

## 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:- SAGAR JAIN

UPSC Roll no:-

Mobile Number.

Date :- 18/08/2024 (4:00 - 7:15 PM).

Dias Roll No.

#### Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	30	X	33	Y	27	31	31	

Signature of invigilator

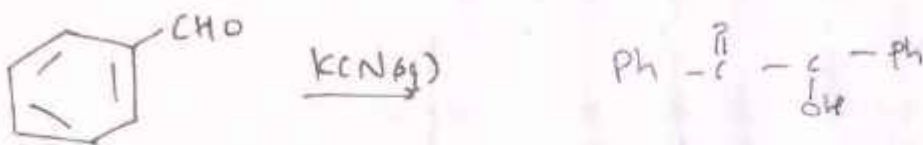
152  
Signature of  
Examiner

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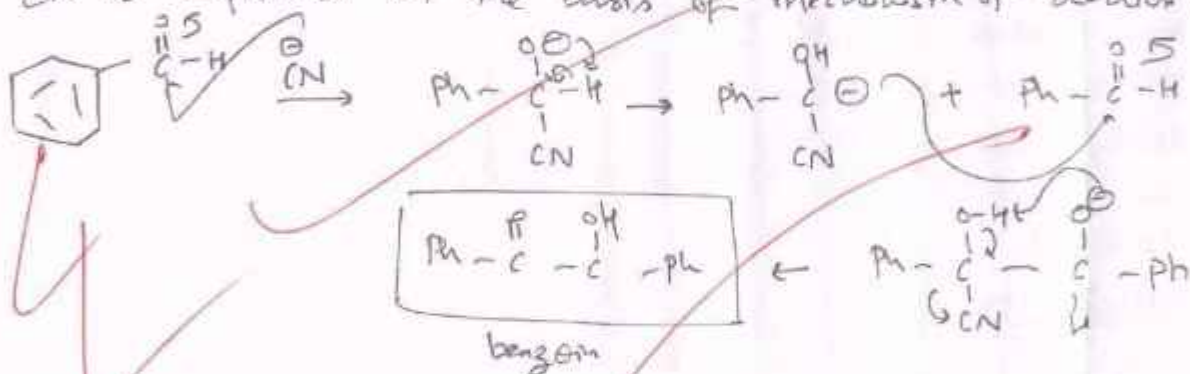
## Section- A

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

Benzoin condensation is a condensation reaction of carbonyl compound specific to benzaldehyde.



In this substitution of both electron withdrawing groups & electron donating groups reduces the rate of reaction. This can be explained on the basis of mechanism of reaction.



The reaction proceeds with nucleophilic attack of cyanide over carbonyl, then intramolecular proton transfer to give carbanion and then attack of this carbanion over other molecule.

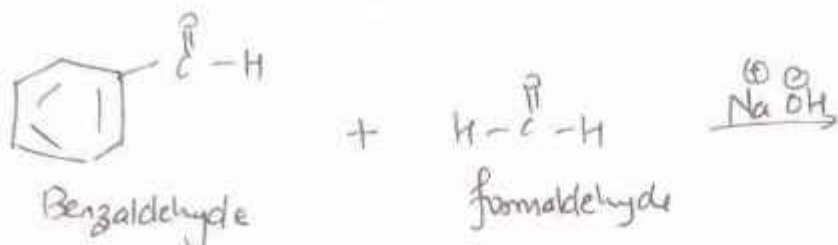


NO<sub>2</sub> being an ewg, reduces the nucleophilicity of carbanion formed, thus reduces the rate of attack. Thus, p-nitro

benzaldehyde does not follow benzoin condensation

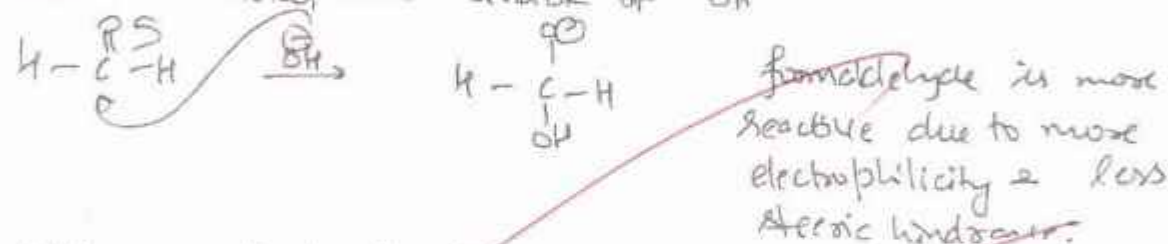
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(ii)  $C_6H_5CHO$  is refluxed in the presence of  $NaOH$  and excess  $HCHO$ . Write the major aromatic product. (5)

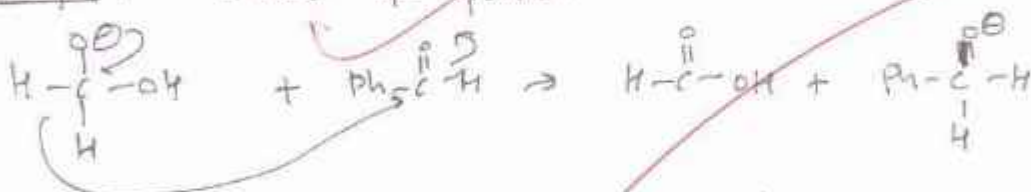


It is a reaction of non-enolizable aldehydes in basic medium. Cross-Cannizzaro reaction will take place in which more reactive aldehyde will get oxidised preferably.

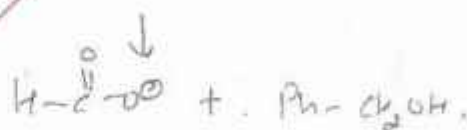
Step 1: nucleophilic attack of  $OH^-$



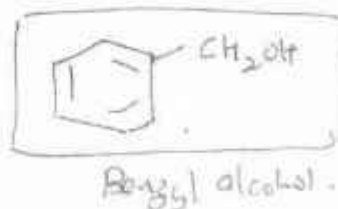
Step 2: attack of proton



Step 3: proton transfer

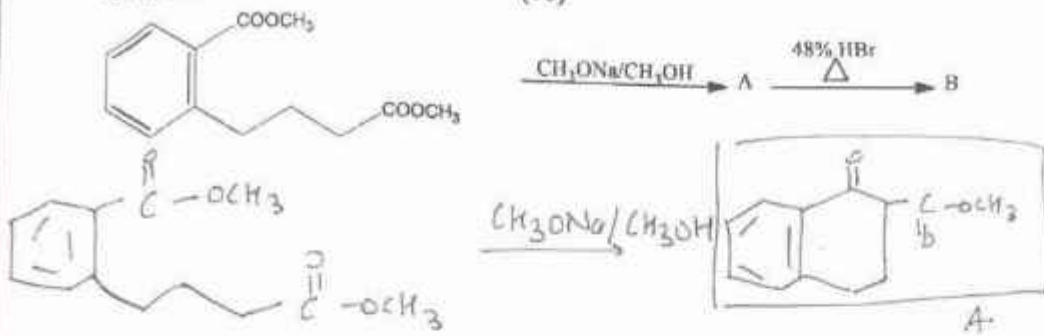


$\therefore$  major aromatic product  $\Rightarrow$

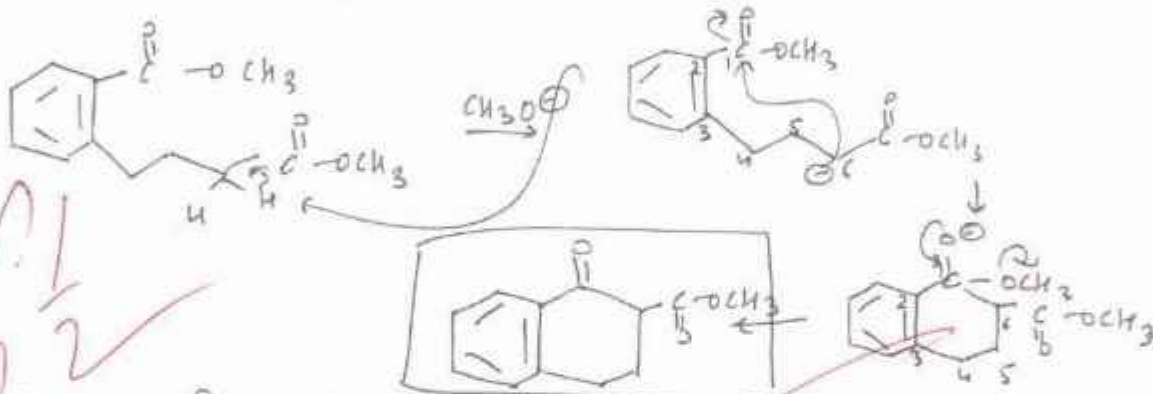


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(b) In the following reactions, identify the products A and B. Explain the mechanism of formation of A: (10)

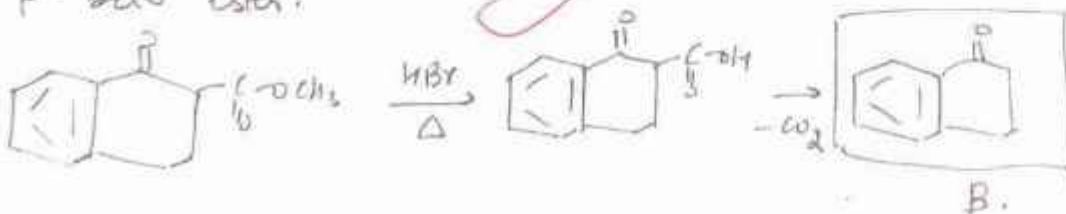


This is an example of dieckmann condensation.



Explanation for mechanism: A  $\beta$ -ester

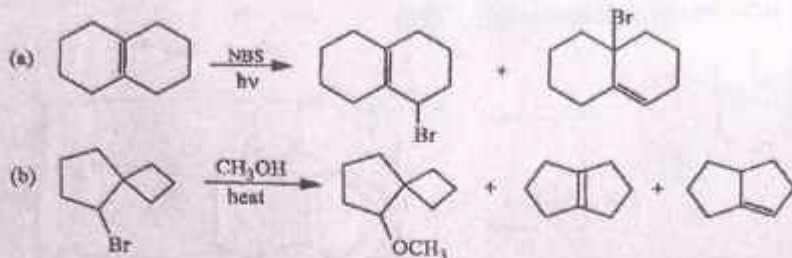
The reaction proceeds with abstraction of most acidic 'H' by base and results in formation of a carbanion intermediate. This carbanion leads to intramolecular nucleophilic attack over carbonyl carbon leading to formation of alkoxide ion, then departure of alkoxy group takes place and we get  $\beta$ -beta ester.



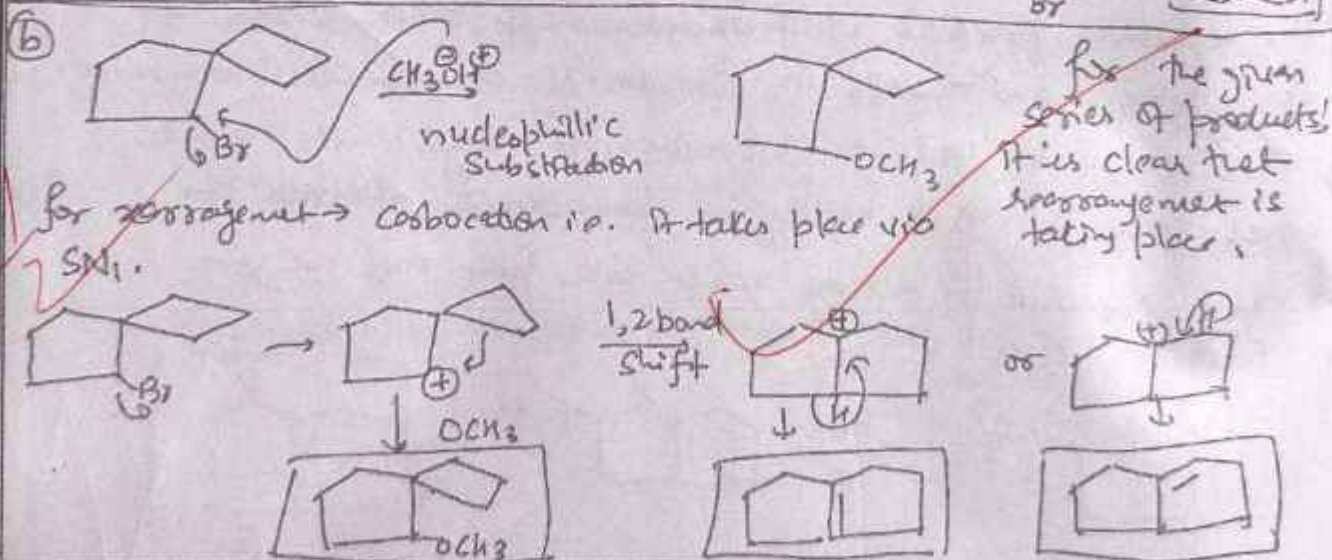
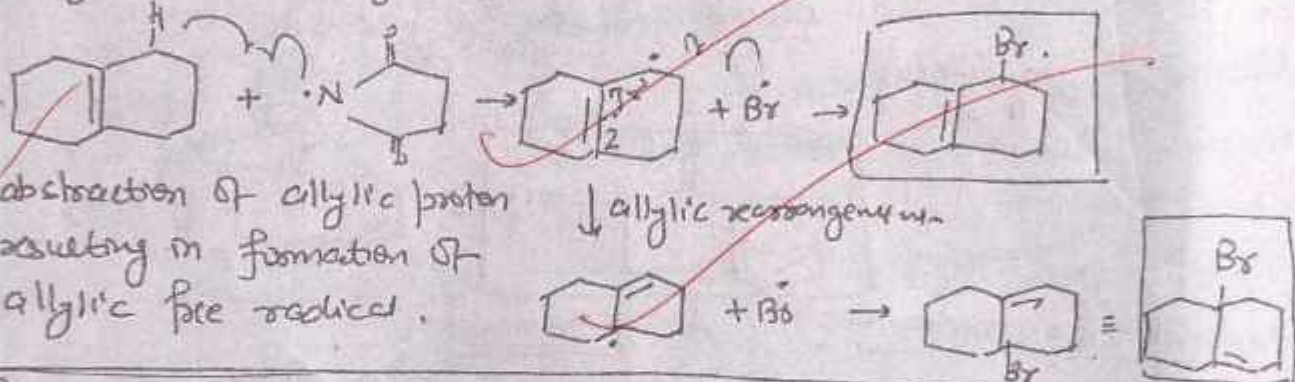
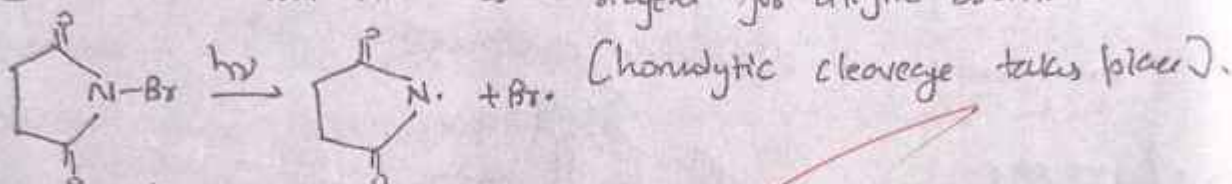


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(c) Propose mechanism to account for the observed products in the following reactions. In some cases more products are formed, but you only need account for the ones shown here. (10)

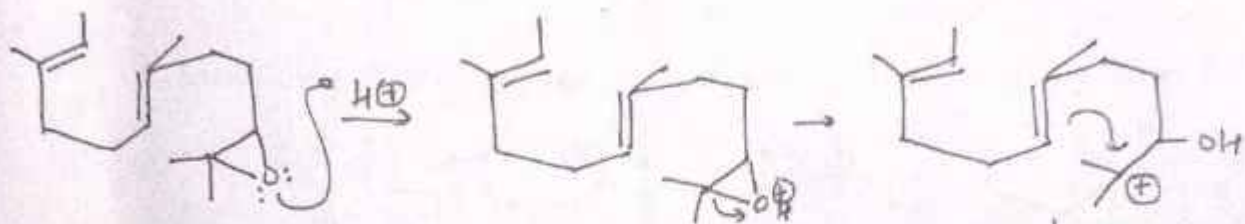
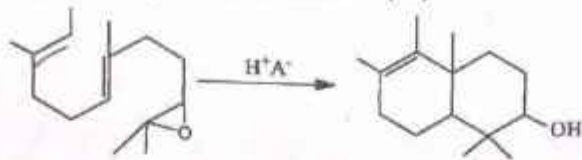


(a) N-bromo succinimide is a reagent for allylic bromination.



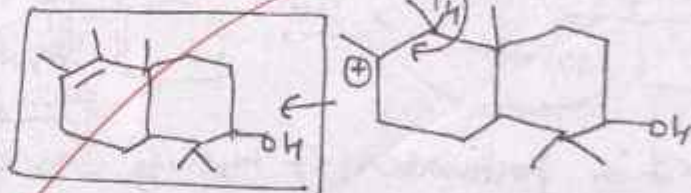
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(d) Under the right conditions, following acid-catalyzed double cyclization proceeds in remarkable good yields. Propose a mechanism. Does this reaction resemble a biological process you have seen? (10)



The reaction proceeds with epoxide ring opening. The ring opens in such a manner that more stable carbocation is formed.

Then Wagner rearrangement takes place twice leading to cyclisation.



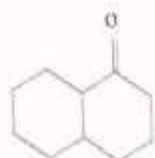
The final step is elimination to give the desired product.

Biological process resemblance: breakdown of products of incomplete oxidation.



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

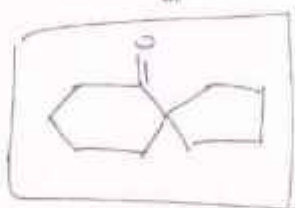
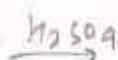
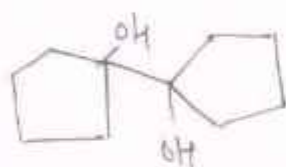


A.

B.

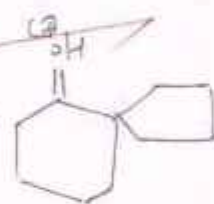
C.

D.



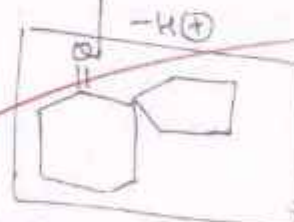
Vicinal diol

The given substrate is a 1,2 diol which in acidic medium undergoes Pinacol - Pinacolone rearrangement



push-pull effect

Step 1 is protonation of hydroxy (as both hydroxy groups are equivalent), attack can take place on any of them



then 1,2 bond shift takes place because of push pull effect. and then deprotonation gives ketone, which is a thermodynamically more stable product because of strong  $(C=O)$  bond.

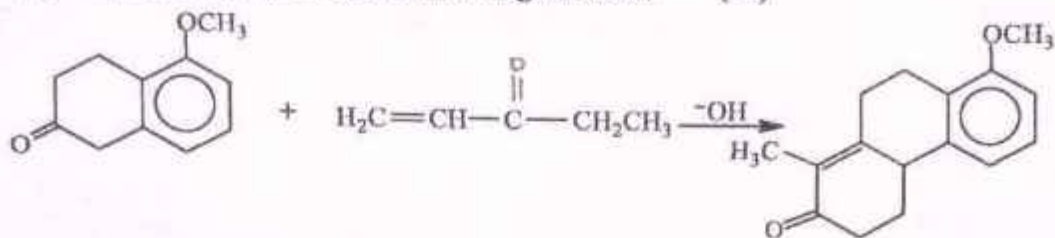
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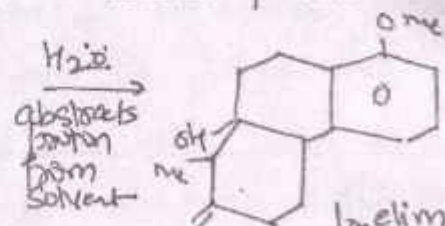
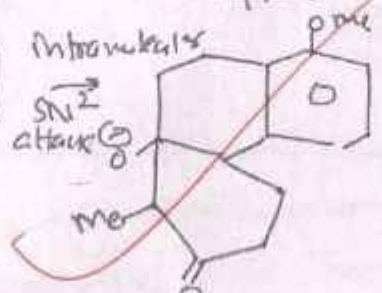
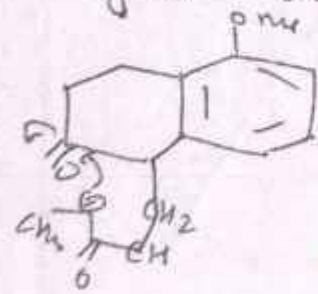
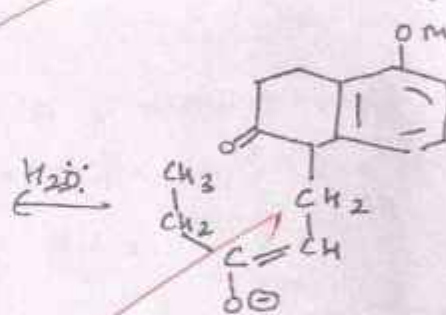
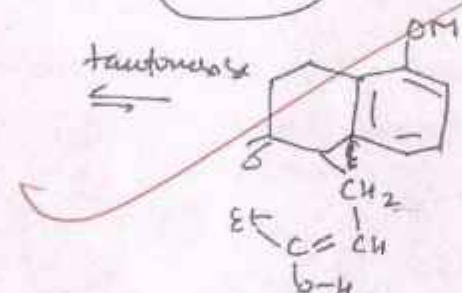
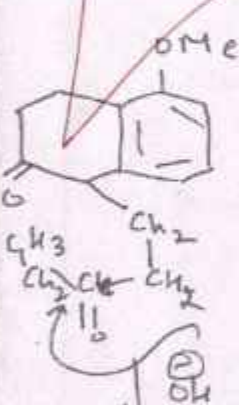
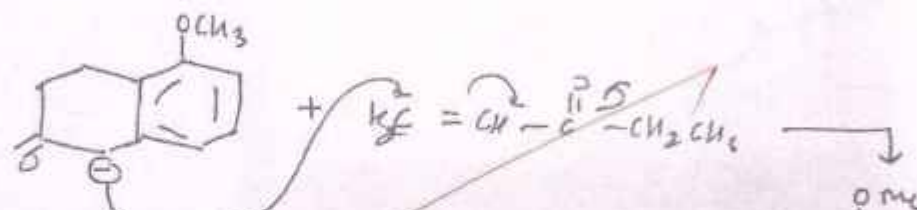
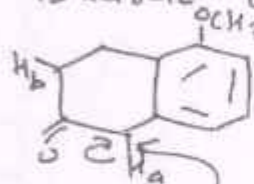
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3(a). Propose mechanism for the following reactions. (10)

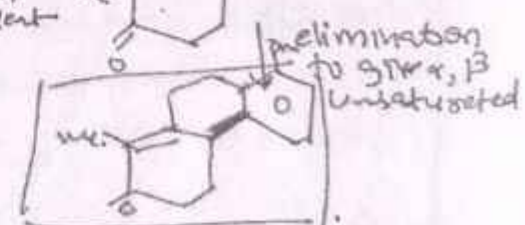


The reaction will proceed with Michael addition over  $\alpha, \beta$  unsaturated compound.

[ $\alpha$  is more acidic (H) because its conjugate base is resonance stabilized].



$\beta$ -hydroxy keto



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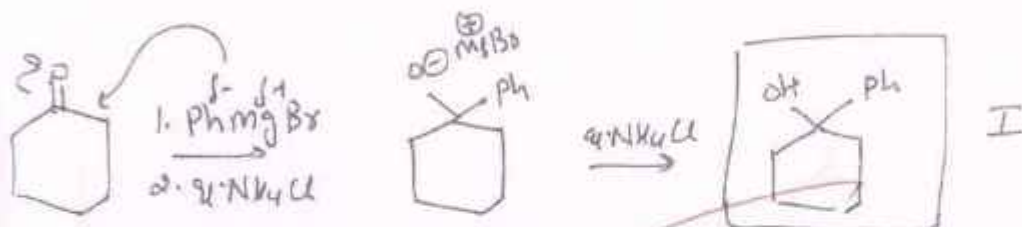
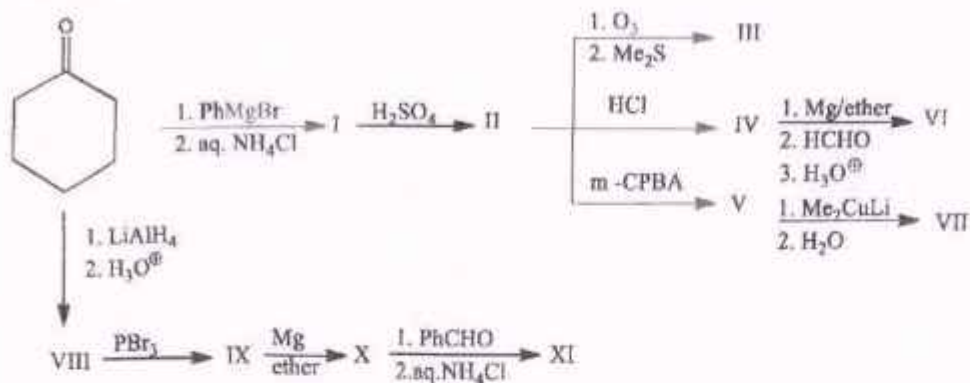
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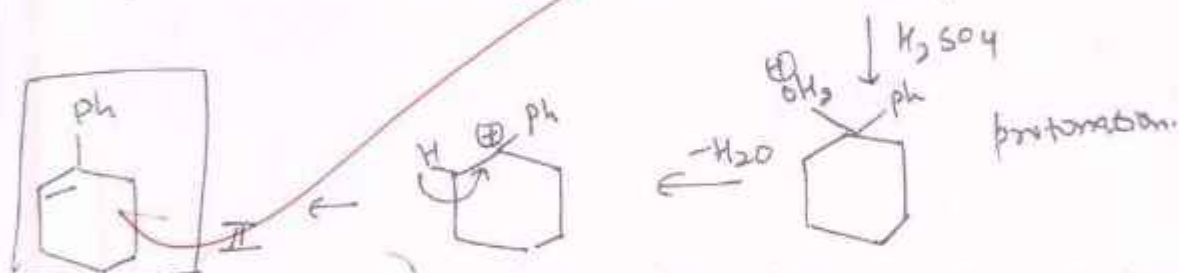


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(b) Identify the compounds I-XI in the following reaction sequence and indicate which of them are isomeric: (30)



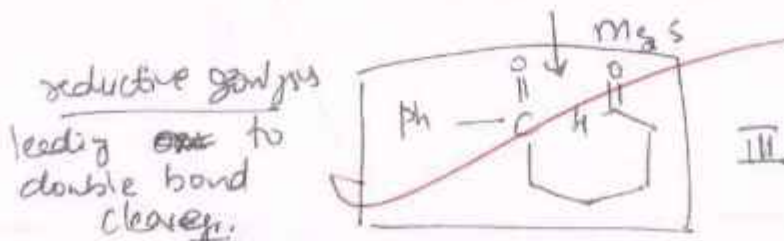
Grignard addition over polar C=O bond takes place.



acid catalysed dehydration takes place via E<sub>1</sub> mechanism.



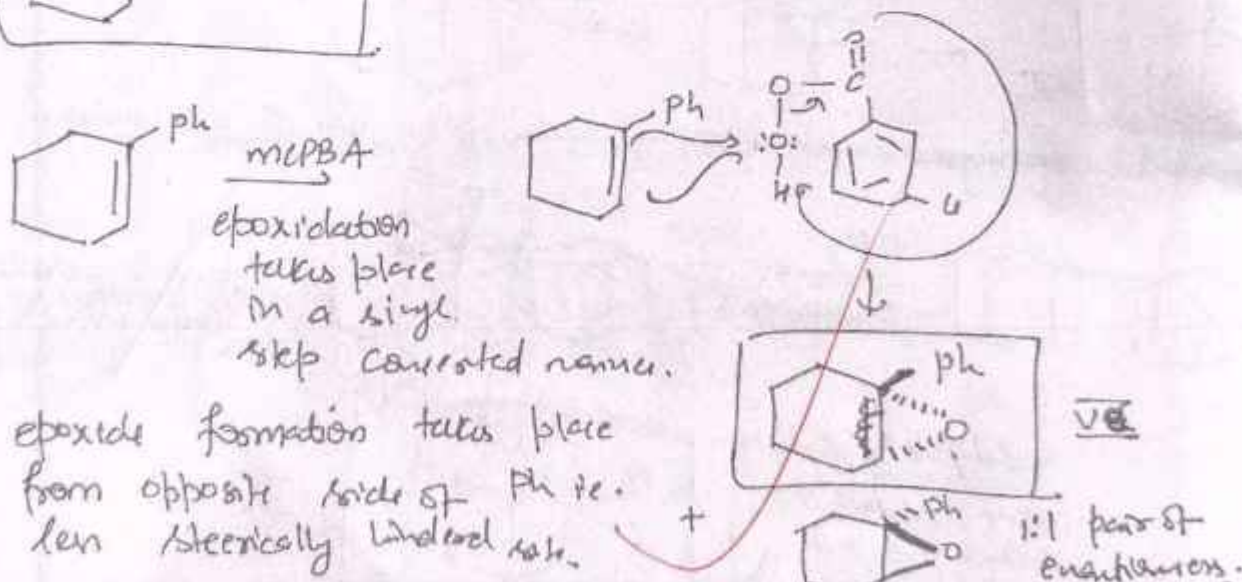
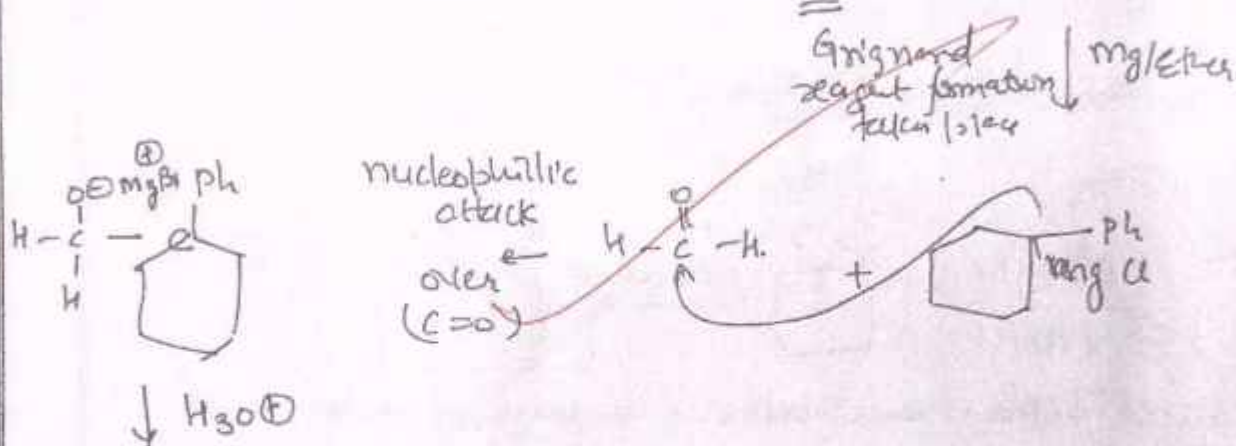
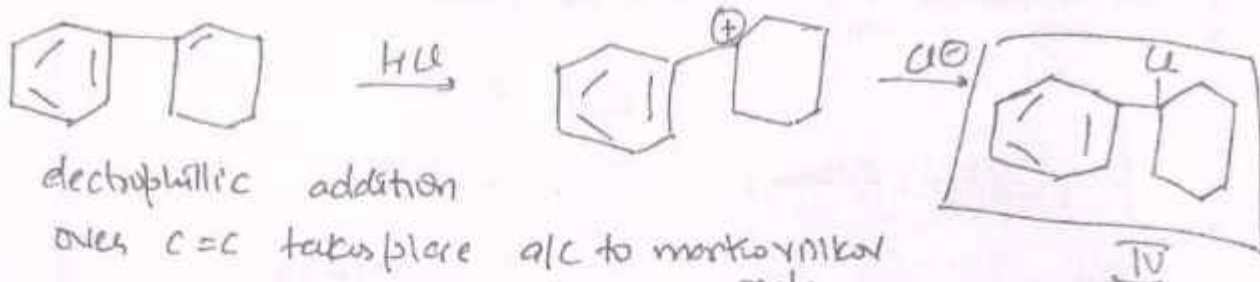
ozonide formation takes place



reductive analysis leading to double bond cleavage.

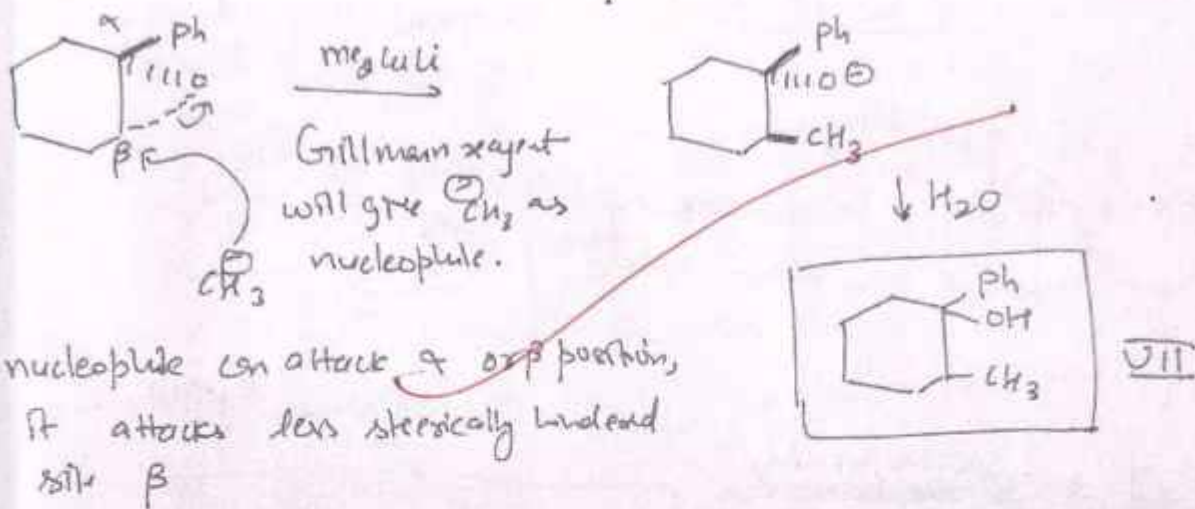
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# DIAS

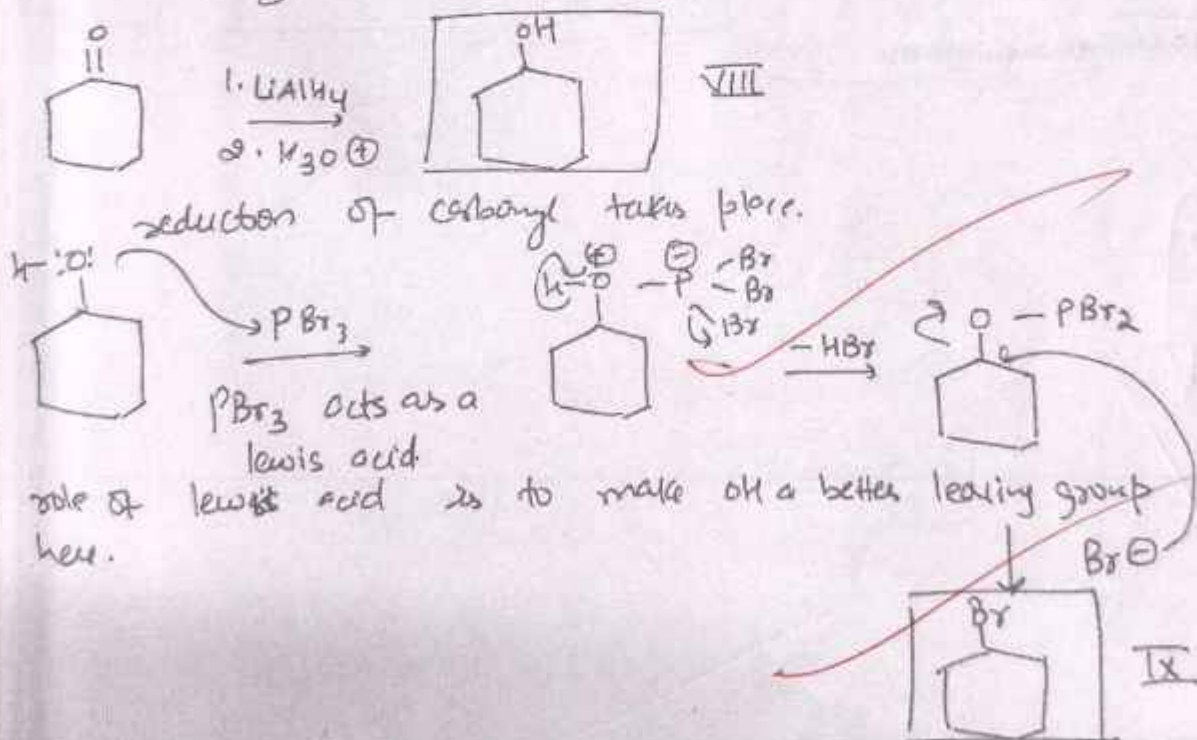


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As enantiomers are energetically similar, we can proceed with taking any one of them

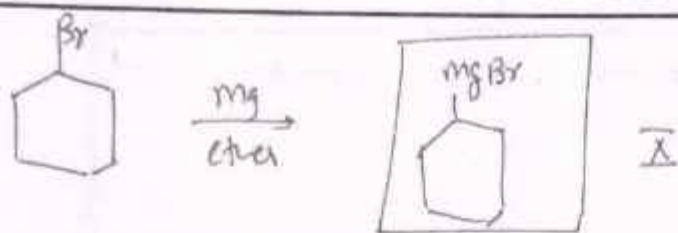


now, analysing the 2nd pathway

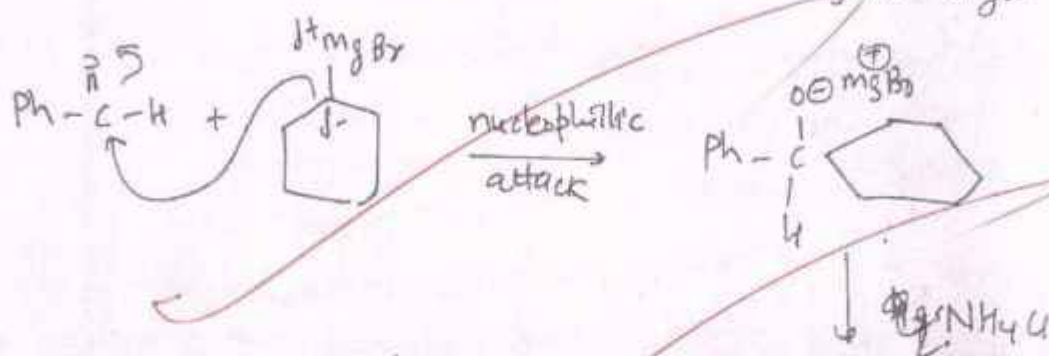




# DIAS

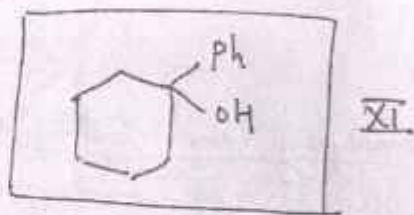


formation of organometallic compound which is Grignard reagent



XI & I are similar

IV & VII are formed in 1:1 molar ratio



22

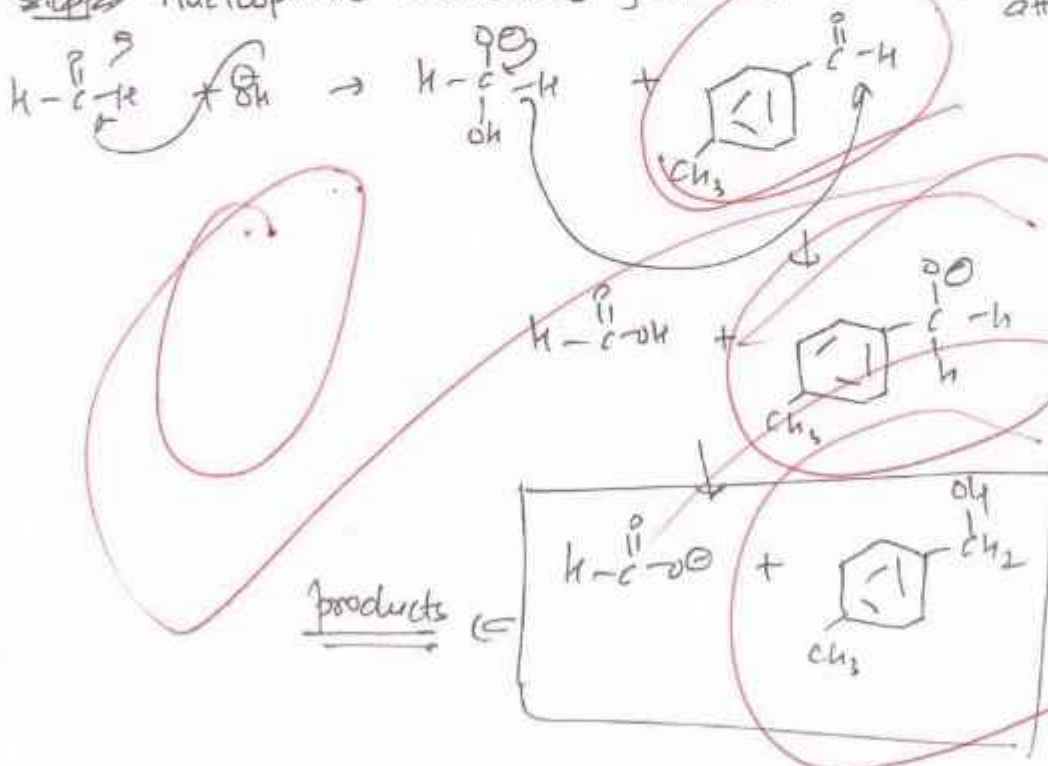
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(c) A mixture of formaldehyde and p-methoxy benzaldehyde is treated with Conc. KOH. Write the products of reaction. (5)



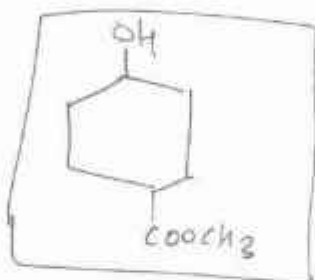
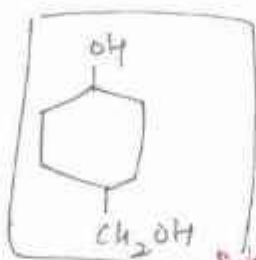
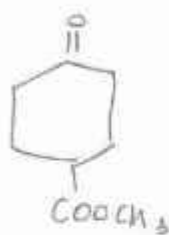
This is a case of cross-Cannizzaro reaction i.e. a disproportionation reaction in which more reactive aldehyde undergoes oxidation.

~~Step 1~~ nucleophilic attack over formaldehyde, then, proton attack



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



Aluminium  
Lithium is max electropositive metal; therefore corresponding hydride ion is max nucleophilic. It is more reactive & reacts with less reactive ester as well.

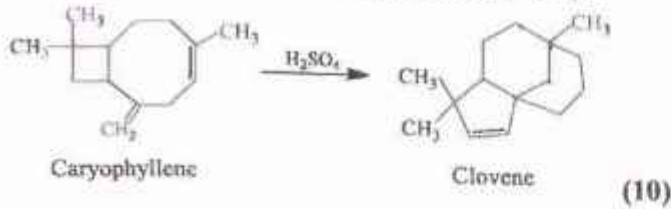
Boron is less electropositive, therefore, corresponding hydride is less reactive & attacks only more reactive aldehyde/ketone/acid chloride.



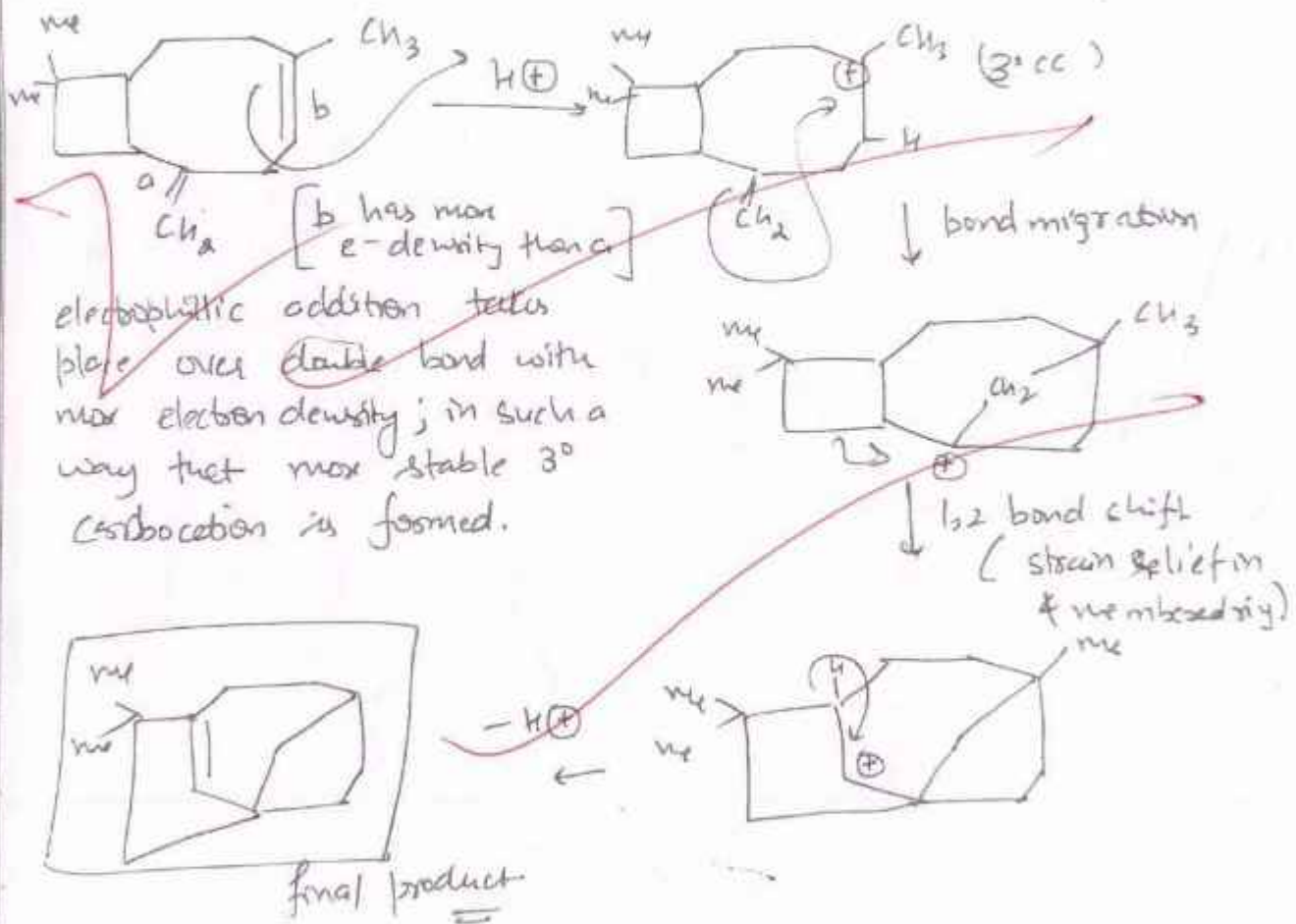
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## Section- B

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



This is a case of Wagner-Meerwein rearrangement.



# DIAS

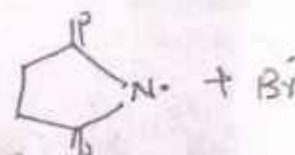
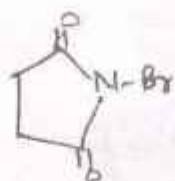
(b) Bromination of 1,5-cyclooctadiene with N-Bromo succinimide (NBS) gives a mixture of two constitutional isomers of  $C_8H_{11}Br$ . Suggest reasonable structures for these two isomers. (10)



1,5-Cyclooctadiene



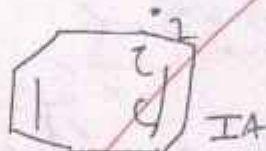
NBS (N-bromo succinimide)  $\equiv$



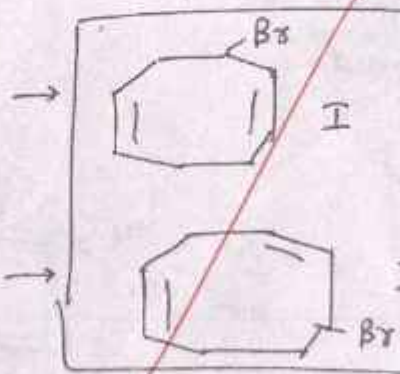
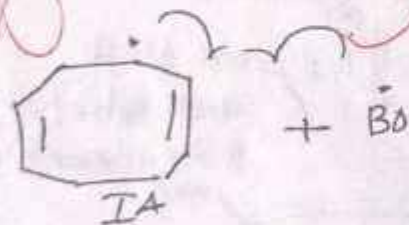
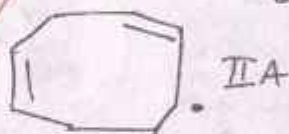
generates free radical on heating.



abstraction of proton from allylic site to give allylic free radical



allylic rearrangement



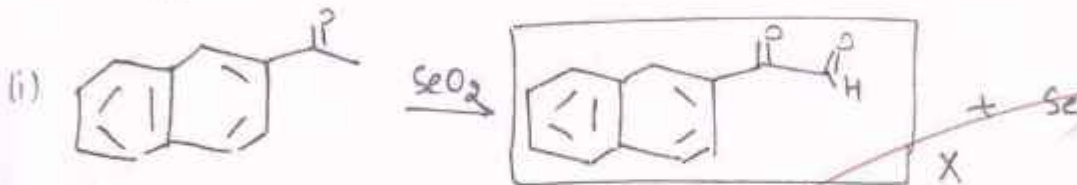
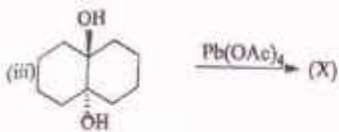
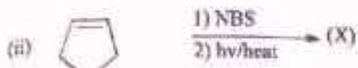
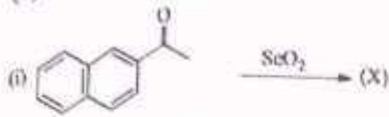
8-bromo 1,5-cyclooctadiene

6-bromo 1,4-cyclooctadiene

the two isomers are formed by ~~addition~~ bromination via free radical intermediate which can undergo allylic rearrangement

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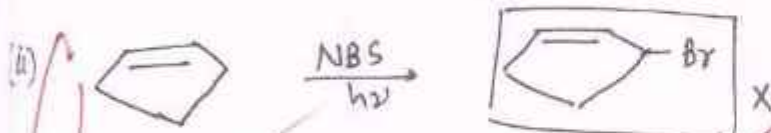
(c) Identify the major product (X) formed in the following reactions: (10)



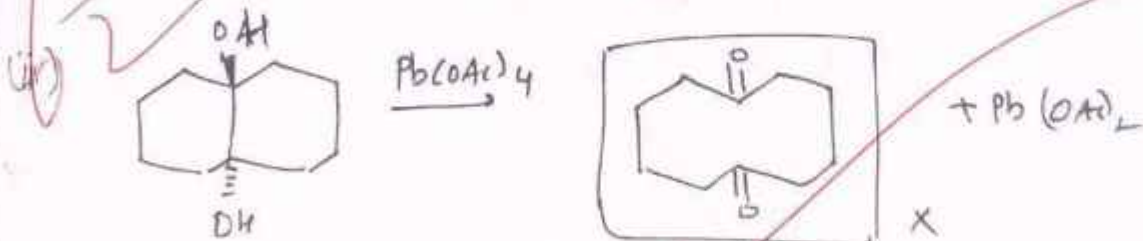
$\alpha$ -oxidation takes place via allylic reaction.

The reaction takes place via enol form.

$\text{SeO}_2$ ;  $\text{Se}^{+4}$ ;  $\text{Se}^0$  Selenium gets reduced from +4 to 0 oxidation state.



allylic bromination via free radical intermediate



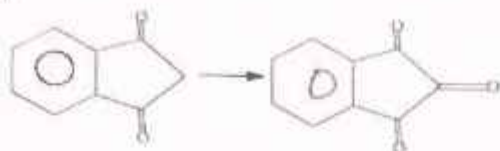
Oxidation takes place as Lead tetraacetate is a strong oxidizing agent. Pb reduces from +4 to +2 o.s.



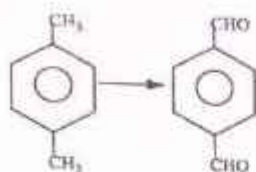
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(d) Write the reagents required for the following conversions. (10)

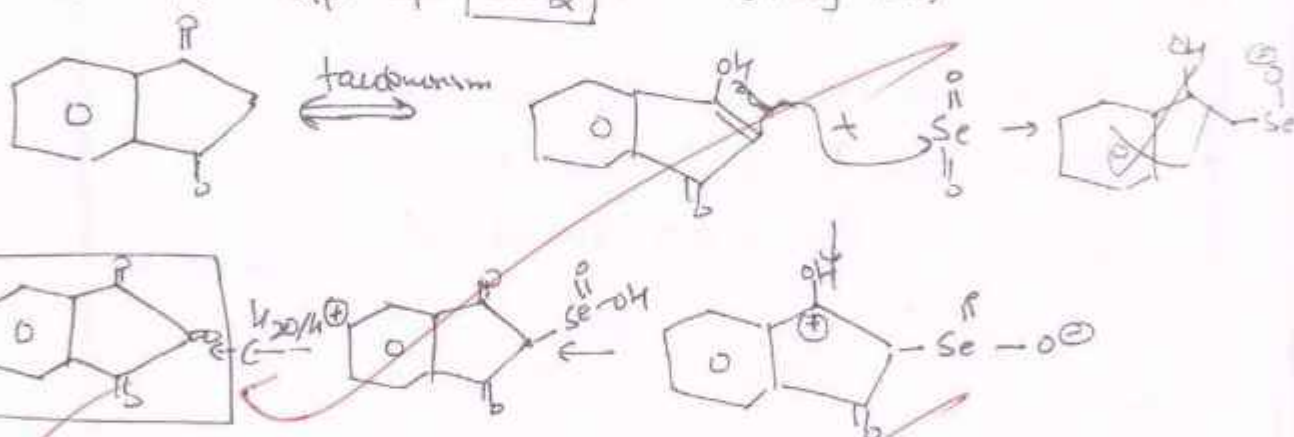
i)



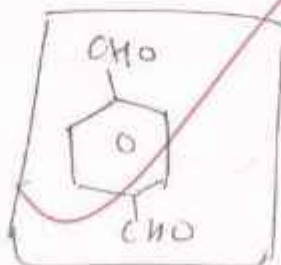
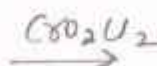
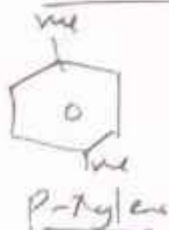
ii)



(i) this is an example of  $\alpha$ -oxidation, it can be done with the help of  $\text{SeO}_2$ . (Riley Pan)



(ii) oxidation of methyl group to aldehyde group is taking place; this can be done with the help of Etard reaction.



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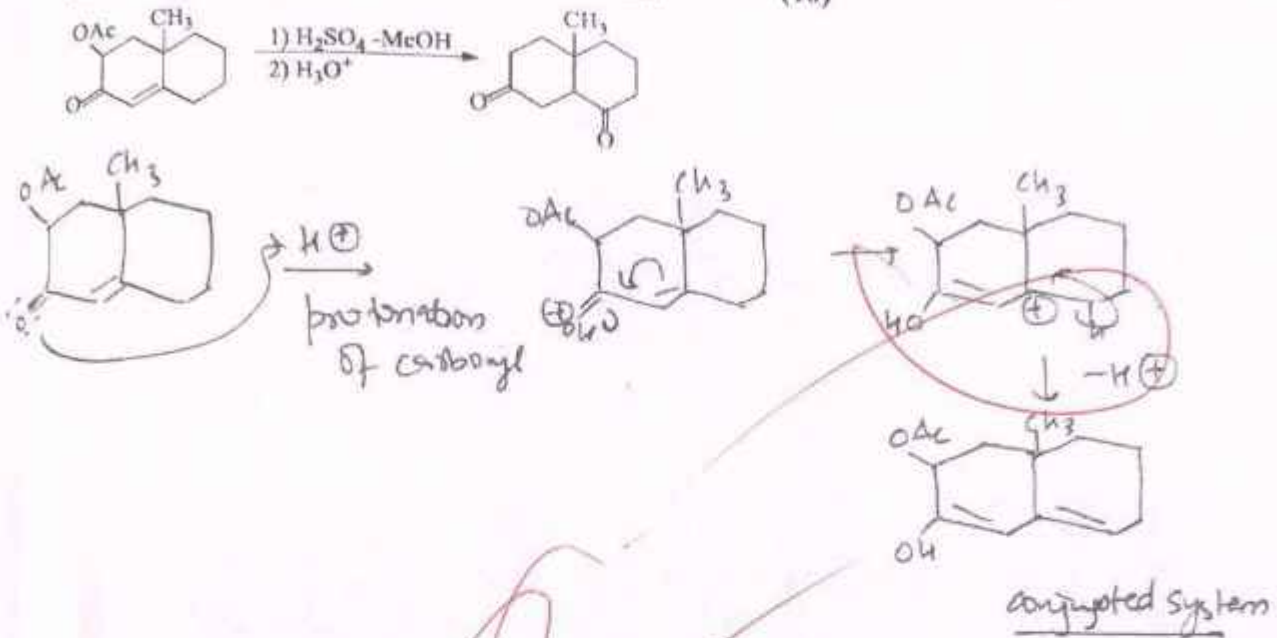
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# DIAS

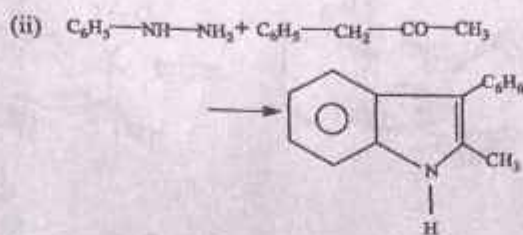
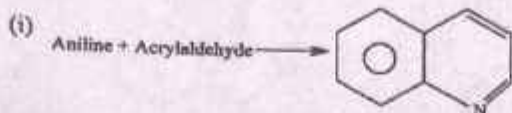
(e) Write down mechanism for below conversion.

(10)

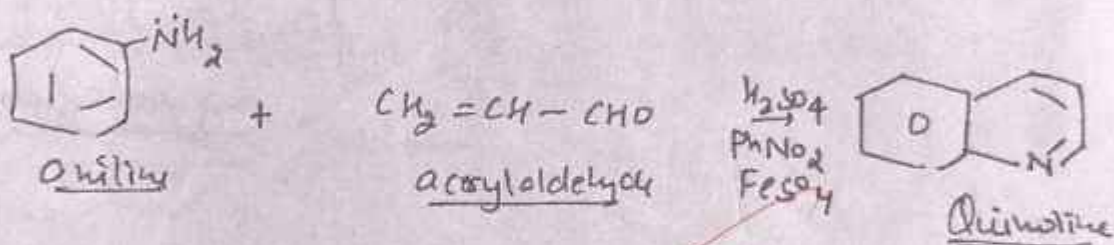


# DIAS

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

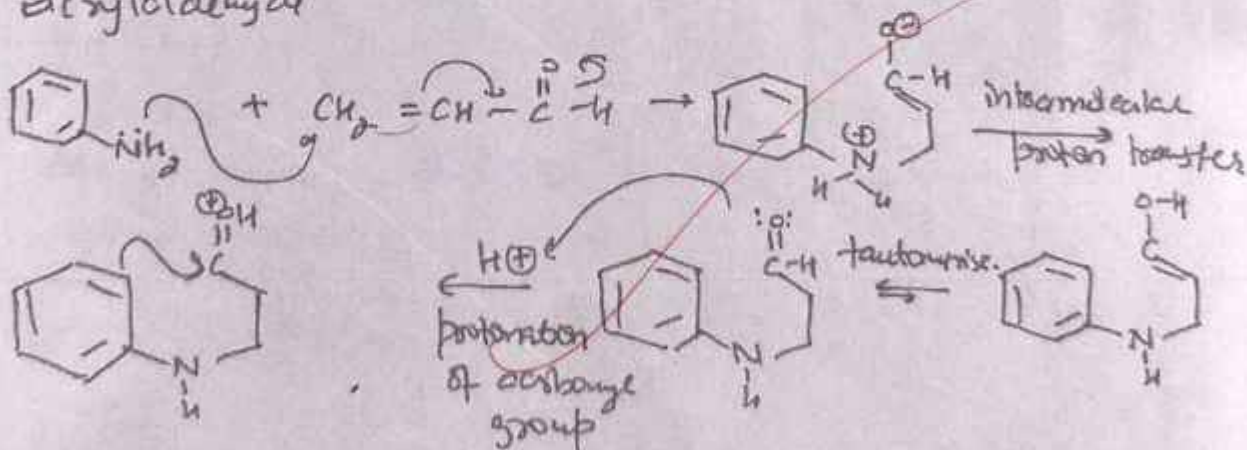


(1)



This is Skraup synthesis of Quinoline.

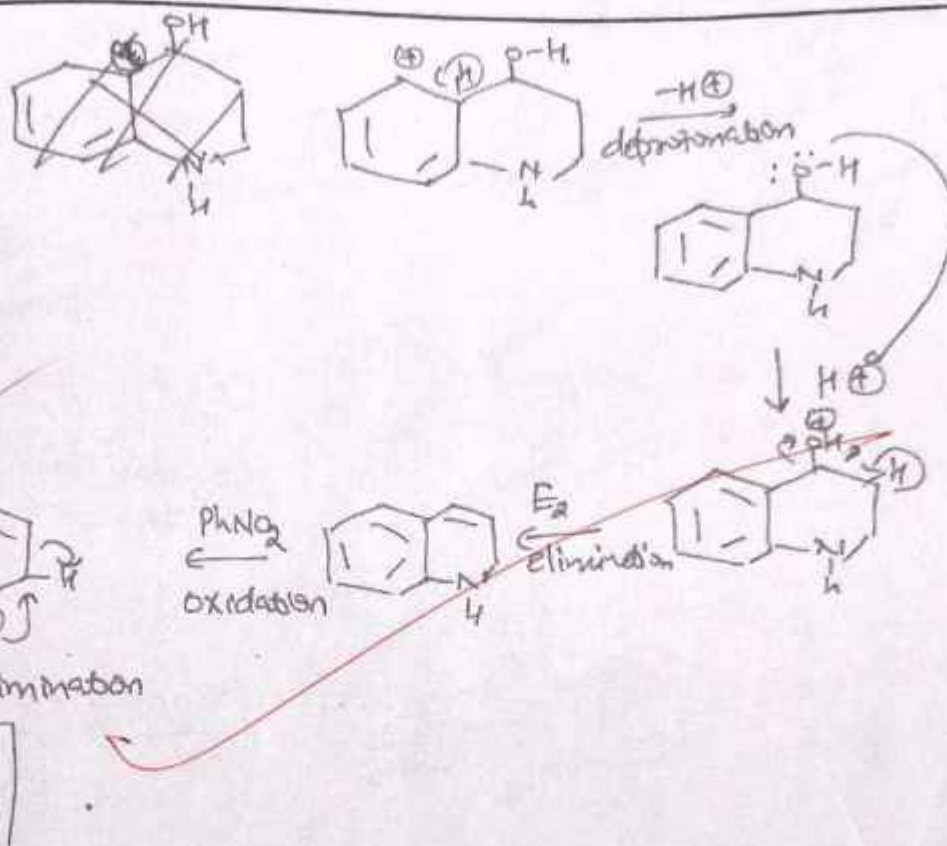
Reaction proceeds with Michael addition of aniline over acrylaldehyde



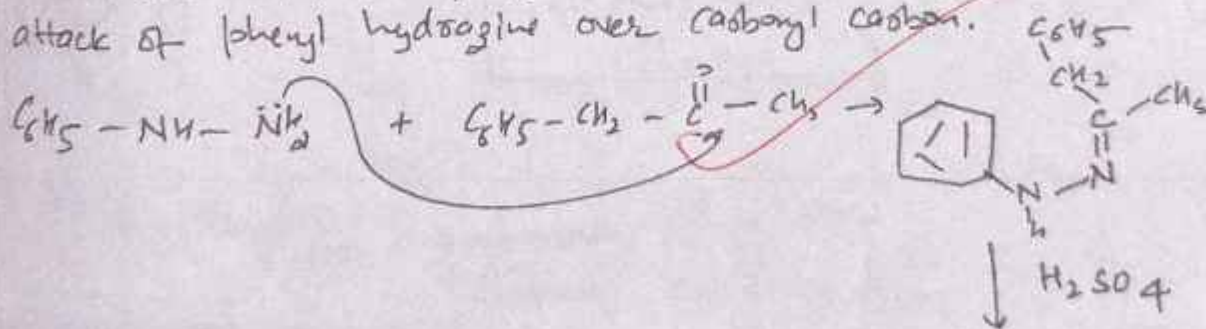


# DIAS

Reidel (soft) ring closing take place.

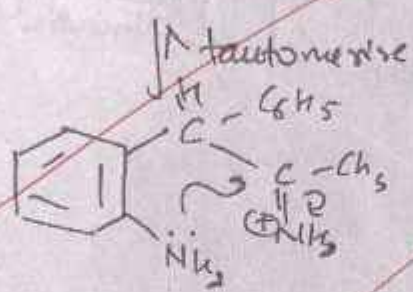
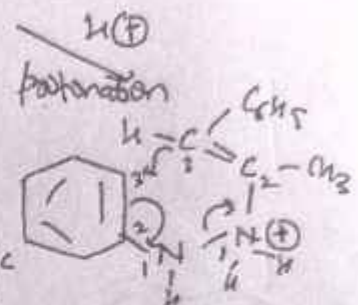
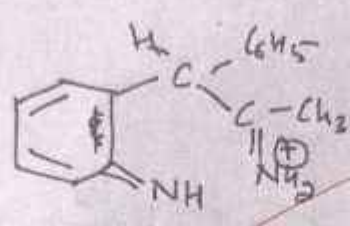
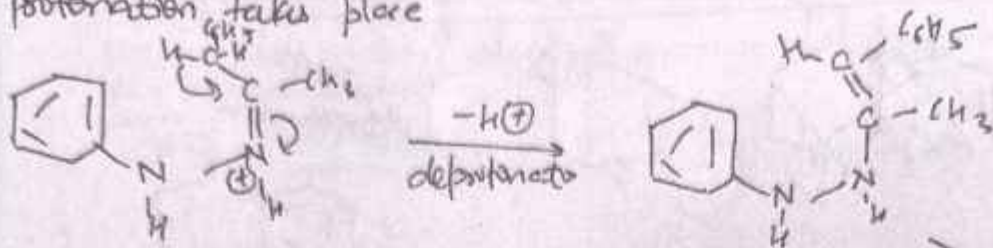


(ii) This is an example of Fischer indole synthesis which take place via series of protonation, deprotonation, [3,3] sigmatropic shift, tautomerism, SN<sup>2</sup> attack & E<sup>2</sup> elimination in the phenyl hydrazine formed by nucleophilic attack of phenyl hydrazine over carbonyl carbon.

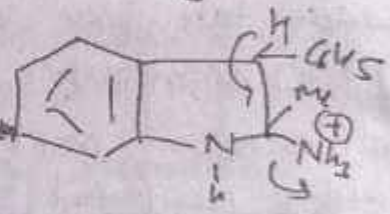
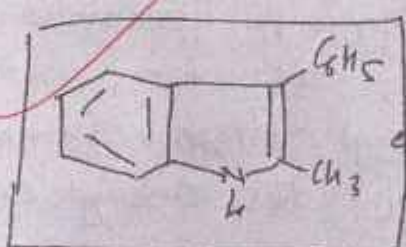
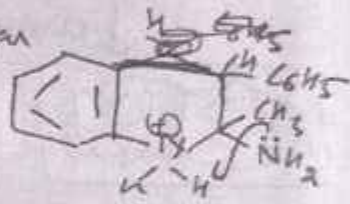


# DIAS

protonation takes place



intramolecular SN2





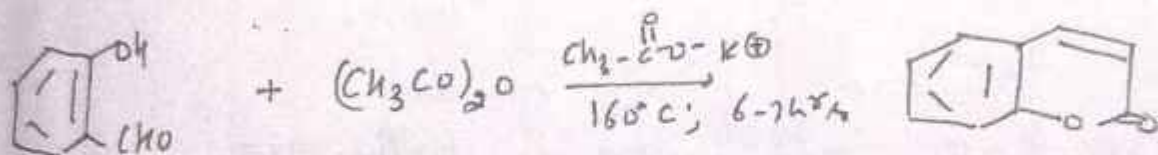
# DIAS

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

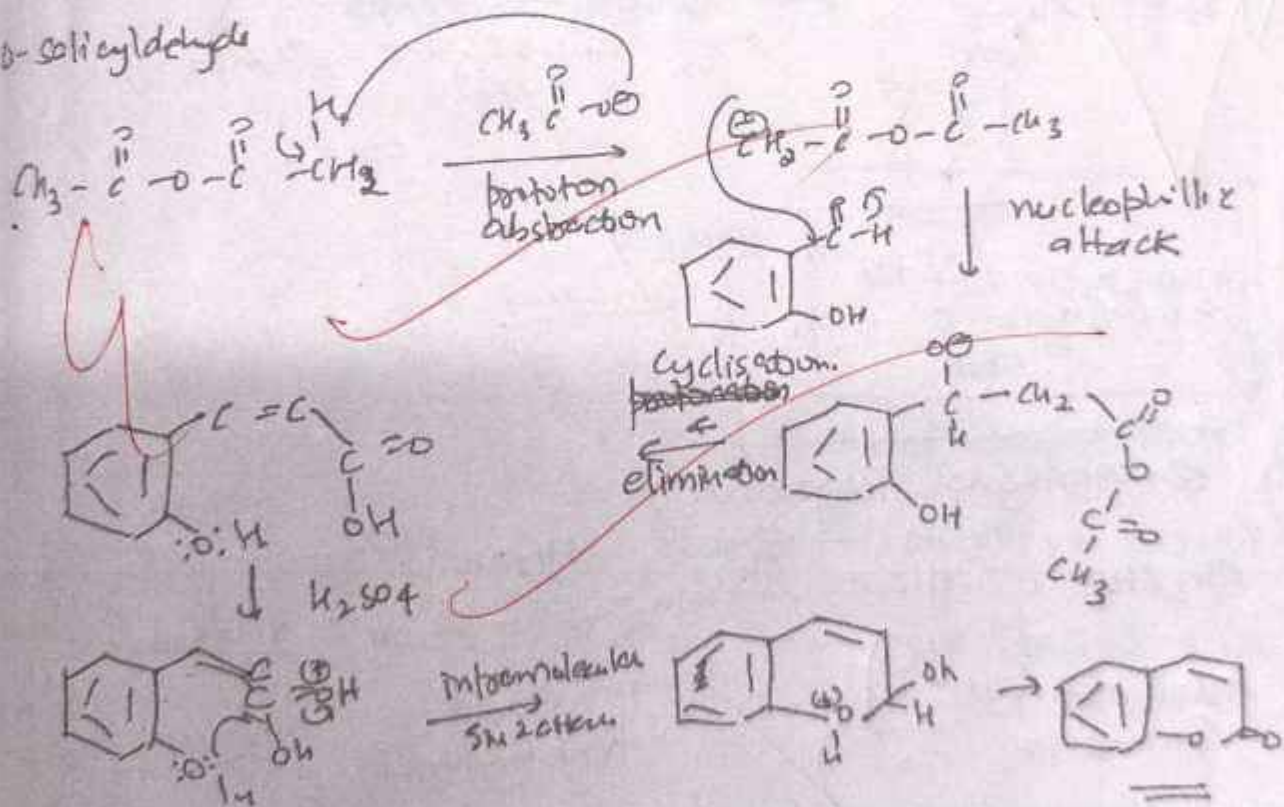
- (i) Coumarin by Perkin condensation
- (ii) Citric acid by Reformatsky reaction.
- (iii) PETN by Aldol condensation.
- (iv) 2-carbethoxy cyclohexanone



It can be synthesized with the help of Perkin condensation.

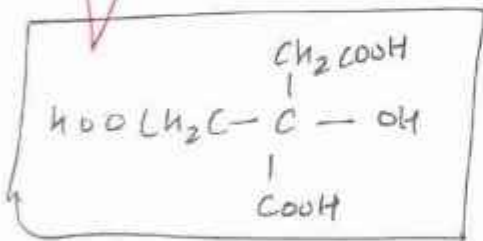
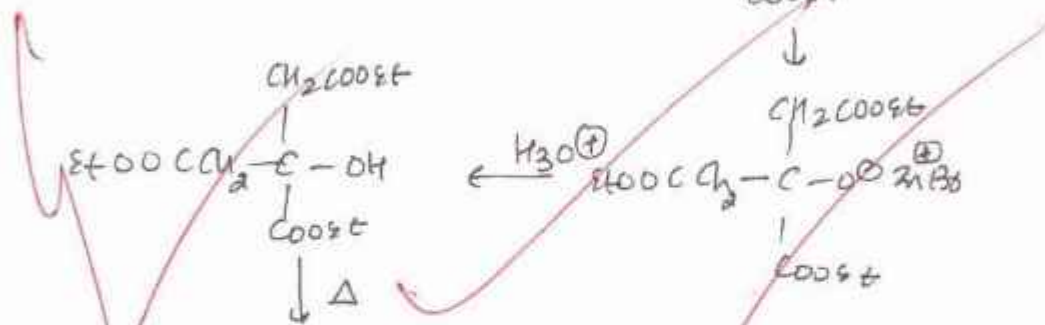
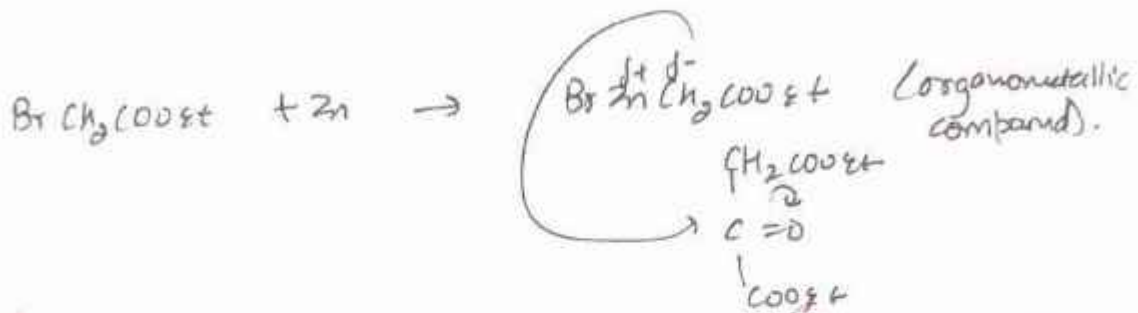
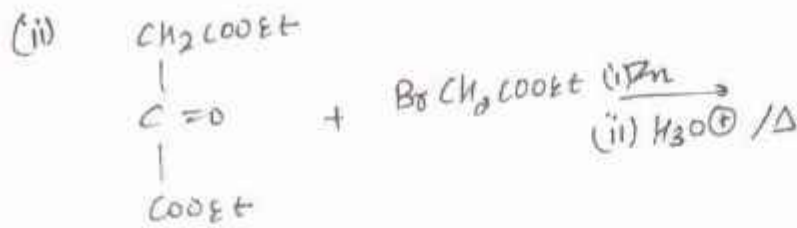


o-salicylaldehyde



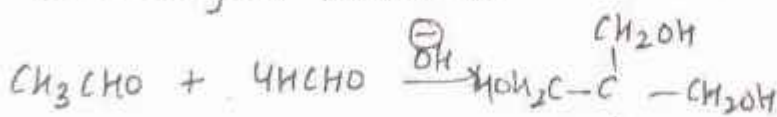


# DIAS



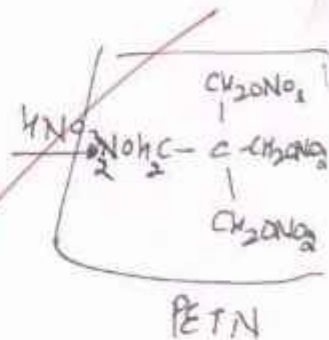
α-HC acid

(iii) Pentaerythritol Tetranitrate

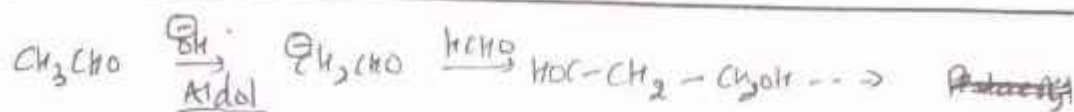


Aldol followed by Cannizzaro

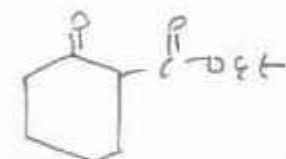
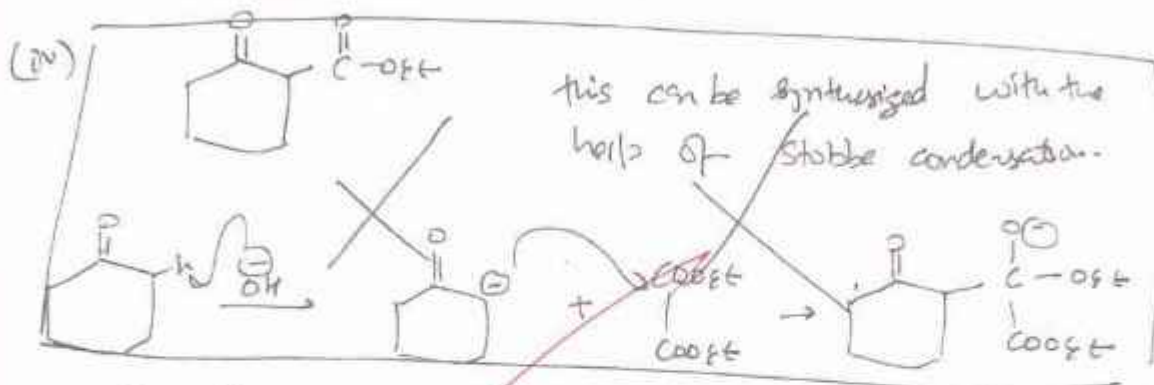
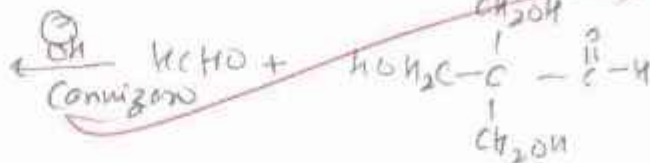
Pentaerythritol



# DIAS



Pentose  
↓ HNO<sub>3</sub>  
PETN.

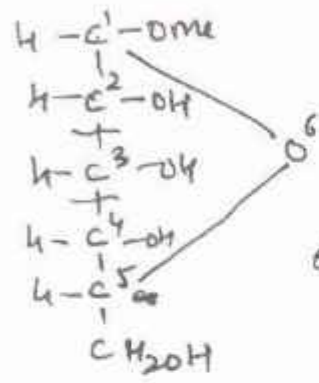


2-cosbethoxy cyclohexanone

# DIAS

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

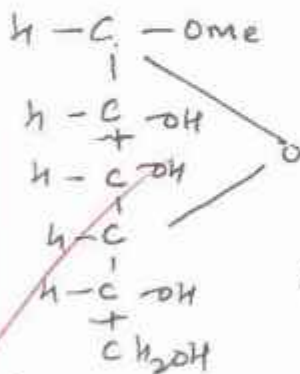
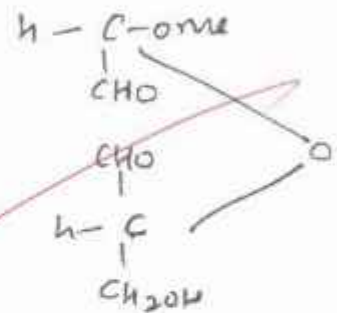
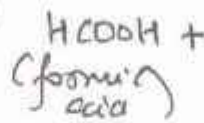
Glucose has different ring sizes in pyranose (6-membered) and furanose (5-membered) and these two can be distinguished with the help of Meerwein reaction.



Glucose pyranose

Periodic acid ( $\text{HIO}_4$ ) leads to oxidative cleavage of vicinal diol.

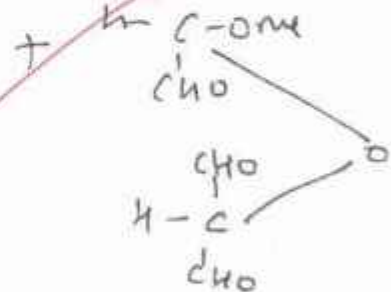
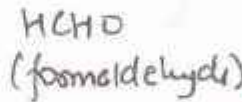
$\xrightarrow{\text{HIO}_4}$   
6 membered ring



Glucose-furanose

$\xrightarrow{\text{HIO}_4}$

5 membered ring



$\therefore$  In case of pyranose, we get formic acid and in case of furanose we get formaldehyde. In case of glucose, we get formic acid,  $\therefore$  we can say that it exists in pyranose structure.



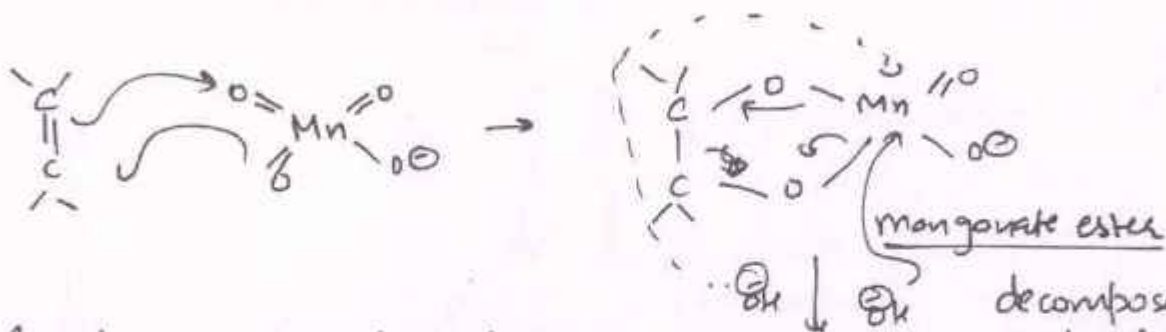
# DIAS

7. (a) Discuss the stereo specificity of diol formation by  $\text{KMnO}_4$  &  $\text{OsO}_4$ . Which is more better. How will you differentiate cis & trans isomer of 1,2-cyclohexane diol. (15)

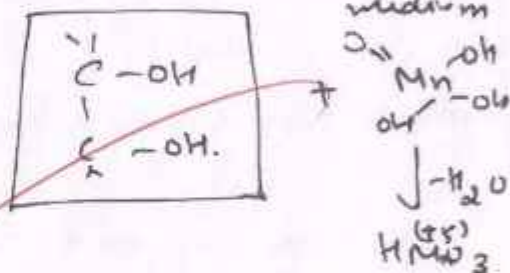
Both  $\text{KMnO}_4$  &  $\text{OsO}_4$  are oxidative agents which do dihydroxylation over  $(\text{C}=\text{C})$  bond in a syn-manner.

(17)

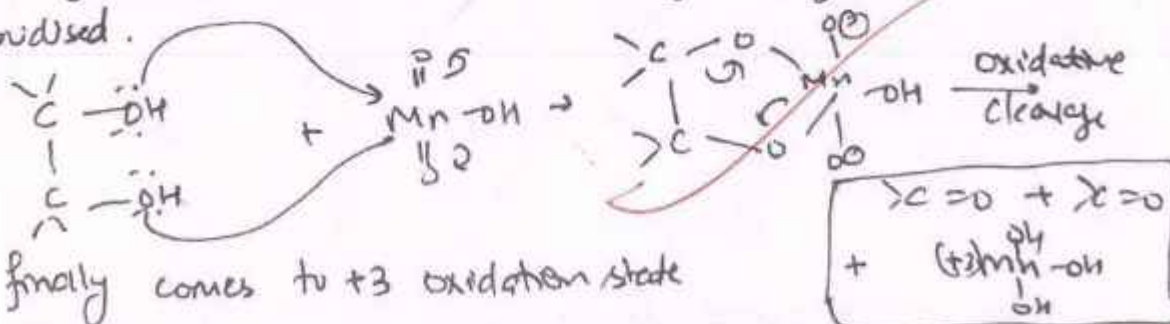
Diol formation by  $\text{KMnO}_4$



As the reaction proceeds via formation of manganate ester in a concerted manner, therefore, addition is stereospecifically syn in nature.



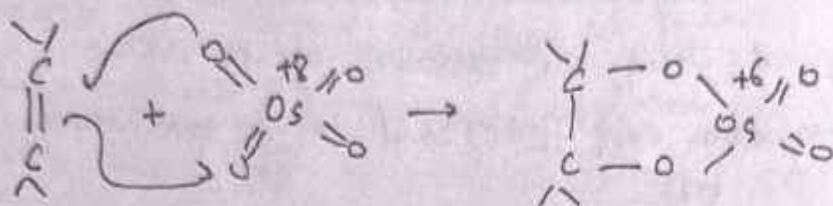
Mn is a member of 3d transition series, therefore, higher oxidation state is less stable and there is a tendency of further attack and the diol formed gets further oxidised.



Mn finally comes to +3 oxidation state

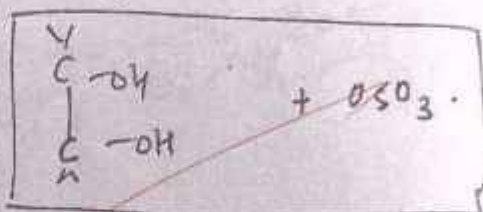
# DIAS

## Diol formation by OsO<sub>4</sub>



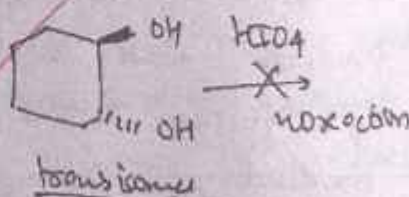
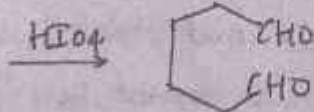
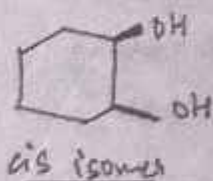
generally, pyridine is used as solvent to increase reactivity of OsO<sub>4</sub>.  
 Osmate ester  
 NaHSO<sub>4</sub>.

As, the dihydroxylation is taking place via formation of an osmate ester with a concerted flow of electrons, therefore, the diol formed is stereochemically syn.



Which one is better? → Os being a member of 5d series can stabilise higher oxidation state because of inverse inert pair effect, therefore, further oxidation of diol doesn't take place.  
 ∴ for diol formation OsO<sub>4</sub> is better.

## Differentiation b/w cis & trans isomers of 1,2 cyclohexane diol



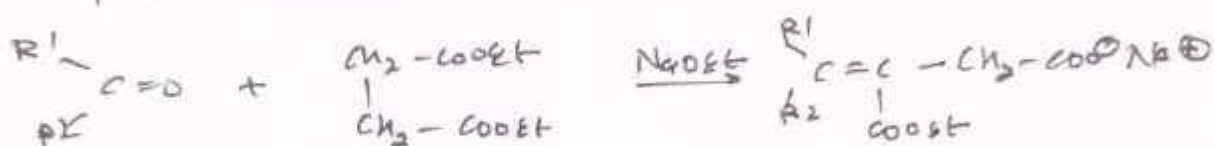
They can be differentiated with the help of HIO<sub>4</sub>. Cis isomer gives product of oxidative cleavage, whereas trans isomer does not give this reaction.



# DIAS

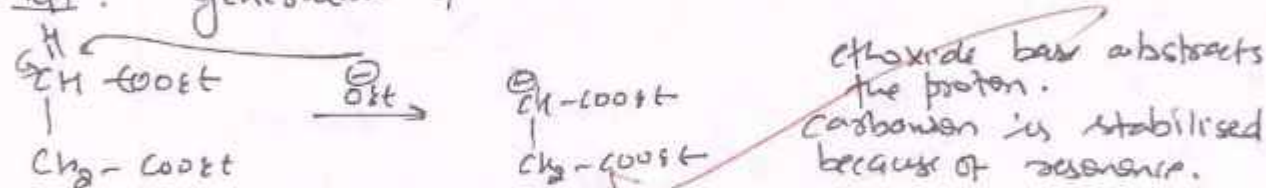
(b) Discuss the mechanism of Stobbe condensation. Why it is not successful with Aliphatic enolizable aldehyde. (15)

Stobbe condensation is a condensation reaction of aldehyde or ketone with Diethyl Succinate, in which the carbanion is given by DES on reaction with base. Product is  $\beta,\gamma$  unsaturated acid.

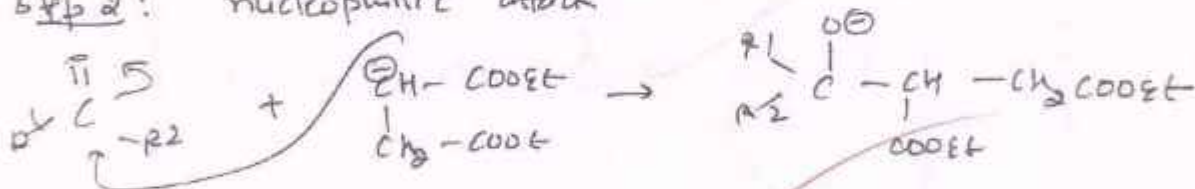


## Mechanism

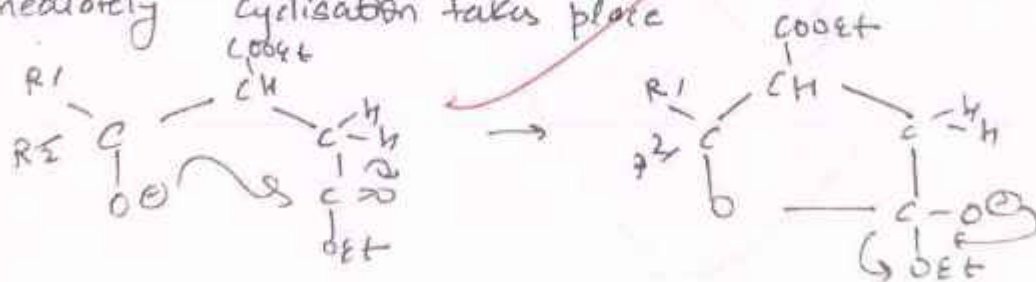
Step 1: generation of carbanion



Step 2: nucleophilic attack



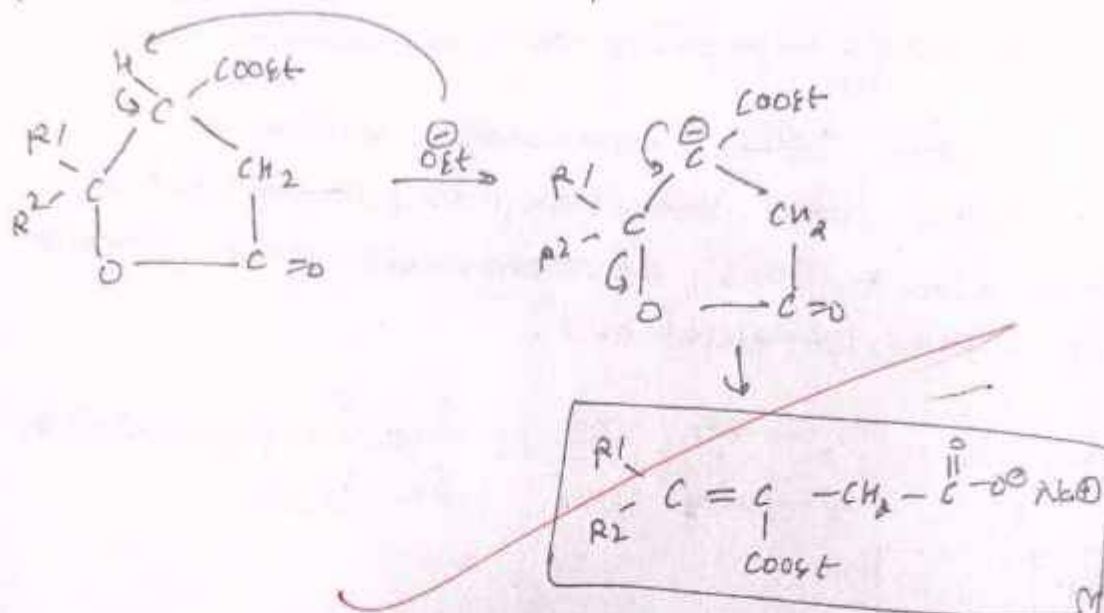
Immediately cyclisation takes place





# DIAS

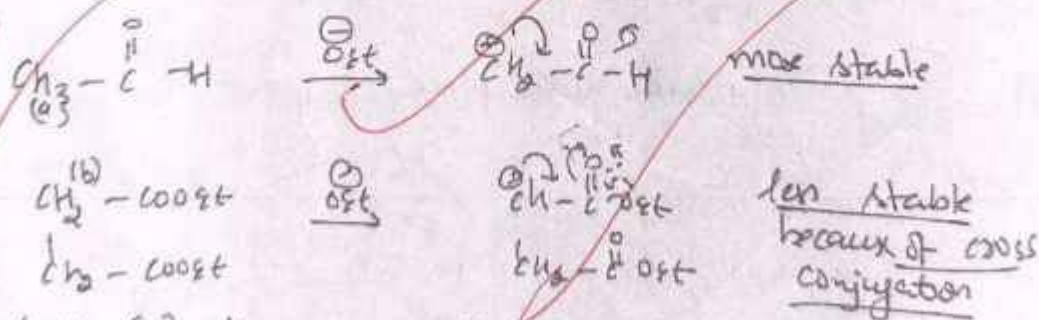
Steps: E1cB elimination takes place



Why not successful with aliphatic enolizable aldehyde

Stobbe condensation is generally successful with aromatic aldehyde & ketone where  $\alpha$ -H is not present and aldol condensation does not take place.

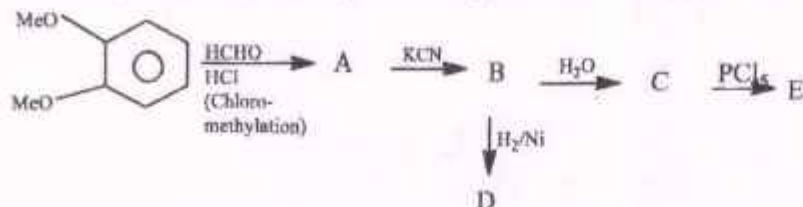
In case of aliphatic enolizable aldehyde, aldol condensation prevails over Stobbe condensation.



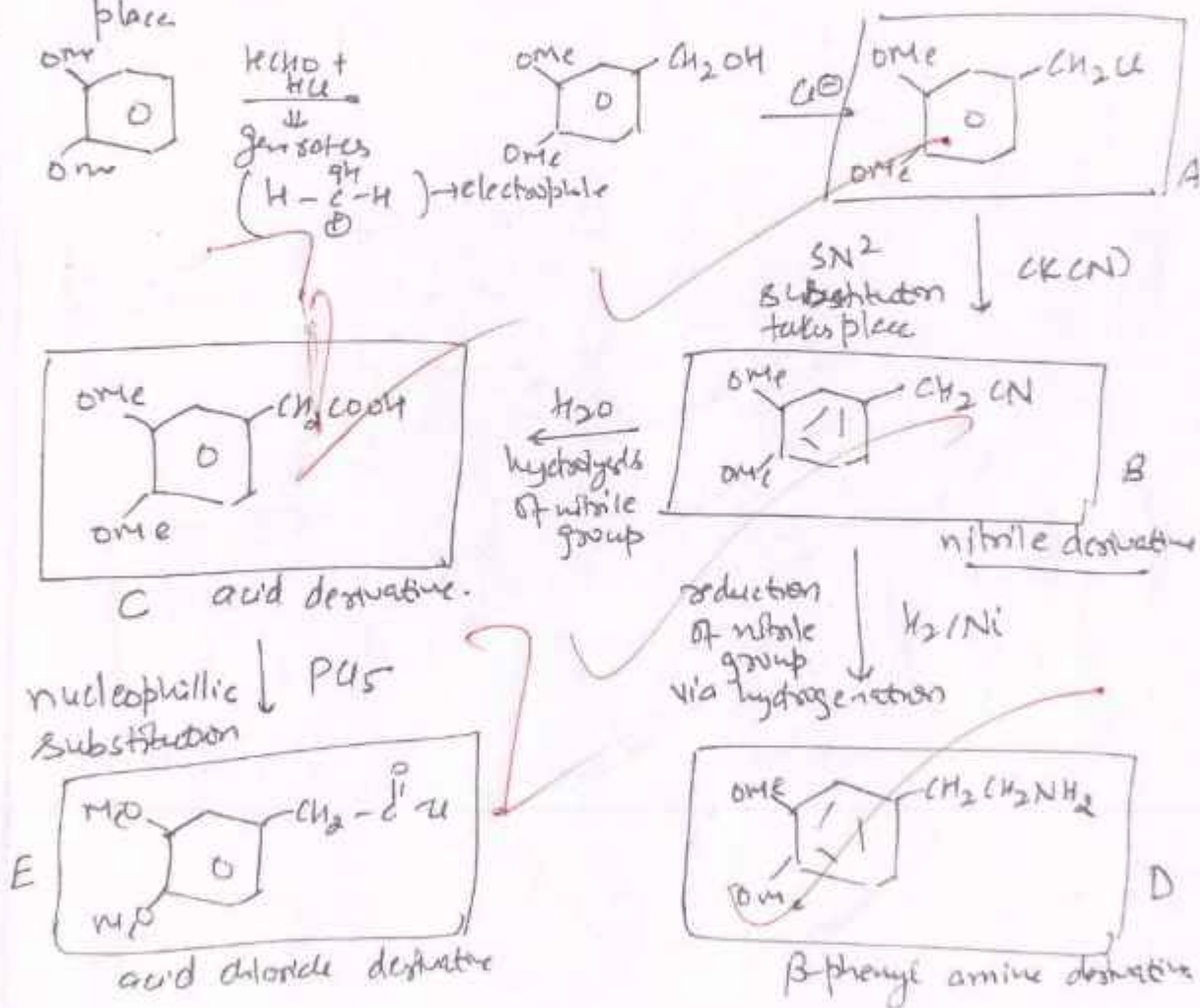
Hydrogen (a) is more acidic because its conjugate base is more stable, therefore, base preferentially attacks it.

# DIAS

(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)



The reaction for formation of A is a variation of Leider Mannose reaction in which electrophilic substitution takes place.





# DIAS

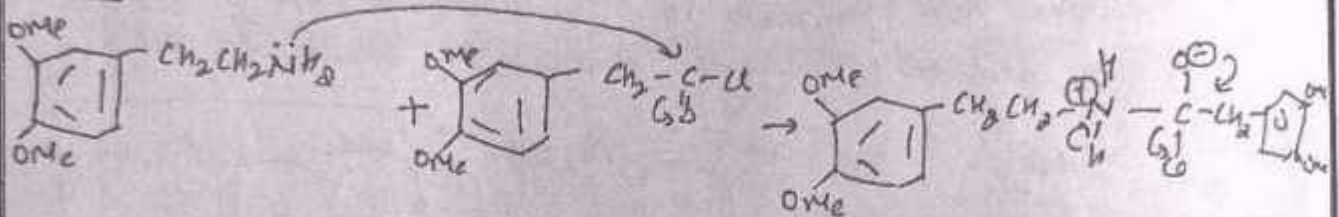
(ii) What happens when D & E Condensed in presence of  $\text{POCl}_3$ . Followed by aromatization.

(10)

If D & E condensed in presence of  $\text{POCl}_3$  & followed by aromatization we get isoguinoline derivative. This rxn sequence is known as

Bischoff-Napieralski synthesis of isoguinoline.

Step 1: Schotten-Baumann Reaction : nucleophilic attack of amine



Step 2: Friedel-Crafts alkylation

