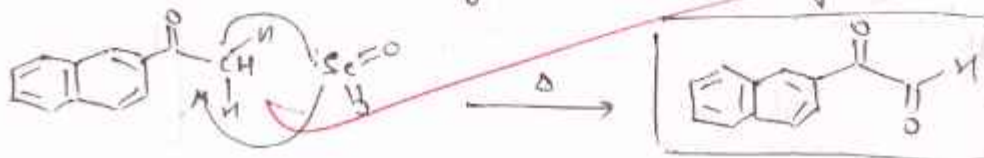
This will form as major Br addition product.

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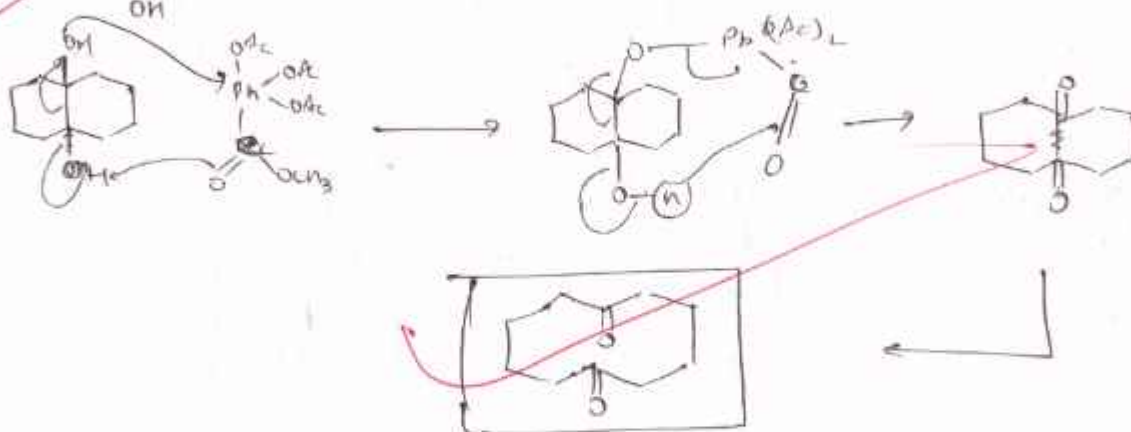
(e) Identify the major product (X) formed in the following reactions: (10)



(i) $\text{SeO}_2 \rightarrow$ add carbonyl at α position of $\text{C}=\text{O}$



(iii) $\text{LTA} \rightarrow$ oxidation in ketone.



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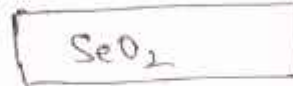
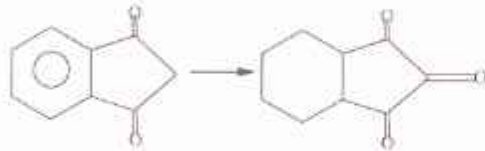
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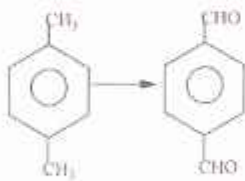
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(d) Write the reagents required for the following conversions, (10)

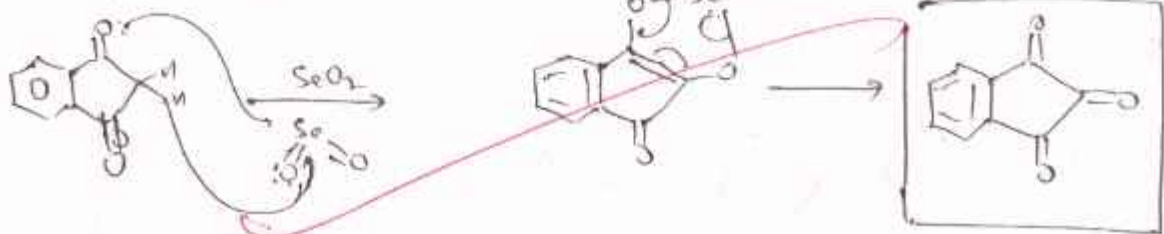
i)



ii)



iii)



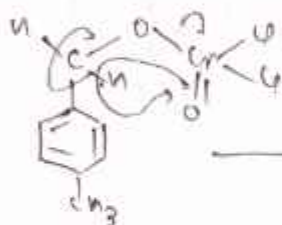
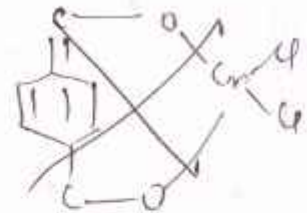
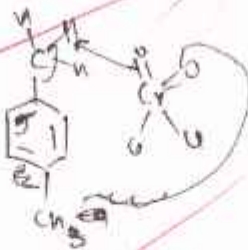
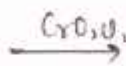
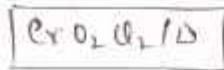
iii)



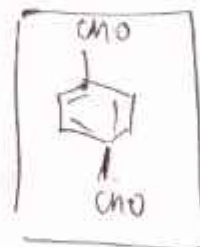
Chromyl Chloride

also known as

etard reaction



hydrolysis



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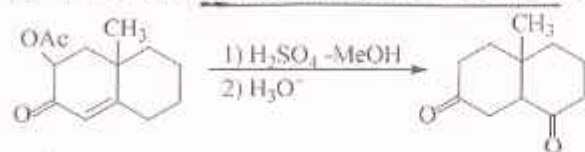
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(e) Write down mechanism for below conversion.

(10)



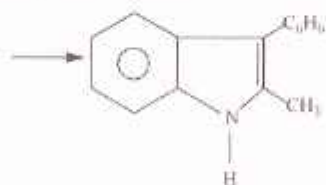
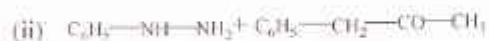
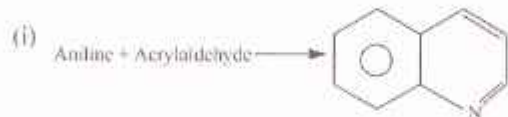
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6(a) How would you carry out the following transformations? Indicate the reagents used and show the mechanisms involved. 10×2 = 20



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(b) How will you synthesize following compound by indicated reaction. (20)

- (i) Coumarin by Perkin condensation
- (ii) Citric acid by Reformatsky reaction.
- (iii) PETN by Aldol condensation.
- (iv) 2-carbethoxy cyclohexanone

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(c)Glucose can exist in pyranose or furanose? How will you justify. (10)

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7. (a) Discuss the stereo specificity of diol formation by KMnO_4 & OsO_4 . Which is more better. How will you differentiate cis & trans isomer of 1,2-cyclohexane diol. (15)

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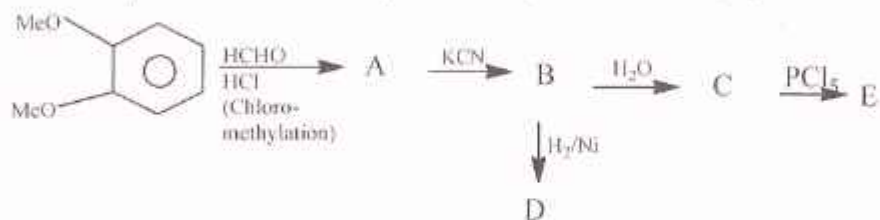
(b) Discuss the mechanism of Stobbe condensation. Why it is not successful with Aliphatic enolizable aldehyde. (15)

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(c)(i) The most economical route to make both the acid chloride and the amine is from the nitrile. Explain the reaction sequence with product. (10)

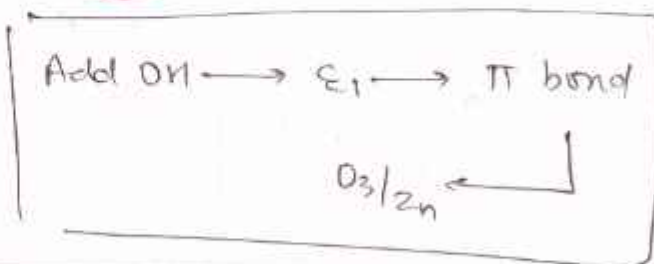
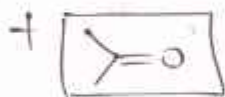
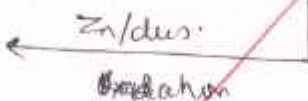
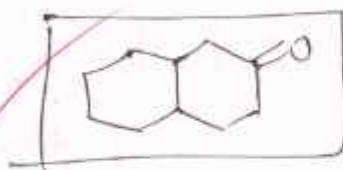
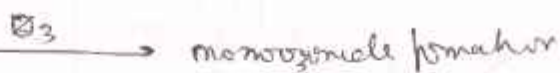
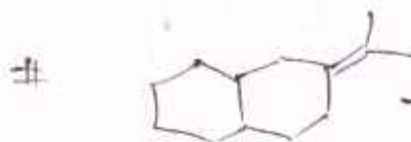
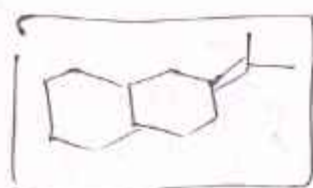
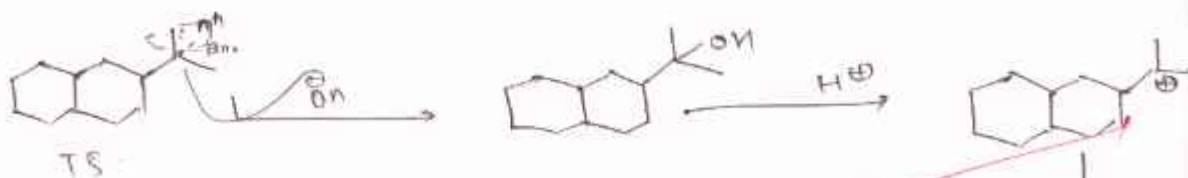
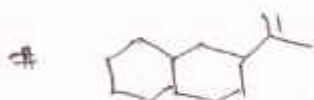


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(ii) What happens when D & E Condensed in presence of POCl_3 . Followed by aromatization.
(10)

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



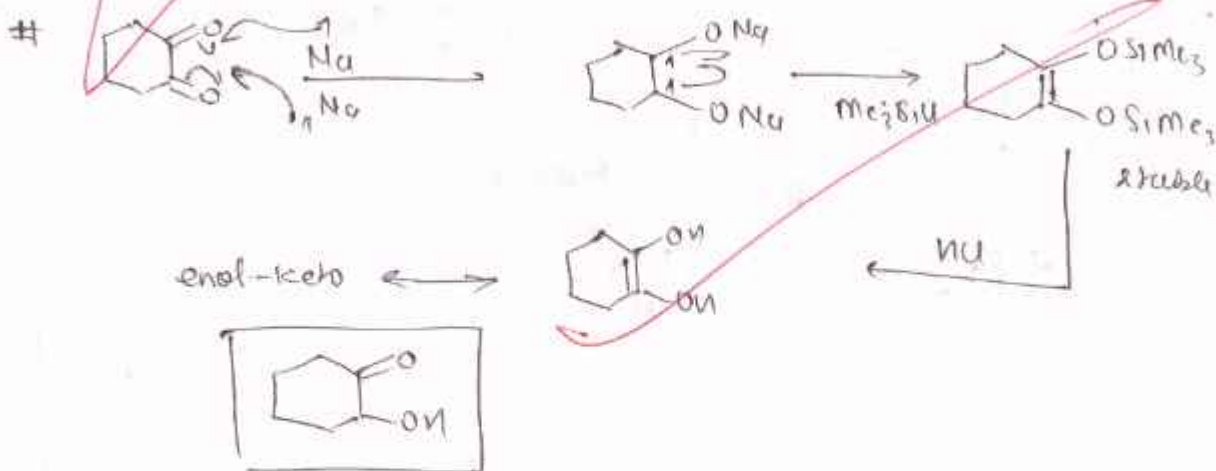
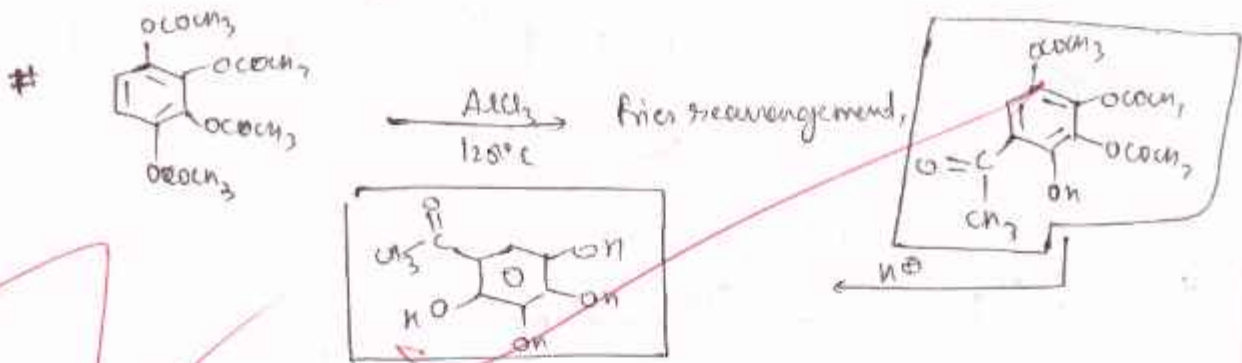
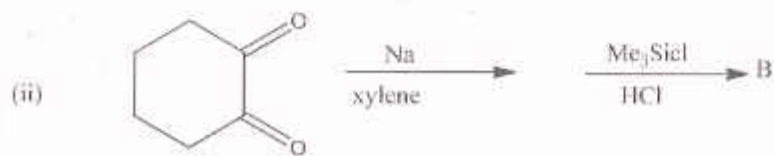
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(b) Write down product give mechanism. (5×2= 10)



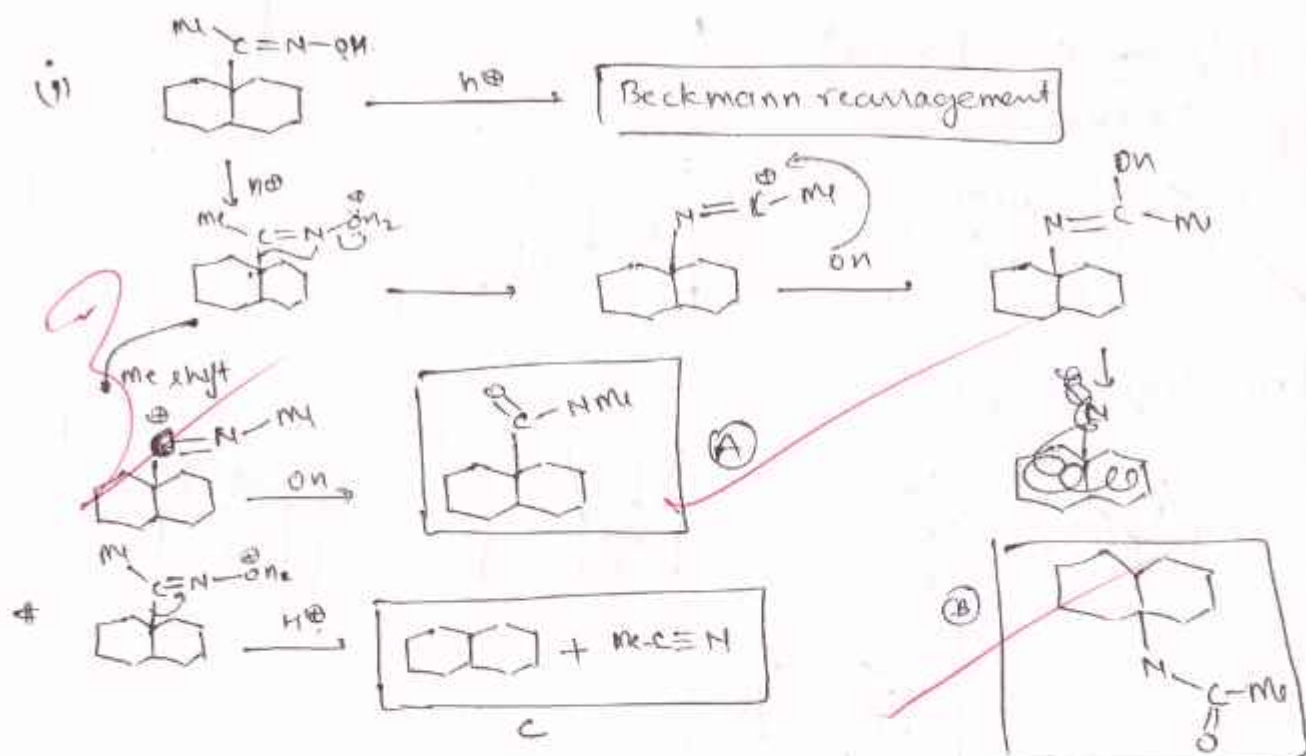
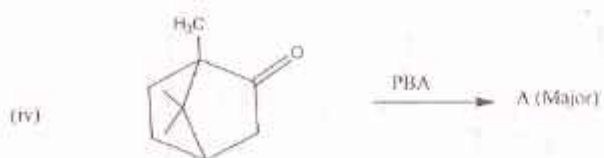
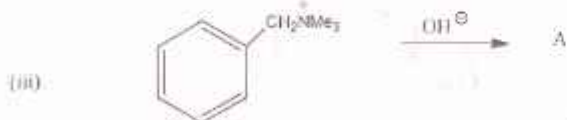
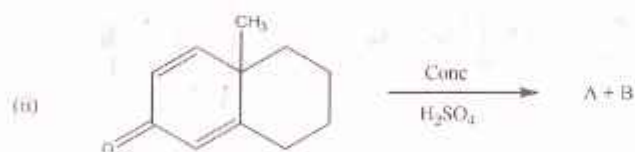
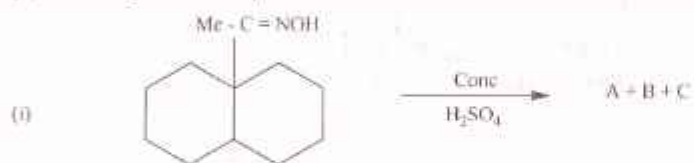
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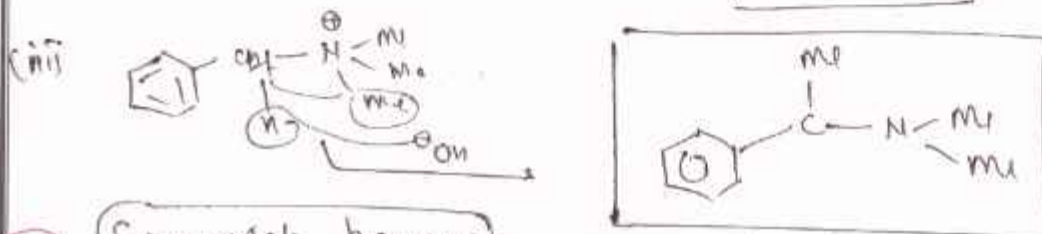
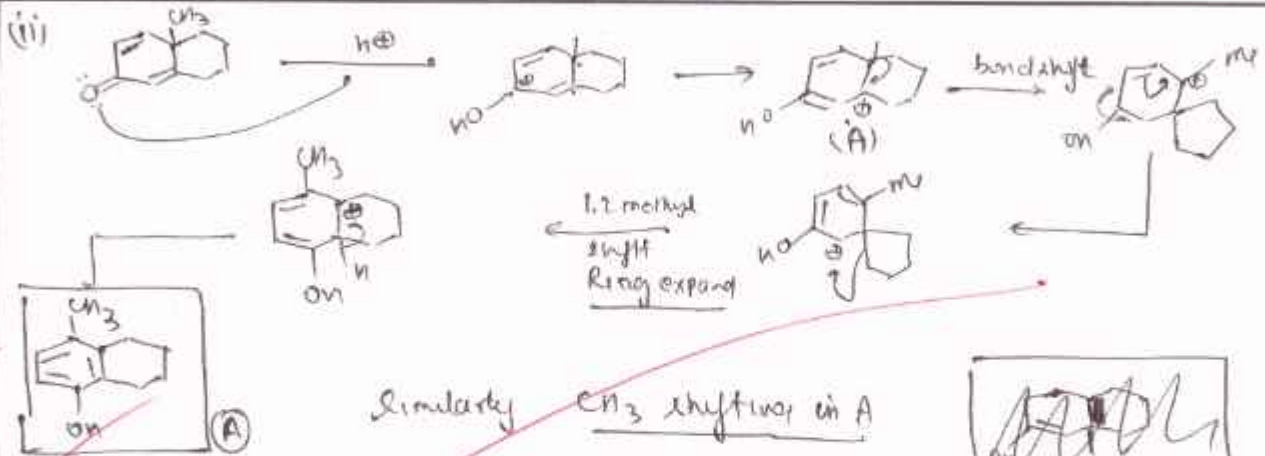
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(c) Identify the compounds and write the name of reaction involved. (20)



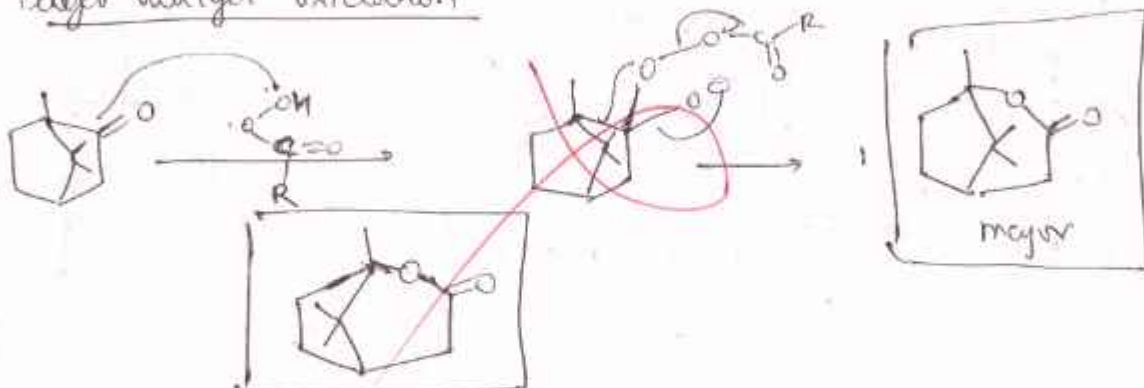
Diene - Phenol ~~Diene~~ **DIAS**



Commeret hauser
→ sigmatropic also



(iv) Bayer viltiger oxidation



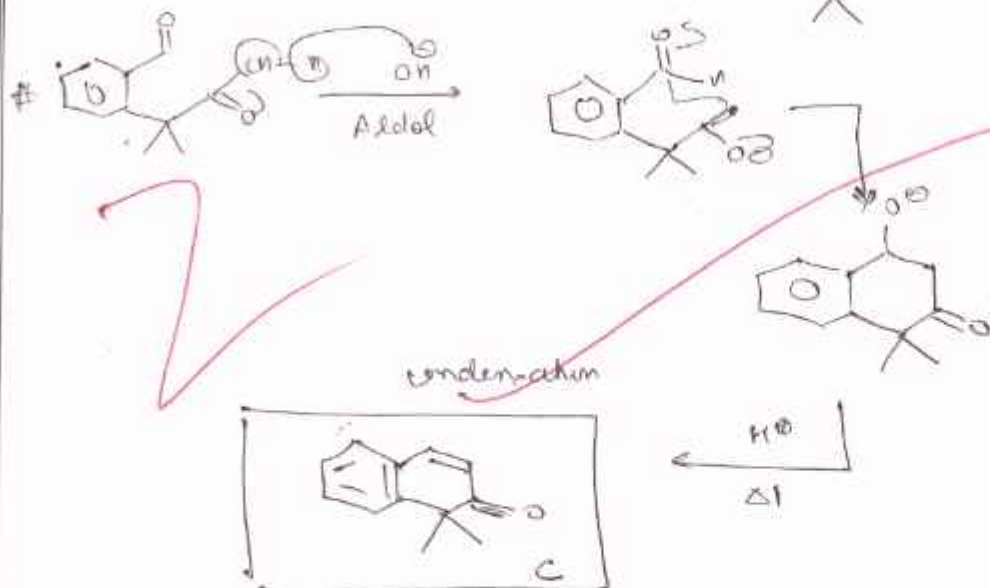
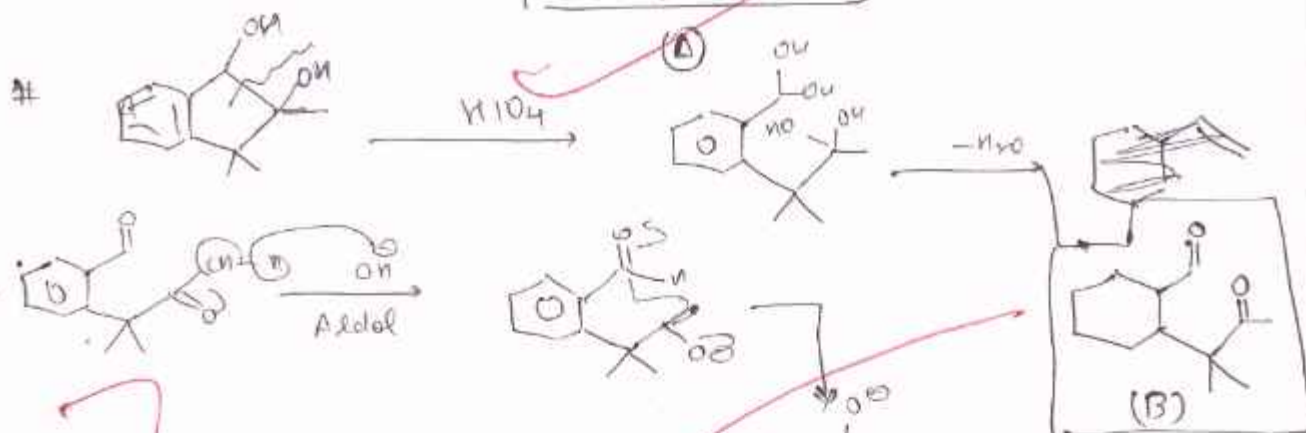
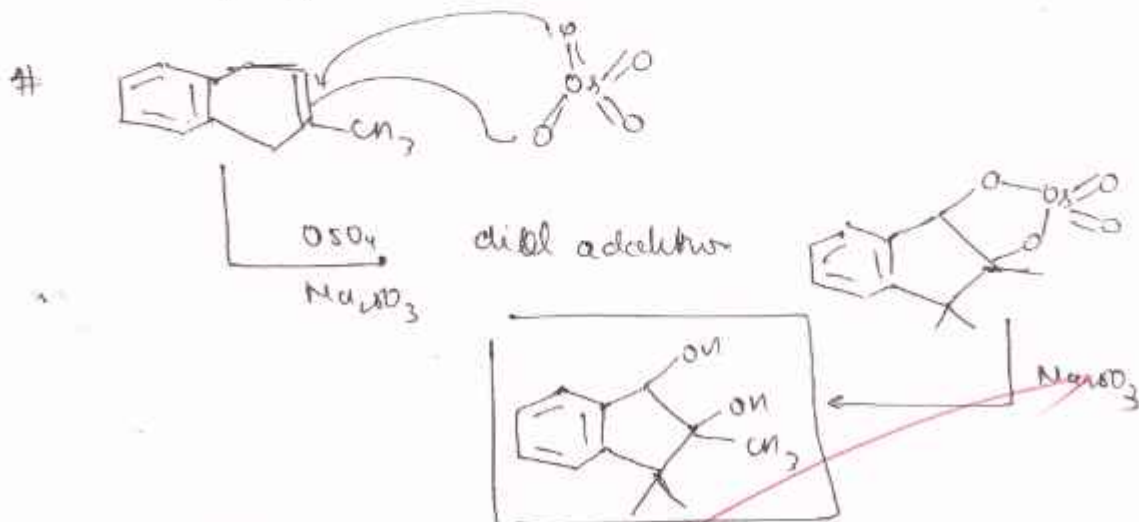
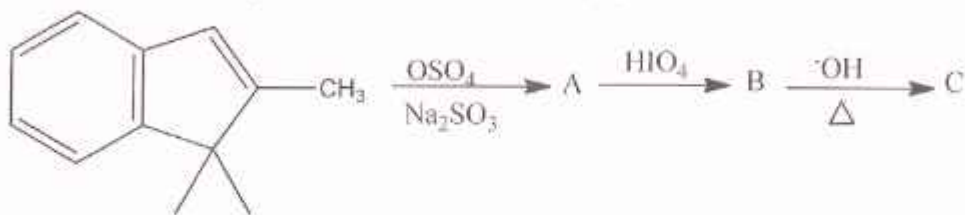
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(d) Complete the sequence of reaction. (10)



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