

DIAS

All India TEST – SERIES CSE – 2024

Test-4

Syllabus -: Aromaticity & Reaction mechanism

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:- Pawan Kumar Pandey

UPSC Roll no:-

Mobile Number.

Date:- 22-07-2024

Attempted 1, 3, 4, 5, 8

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	30½	0	27	34	33	—	—	28

Signature of invigilator

Good

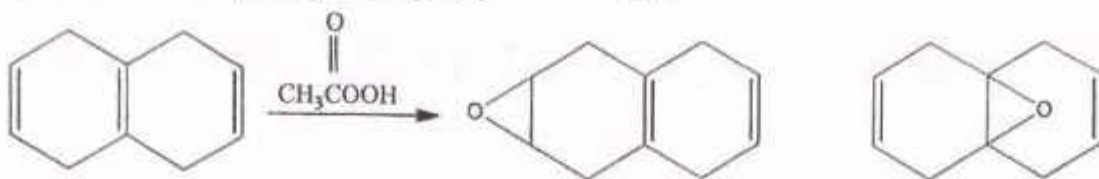
Signature of
Examiner

152½

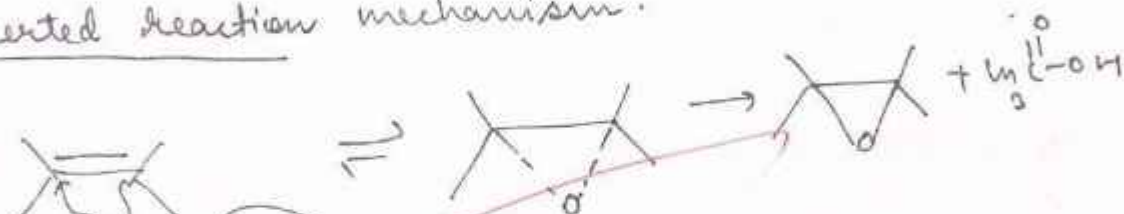
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Section - A

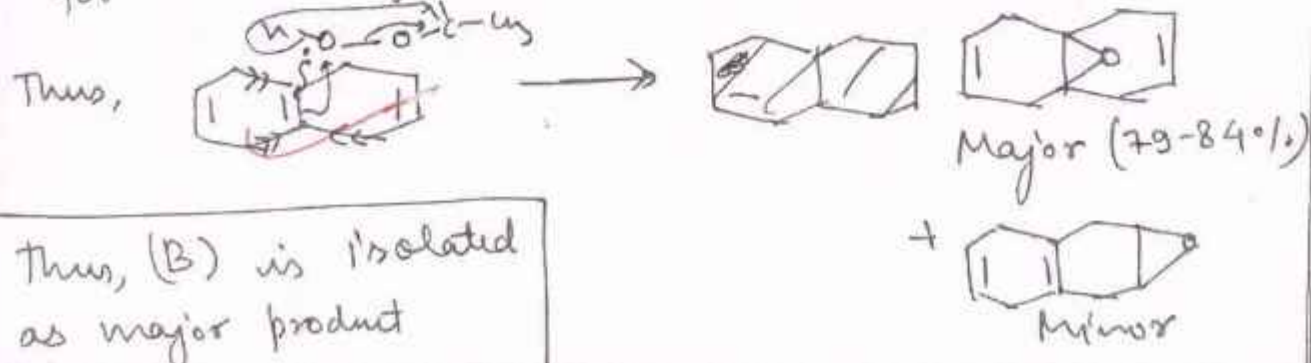
1.(a) A single epoxide was isolated in 79-84% yield in the following reaction. Was this epoxide A or B? Explain your reasoning. (10)



Epoxidation is electrophilic addition of deficient oxygen on double bond. It proceeds via single step concerted reaction mechanism.



Thus, epoxidation takes place at more substituted double bond reaction centre because more substituted double bond has higher e^- density as compared to less substituted. Thus, it is more nucleophilic for attack of electrophilic oxygen of per acid.



Thus, (B) is isolated as major product

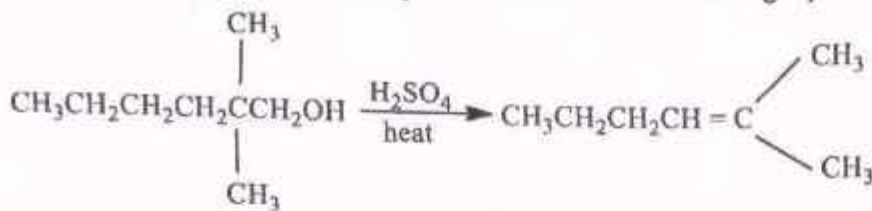
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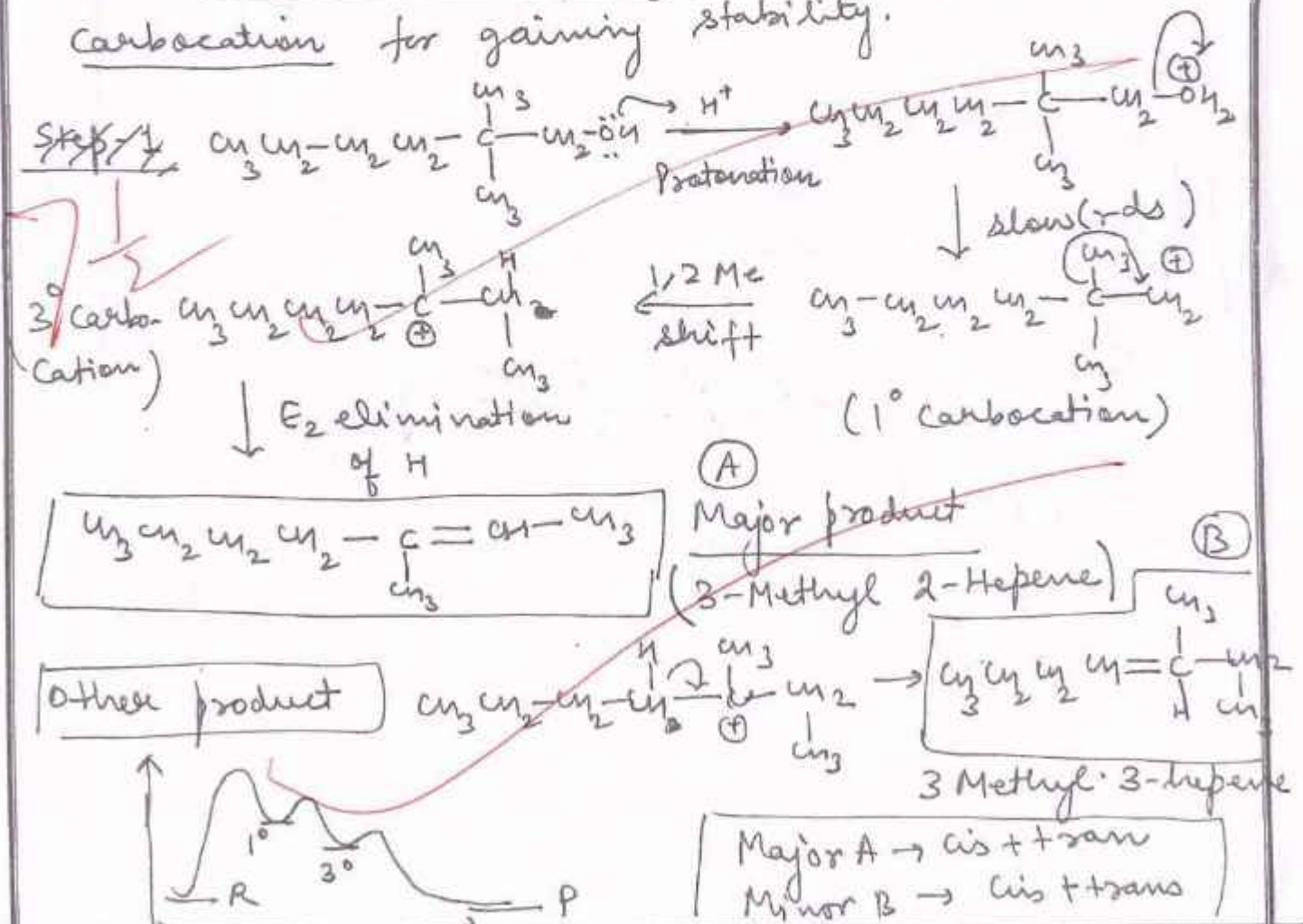
(b) Acid-catalyzed dehydration of 2,2-dimethyl-1-hexanol gave a number of isomeric alkenes including 2-methyl-2-heptene as shown in the following equation. (10)



(i) Write a stepwise mechanism for the formation of 2-methyl-2-heptene, using curved arrows to show the flow of electrons.

(ii) What other alkenes do you think are formed in this reaction?

Acid catalysed dehydration of alcohol takes place via E₁ mechanism via formation of carbocation. Thus, carbocation rearranges to a more stable carbocation for gaining stability.



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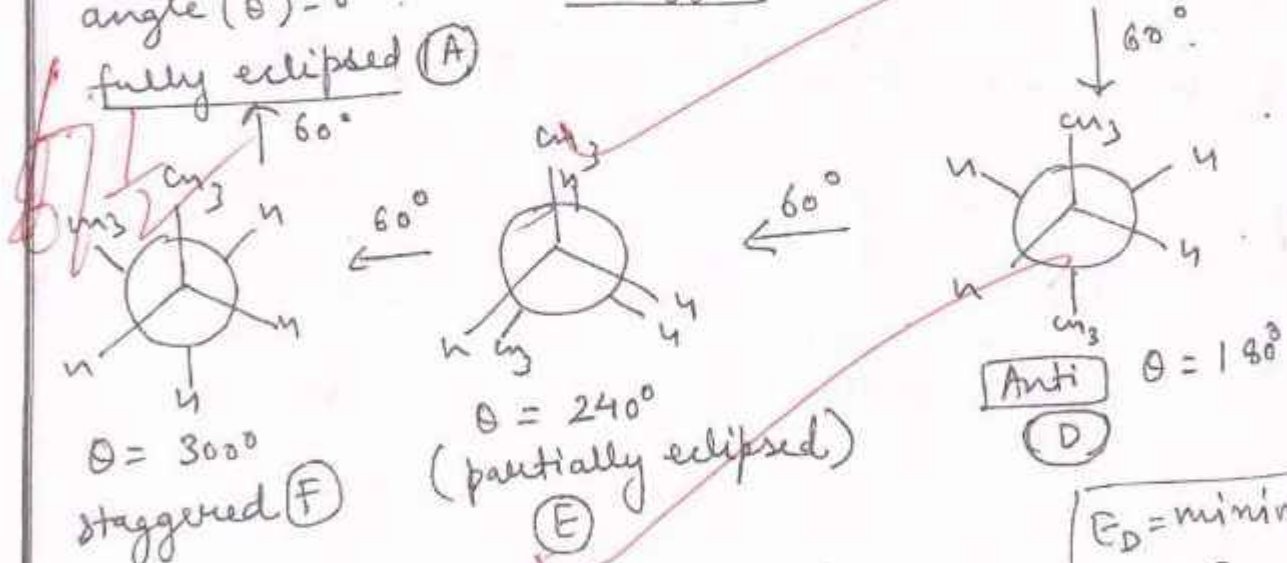
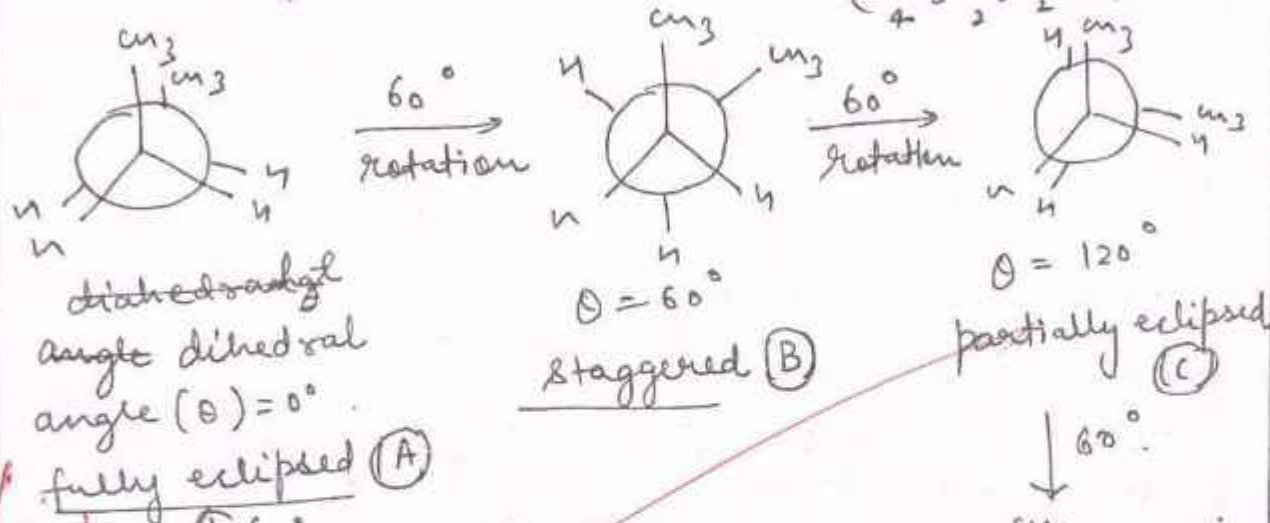
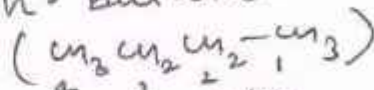
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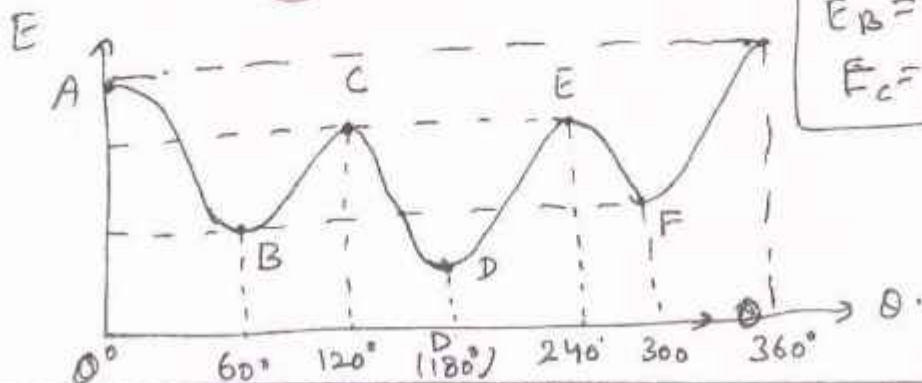
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(c) Potential Energy (PE) change during rotation about C(2)-C(3) bond of n-butane. Present the variation semi-quantitatively with rotation of the bond. (10)

This can be explained on the basis of newman projection structure of n-butane.



(Potential energy)



$$E_D = \text{minimum}$$

$$E_B = E_F$$

$$E_C = E_E$$

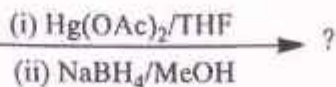
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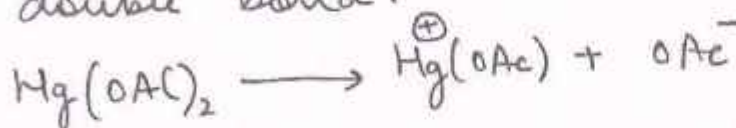
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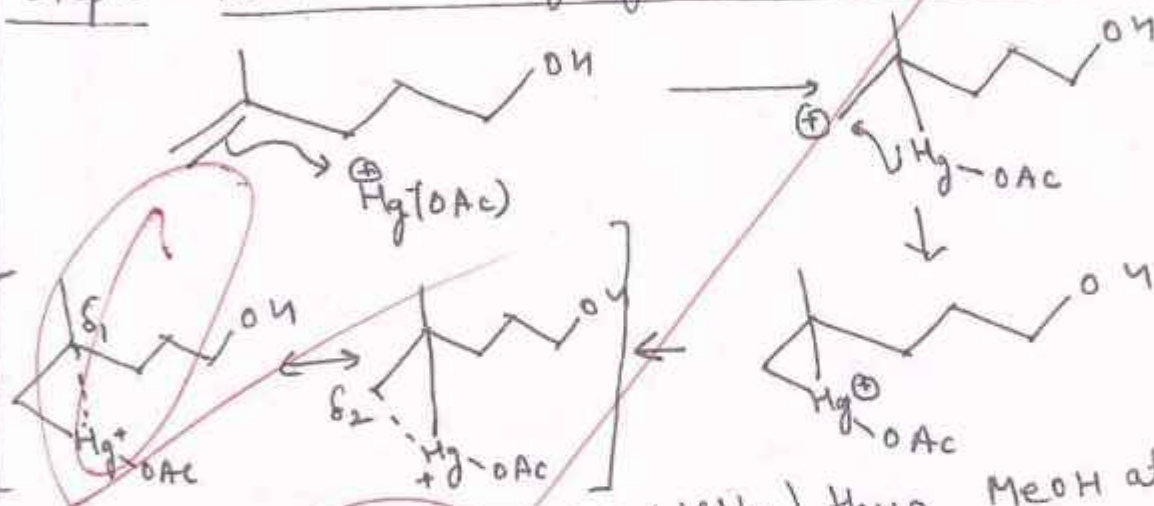
(d) Give the product and mechanism of the following reaction : (10)



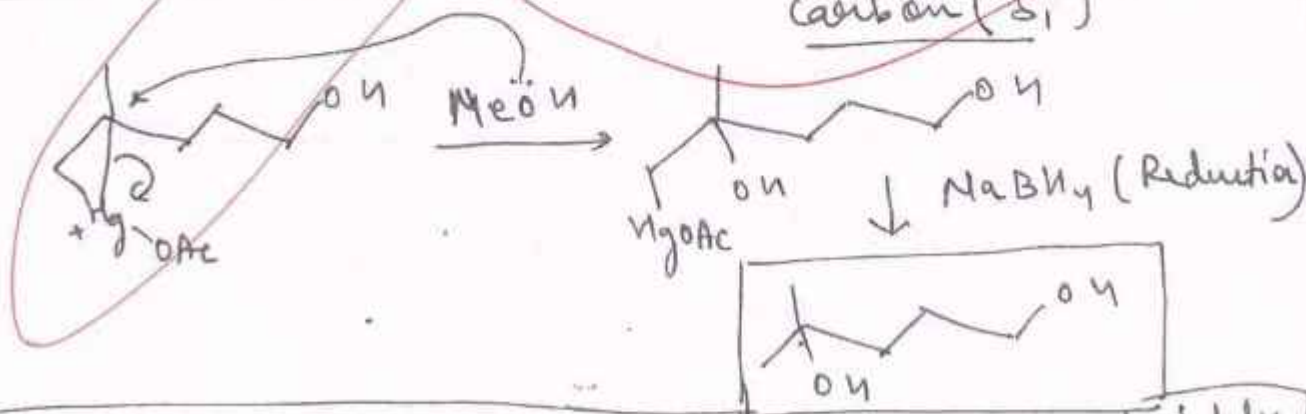
This is oxymercuration-demercuration reaction which involves addition of electrophilic mercury on double bond.



Step 1 Formation of cyclic mercurinium ion



Step 2 Since, $\delta_1 > \delta_2$ (Stability) thus MeOH attack at more substituted carbon (δ_1)



Mercury is highly electrophilic. Thus, reaction is highly stereospecific

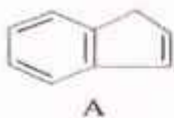
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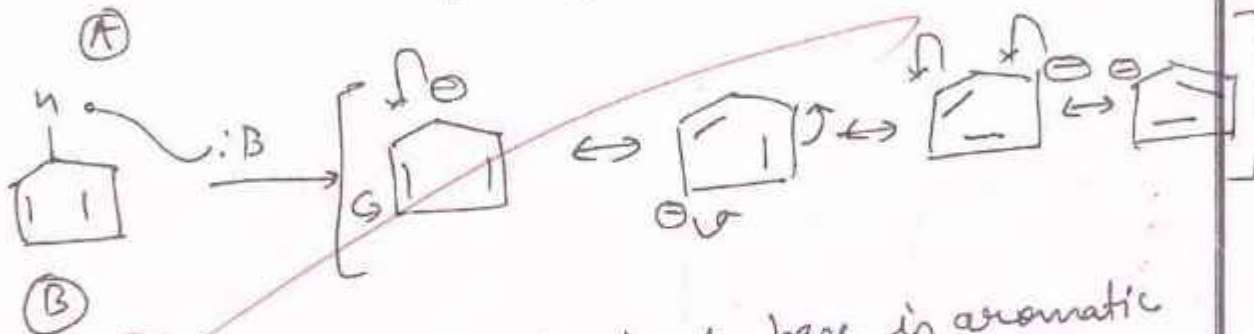
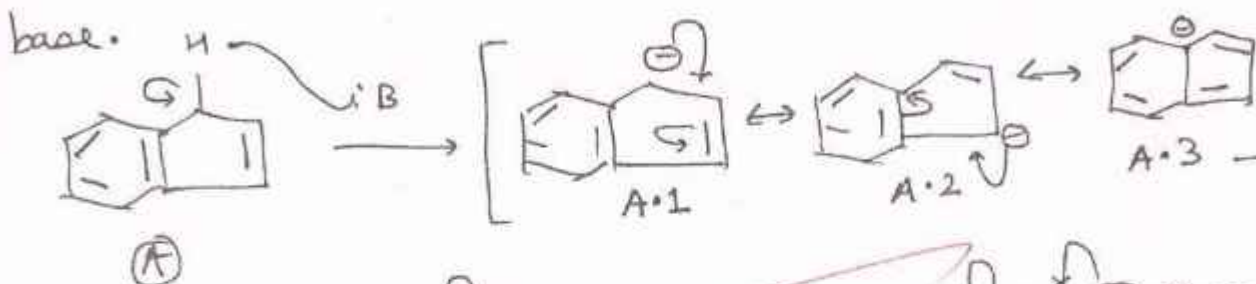
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(e) (i) Which one of the above compounds is more acidic and why? (5)



Acidity of A and B can be explained on the basis of aromaticity (i.e. stability) of conjugate base.



In A, although conjugate base is aromatic (no πe^- system) but benzoid character is lost in A.3 conjugate structure and other subsequent resonating structure.

In B, conjugate base is highly stable due to aromatic circulation $6\pi e^-$.

Stability:- Conjugate Base of B > Conjugate Base of A

Acidic nature:- B > A

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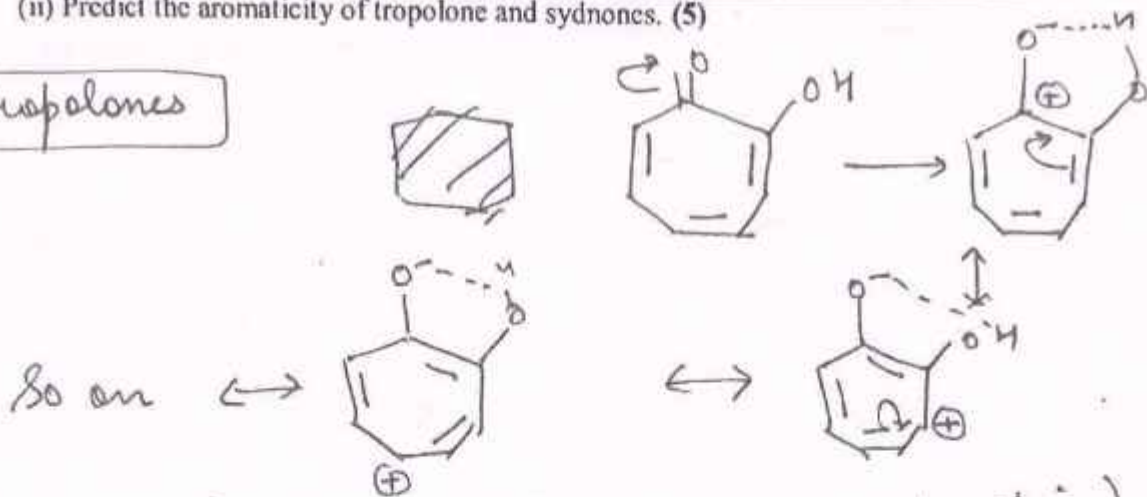
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(ii) Predict the aromaticity of tropolone and sydnone. (5)

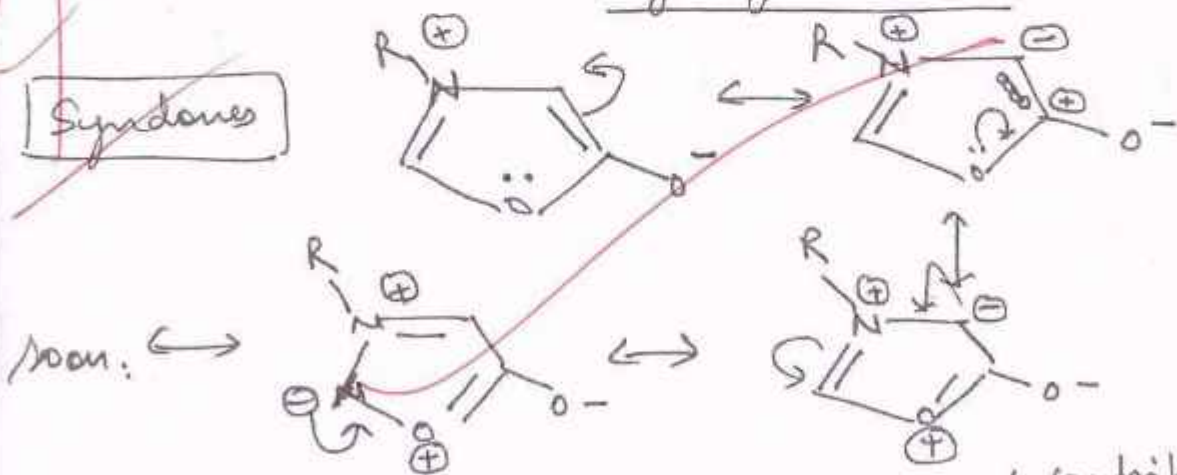
Tropolone



As per huckle rule, (after charge separation), $6\pi e^-$ circulation ($n=1$) and continuous cyclic planar circulation makes tropolone aromatic

Additionally, conjugate base it is stabilised by hydrogen bonding

Sydnone



As per huckle rule, $6\pi e^-$ circulation (contribution of lone pair of oxygen) ($n=1$) and planar \Rightarrow Asomatic

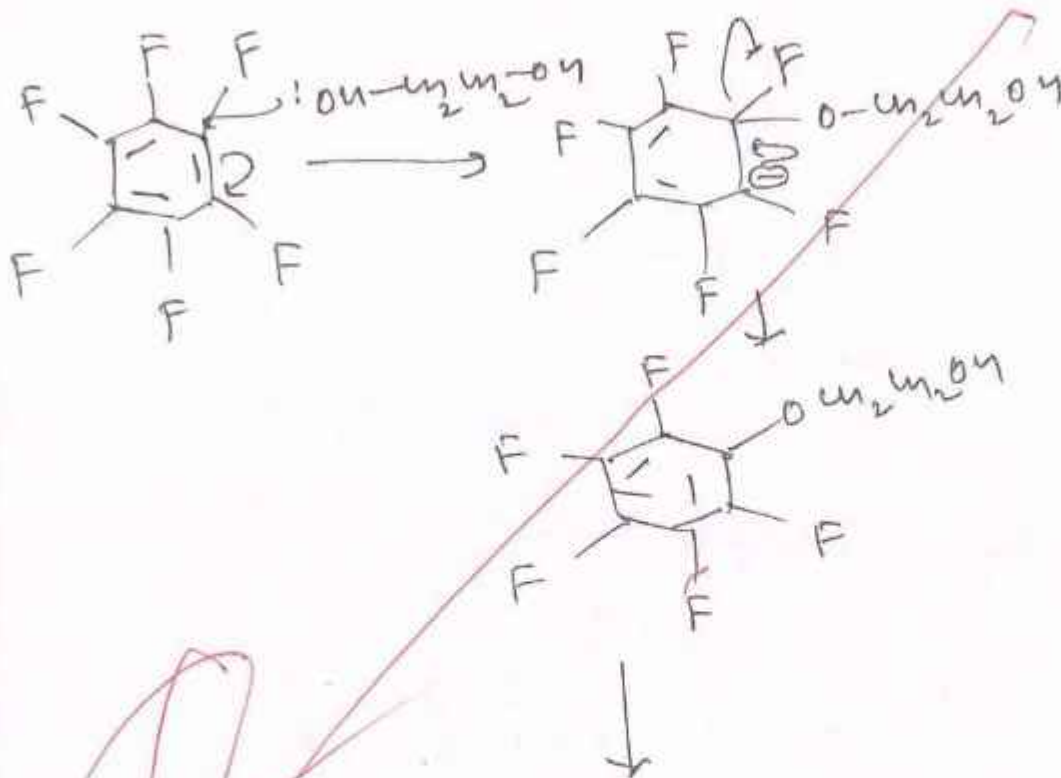
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3.(a) The cumulative effect of their fluorines activate the rings of penta- and hexafluoro benzene toward nucleophilic aromatic substitution. What is compound X in the following synthesis? (10)

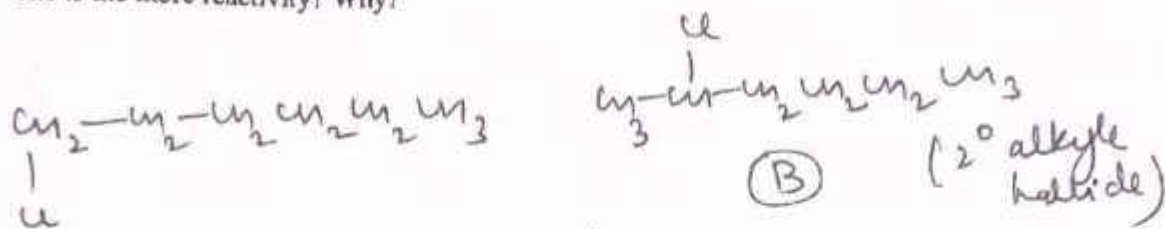


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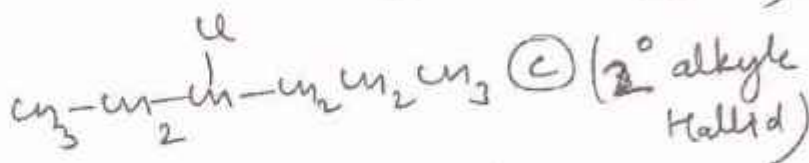
(b). There is an overall 29-fold difference in reactivity of 1-chlorohexane, 2-chlorohexane, and 3-chlorohexane toward potassium iodide in acetone. (10)

(i) Which one is the most reactive? Why?

(ii) Two of the isomers differ by only a factor of 2 in reactivity. Which two are these? Which one is the more reactivity? Why?



(A) (1° alkyl halide)



① Since I^\ominus is strong nucleophile and solvent is polar aprotic $\Rightarrow \text{S}_\text{N}2$

For $\text{S}_\text{N}2$ 3° is least reactive and 1° is most reactive due to steric hindrance in transition state. Thus (A) is most reactive.

② (B) and (C) differ only by factor of 2 in reactivity and steric hindrance is almost same in both as both are 2° alkyl halide.

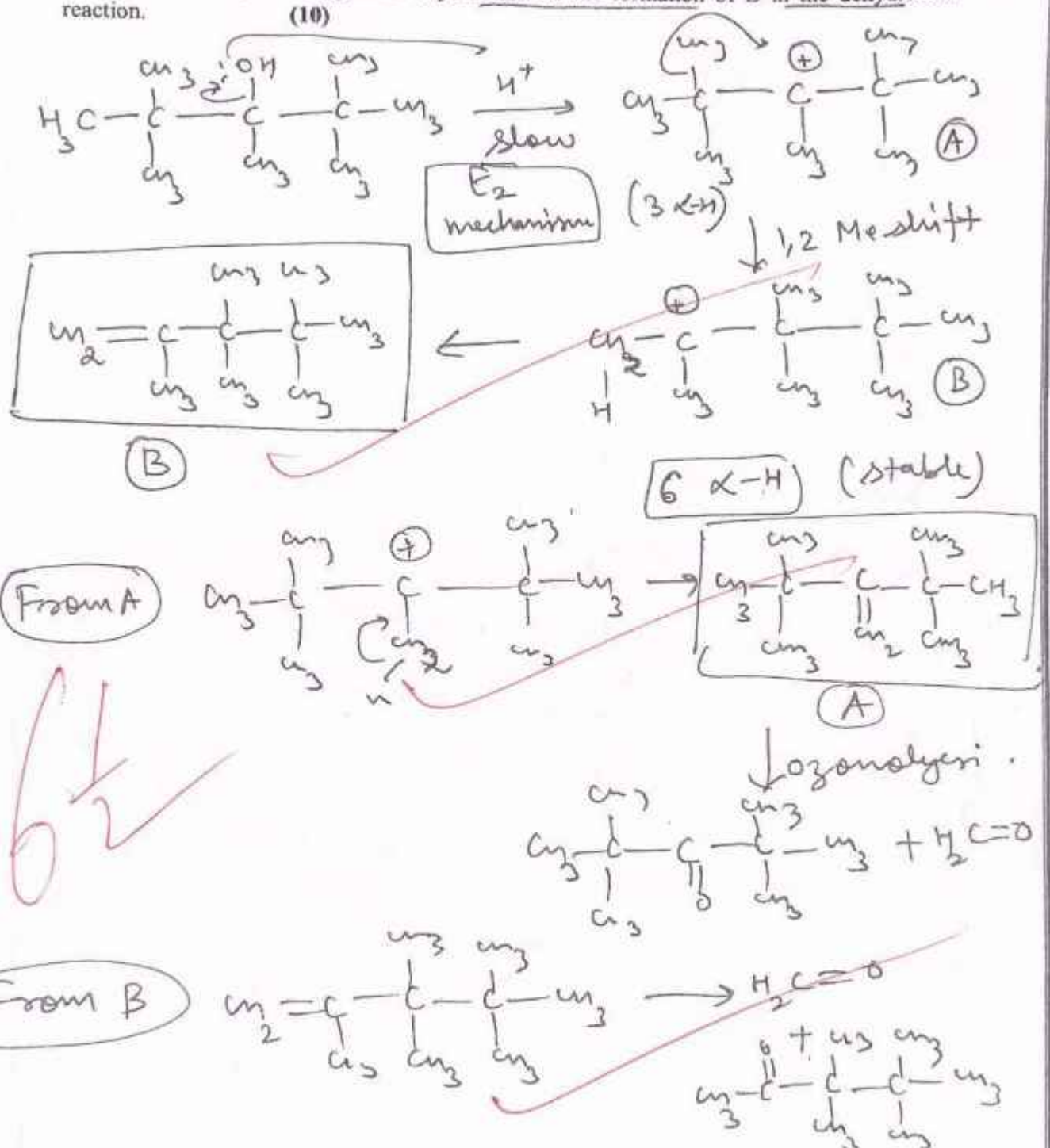
Thus, (B) is slightly more reactive due to smaller $-\text{CH}_3$ group.

Read Quest.

Aqum

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(c) Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol gave two alkenes A and B. Ozonolysis of the lower boiling alkene A gave formaldehyde ($H_2C=O$) and 2,2,4,4-tetramethyl-3-pentanone. Ozonolysis of B gave formaldehyde and 3,3,4,4-tetramethyl-2-pentanone. Identify A and B, and suggest an explanation for the formation of B in the dehydration reaction.



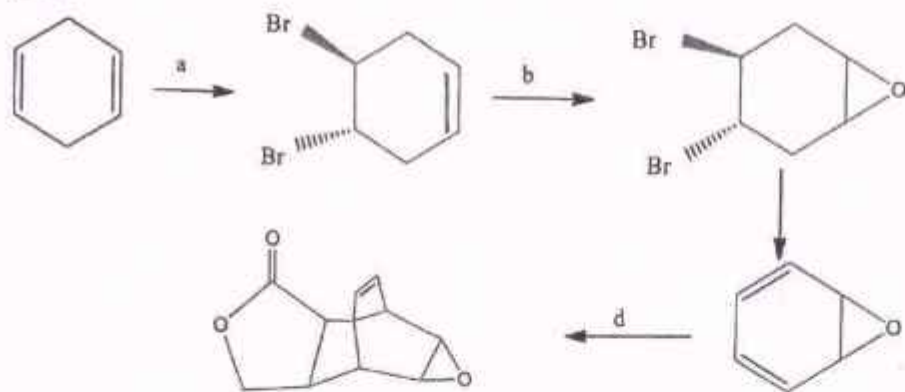
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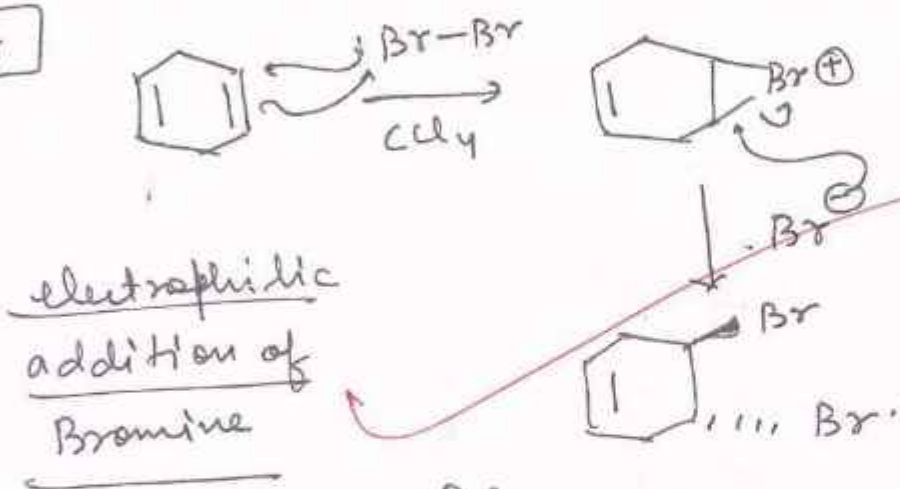
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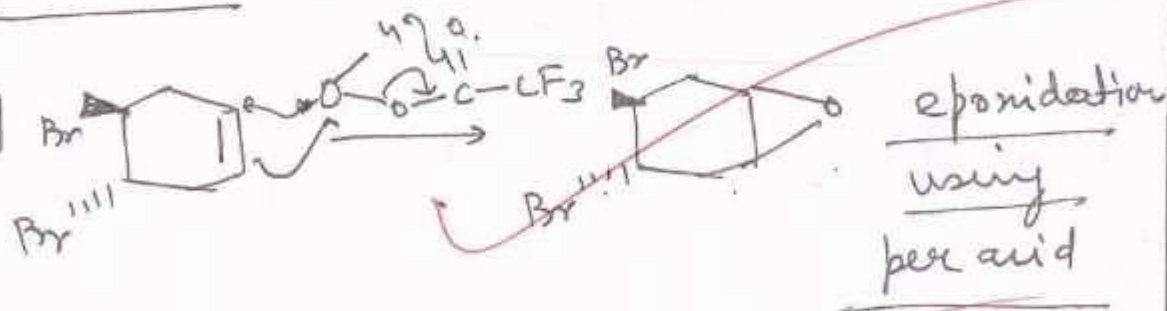
(d) Suggest reagents suitable for carrying out each step in the following synthetic sequence:
(20)



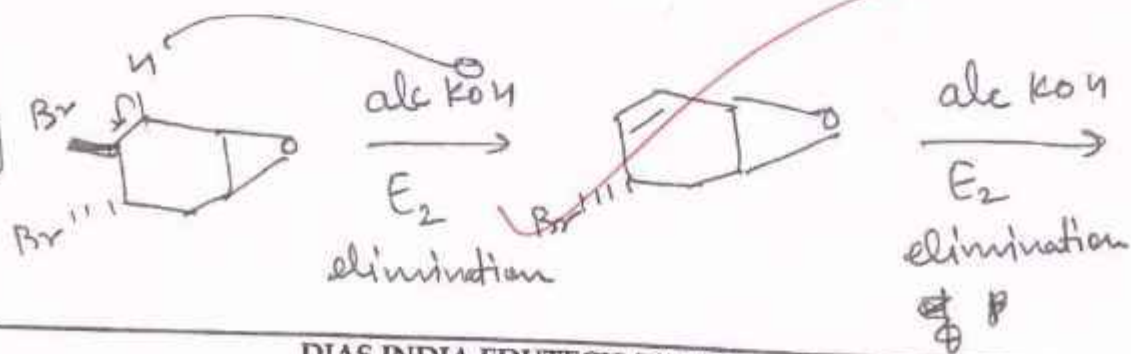
A



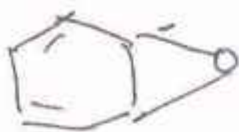
B



C

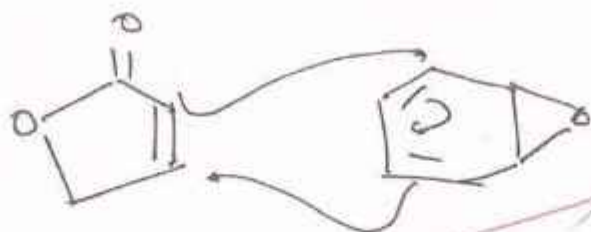


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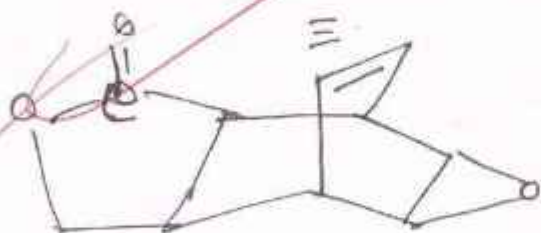
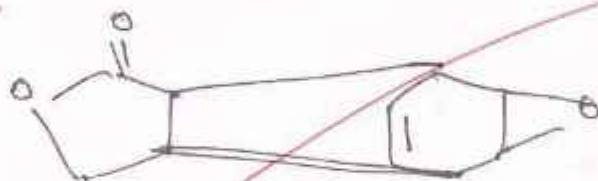


2 successive dehydrobromination

D



Δ \rightleftharpoons 2,4 cycloaddition

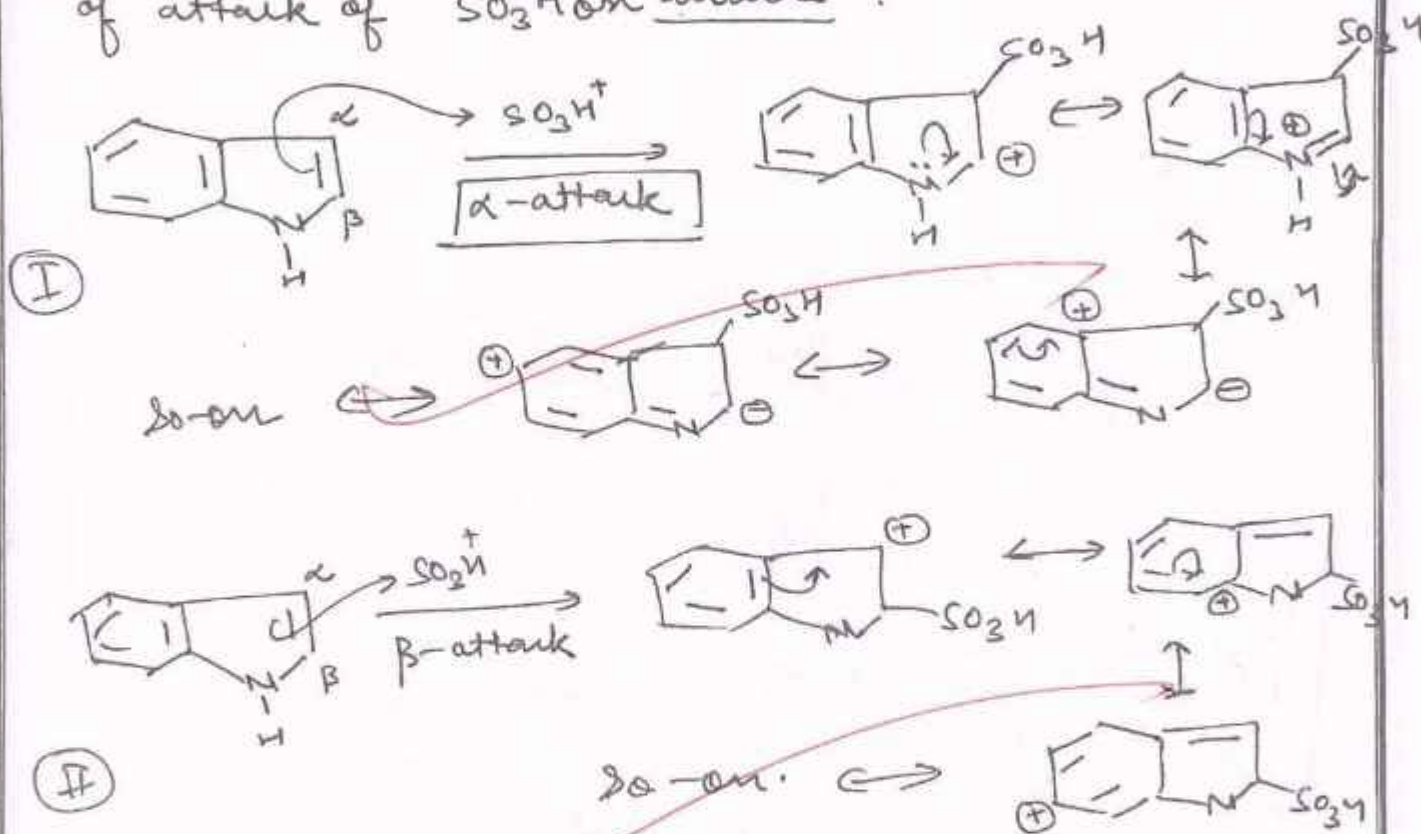


Diels Alder reaction

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4.(a) (i) Draw resonating structures for the attack of SO_3H^+ at different positions of indole, using curved arrows. At which position attack occurs preferentially? Draw an energy profile diagram for the position of preferential attack. (15)

Attack of SO_3H^+ on indole is electrophilic substitution reaction with SO_3H^+ attacking as electrophile. There can be two different positions of attack of SO_3H on indole.

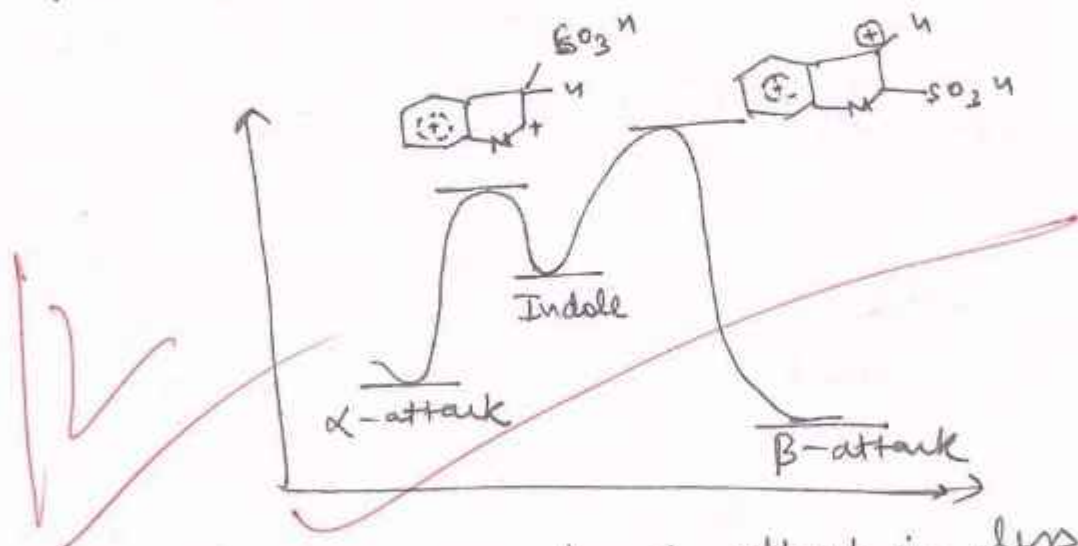
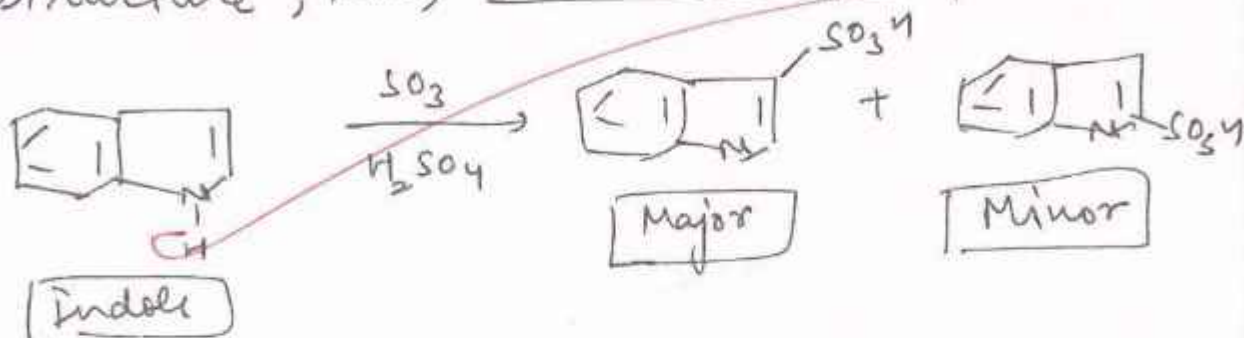


(II) \Rightarrow In **(I)** (α -attack), before benzoid character is lost due to delocalization, there exist one extra resonating structure due to delocalization

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of lone pair of N. But in β -attack (II), directly benzoid character is lost.

Thus, α -attack ~~is~~ has more stable resonating structure, thus, α -attack is preferred.

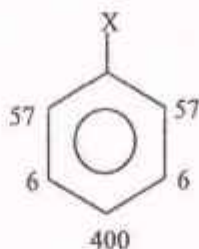


Activation energy for α -attack is less, thus formed preferentially.

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(ii) Of the groups shown. Which is the most likely candidate for substituent X based on the partial rate factors for chlorination? (5)

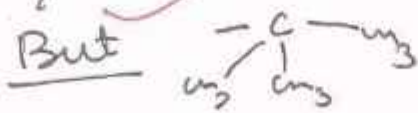
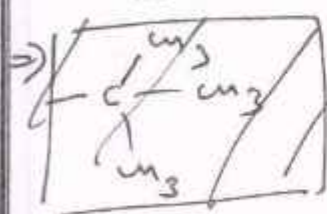
$-\text{CF}_3$, $-\text{C}(\text{CH}_3)_3$, $-\text{Br}$, $-\text{SO}_3\text{H}$, $-\text{CH}=\text{O}$



Since, Chlorination is electrophilic substitution reaction, e^- donating group increases partial rate factor at ortho and para position where as e^- withdrawing group deactivates ring and act as meta director.

Thus, $-\text{CF}_3$, $-\text{SO}_3\text{H}$, $-\text{CHO}$ are ruled out as they are e^- withdrawing.

Now $-\text{Br}$ is ortho, para director but activates de-activates the ring.

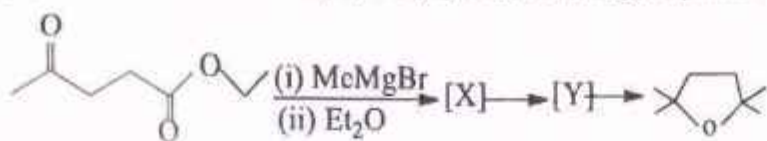


is most suitable as due to steric hindrance only acts as activator through +I not hyperconjugation (no α -H).

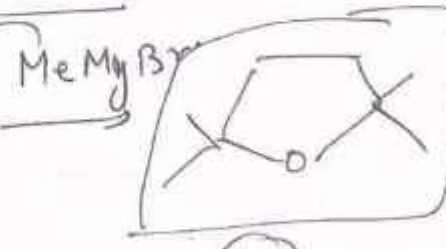
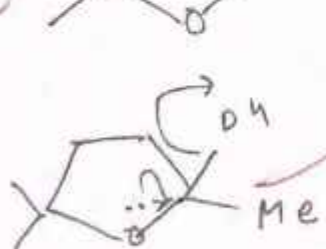
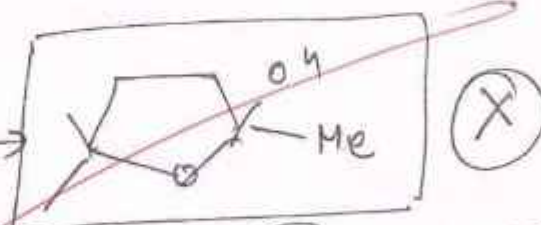
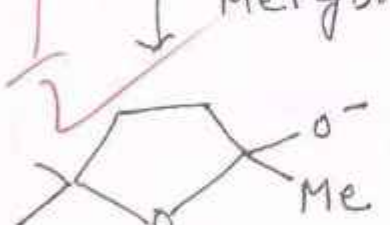
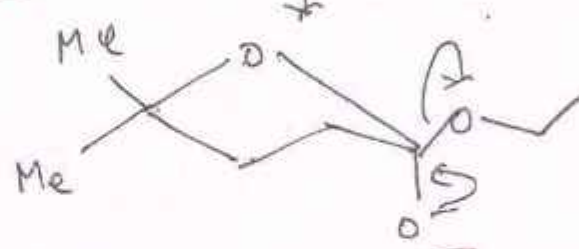
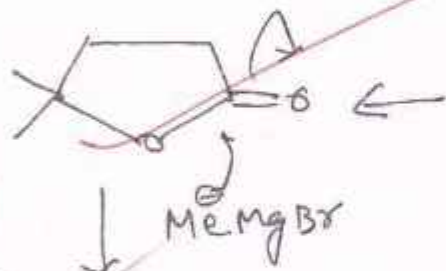
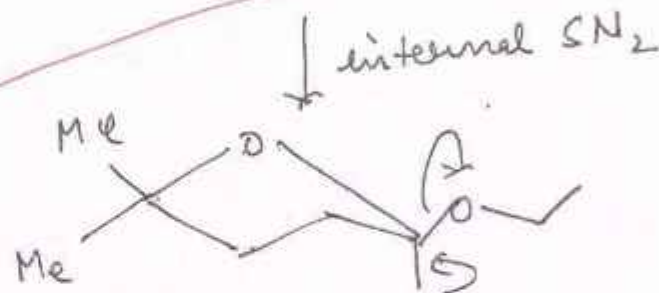
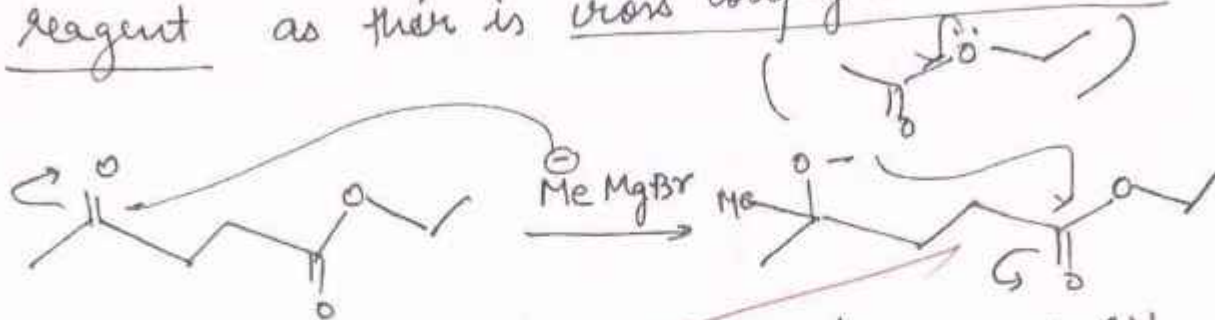
Thus, $-\text{Br}$ is most suitable ⇒ Para activated more due to steric hindrance.

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(b) Predict the structure of (X) and (Y) in the following sequence: (10)



Ketone will be more reactive towards Grignard reagent as there is cross conjugation in ester.



(X)

(Y)

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(c) Answer the following:

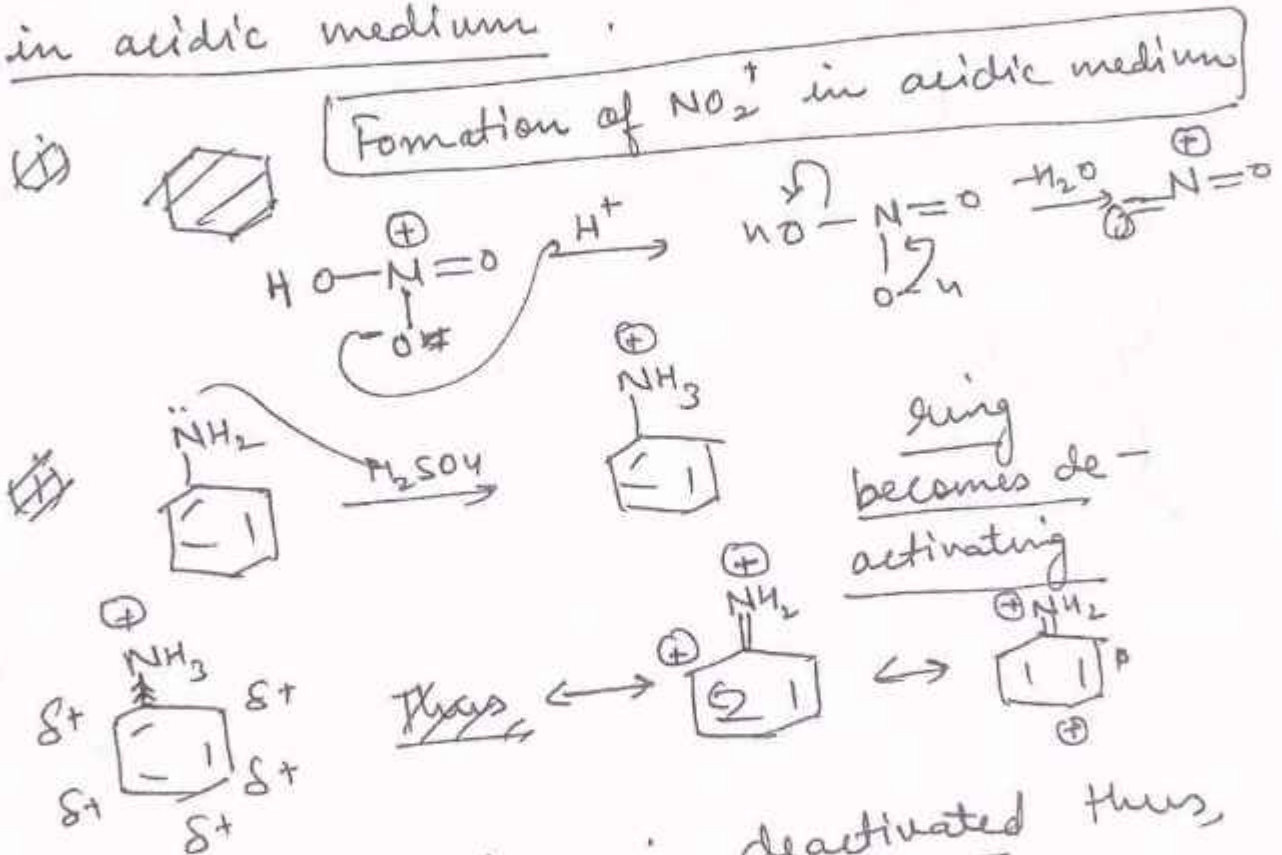
(15)

(i) A student carried out reaction of aniline with concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$. Write the structure of product/s he is likely to obtain.

(ii) Write a mechanism to explain the formation of major product in (i).

(iii) If the reaction in (i) is carried out only in nitric acid, write an equation for the formation of NO_2^+

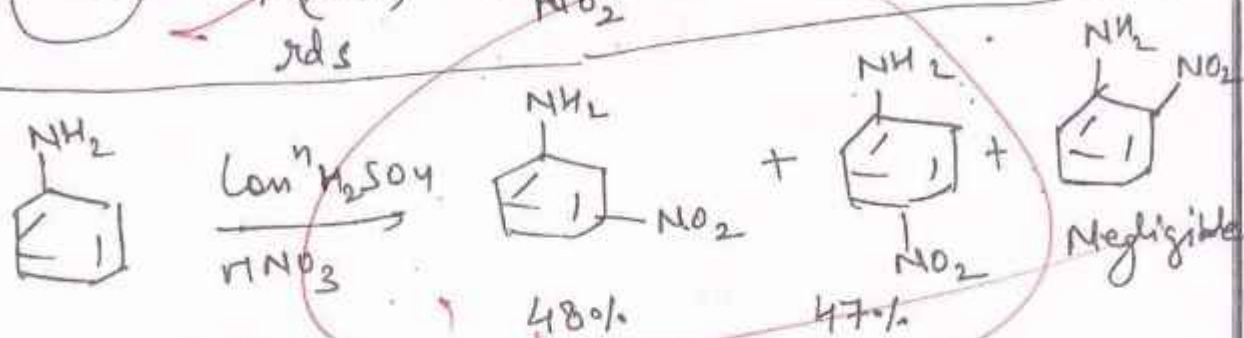
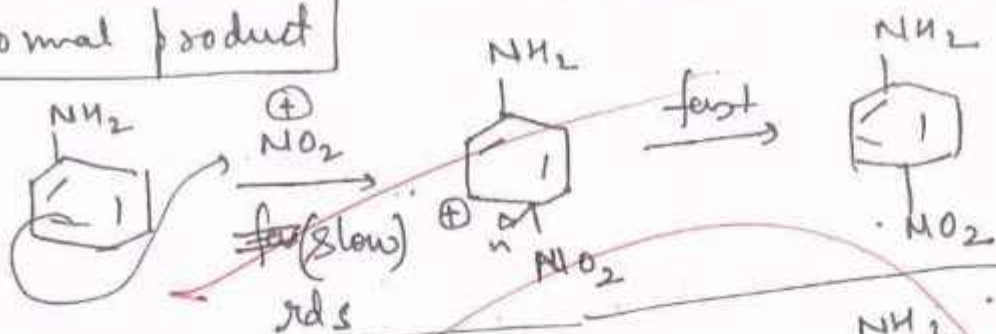
This reaction presents limitations of freed electrophilic substitution on aniline in acidic medium.



Thus, ortho, para is deactivated thus, NH_3^+ become meta directing ~~as well~~.

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Normal product

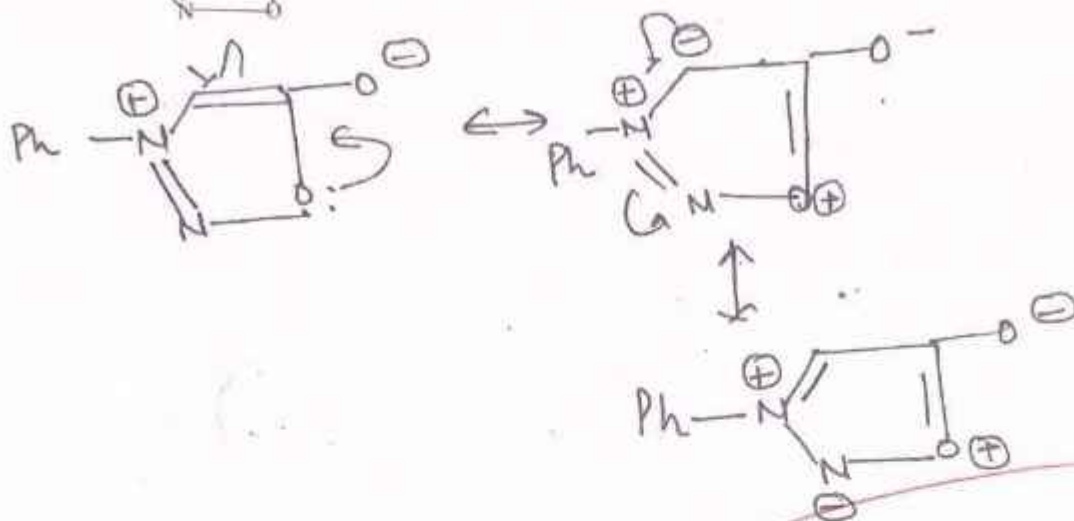
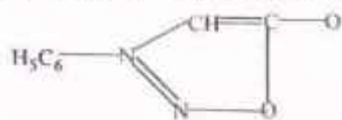


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(d) Write the resonance of the following:

(5)



Conjugation of $6\pi e^-$ (2π bond + 1 lone pair of O)

3

aromatic

due to Huckel's rule.

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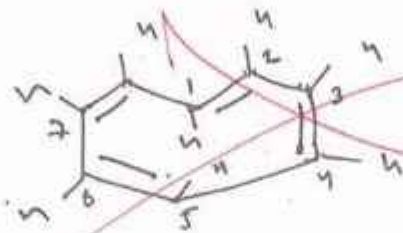
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Section - B

5(a). Draw the structures of [8], [12], [16], and [18] annulenes and discuss their aromaticity. (10)

For $4n$ types of Annulene, they must be ideally ~~non~~ Anti-aromatic subject to condition of planarity but deviation can take place due to certain factors.

8-Annulene
 $n=2$



repulsion of 1,5 H makes it non-planar
↓
non-Aromatic

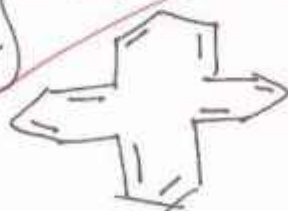
12-Annulene
 $n=3$



perimeter becomes large \Rightarrow circulation of $4n \pi e^-$ is planar
↓
Anti-Aromatic

Higher Annulenes like [16], annulene have both Anti-Aromatic and aliphatic character.

[16]-Annulene
 $n=4$



Perimeter is large \Rightarrow Anti-Aromatic

[18]-Annulene



Aromatic

$$4n+2 = 18 \quad |n=4$$

Perimeter high \Rightarrow Planar

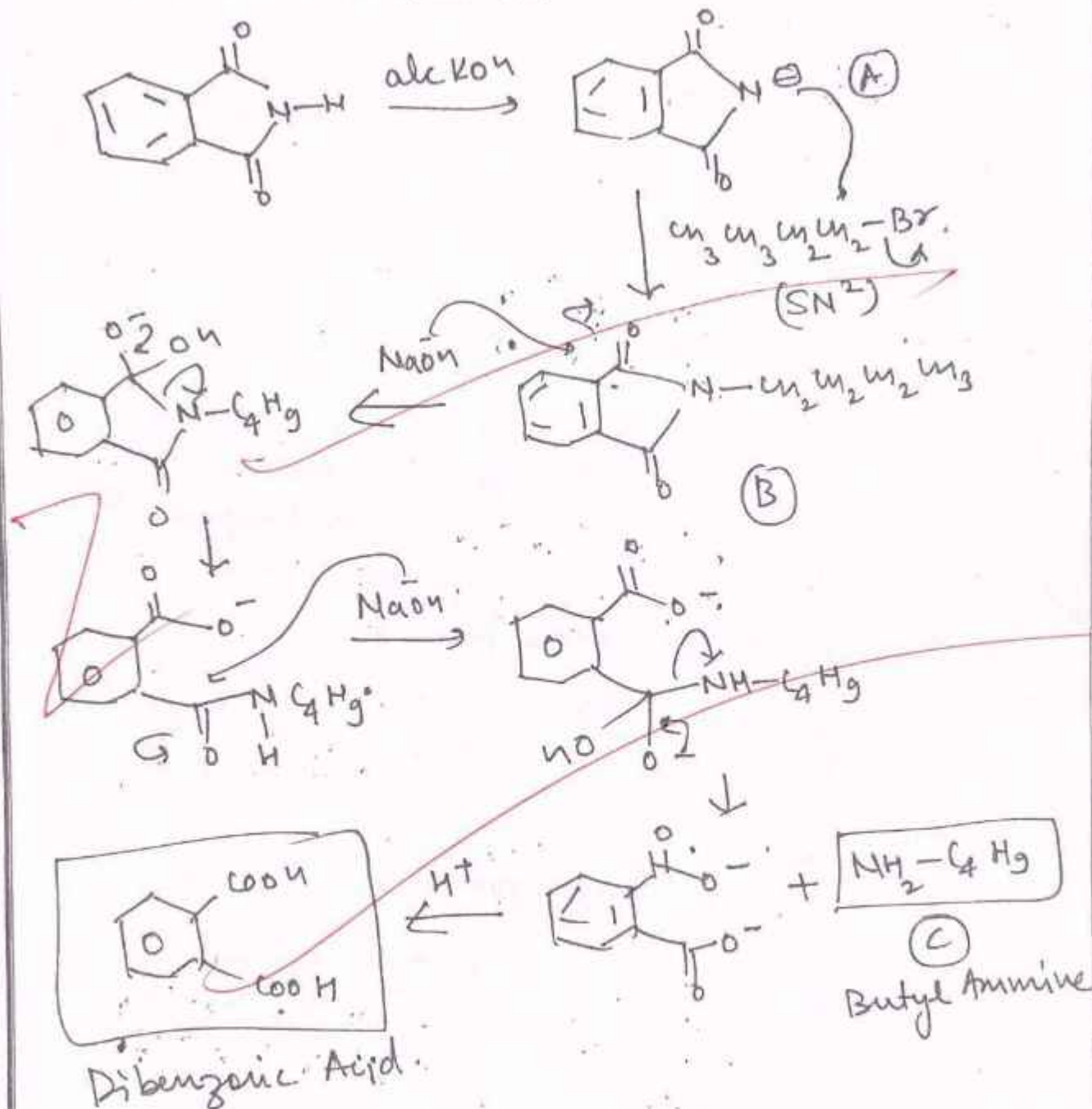
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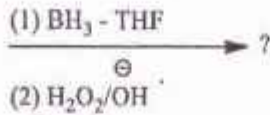
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(b) Phthalimide is treated with alcoholic KOH and it produces product A. A is treated with n-butyl bromide producing B. The product B is boiled with excess NaOH producing a volatile liquid. C after removal of C, the solution on acidification gives a solid organic acid D. What are A, B, C and D? Write with equations. (10)

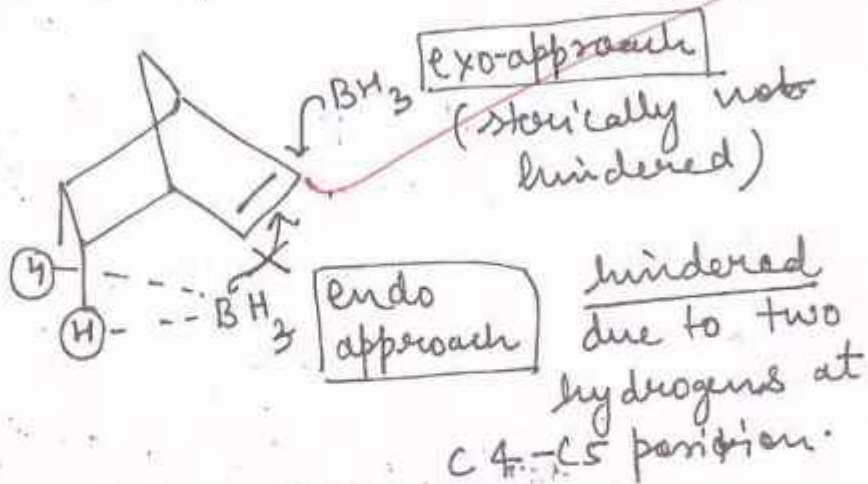


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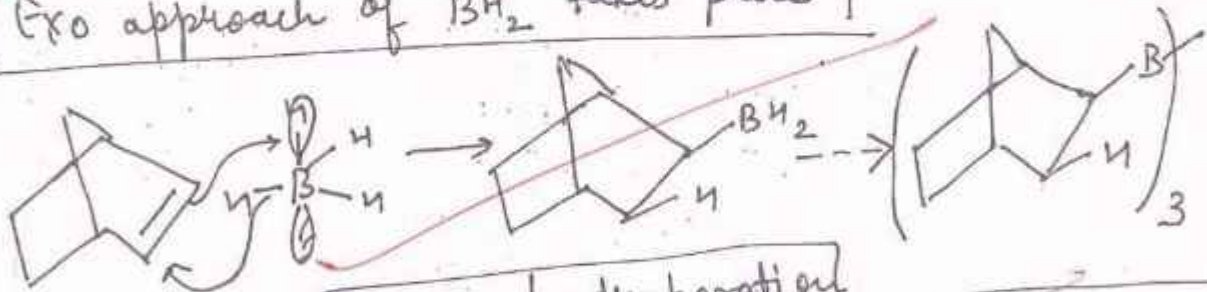
(c) Complete the following reaction and provide suitable mechanism and stereochemistry of the product :
(10)



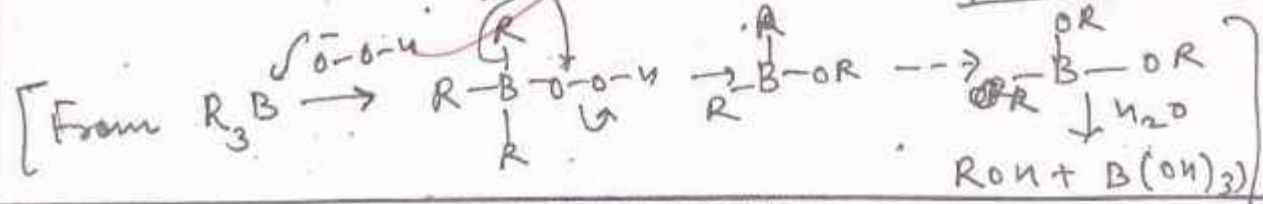
This reaction is hydroboration oxidation reaction



[Exo approach of BH_2 takes place]



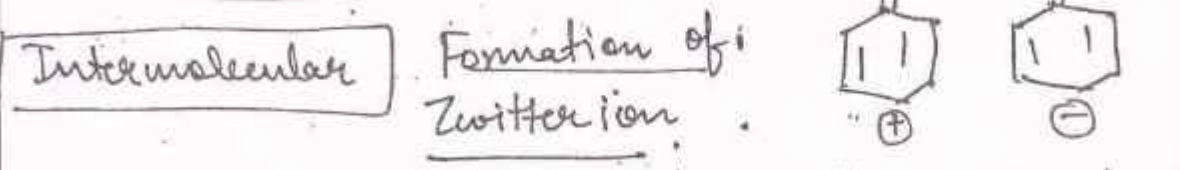
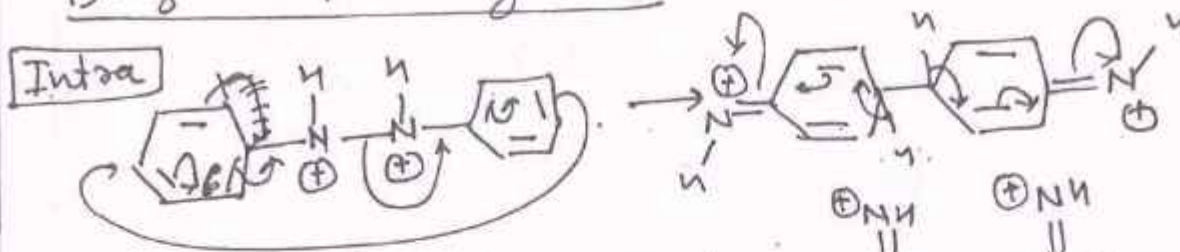
[Step 1 - Hydroboration]



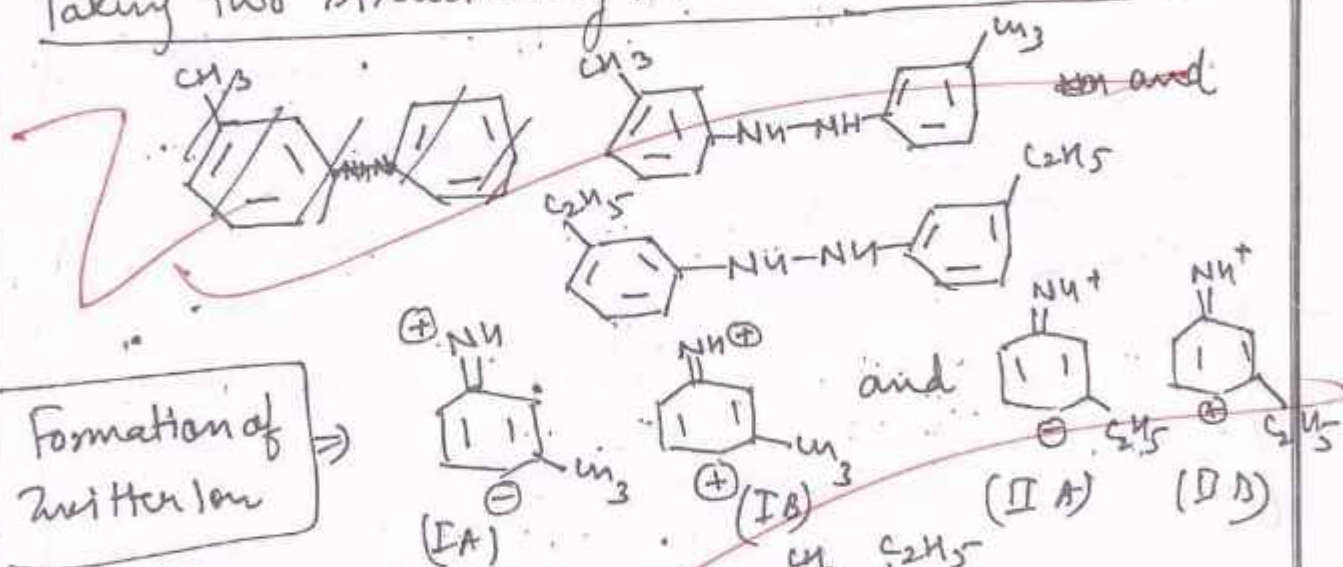
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(d) With a suitable cross-over experiment, prove that benzidine rearrangement proceeds intramolecularly. (10)

Benzidine rearrangement takes place as follows:-



Taking two structurally similar reactants in 1:1

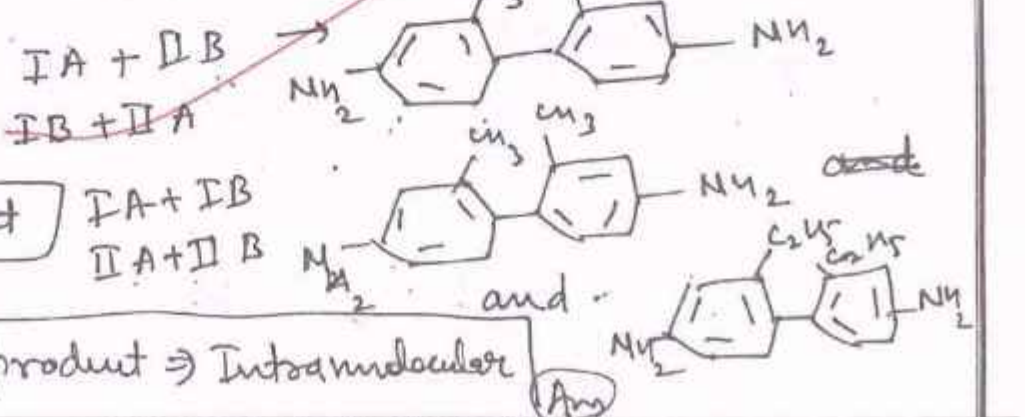


Formation of Zwitterion

Cross over Products

Normal product

No crossover product \Rightarrow Intramolecular



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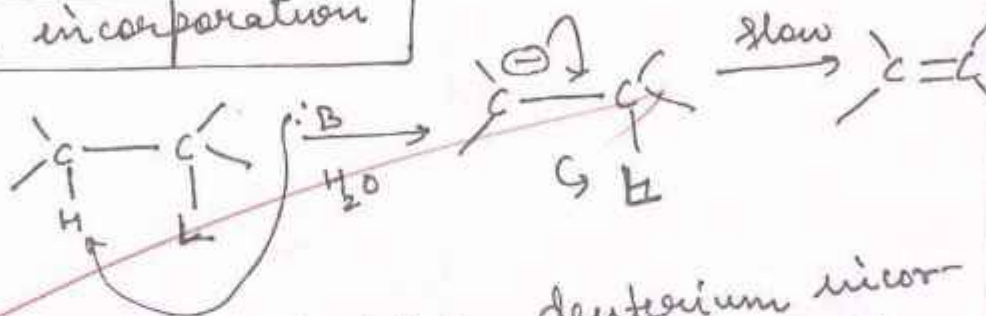
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(c) How will you differentiate E_2 and E_{1cb} mechanism by isotopic effect. (10)

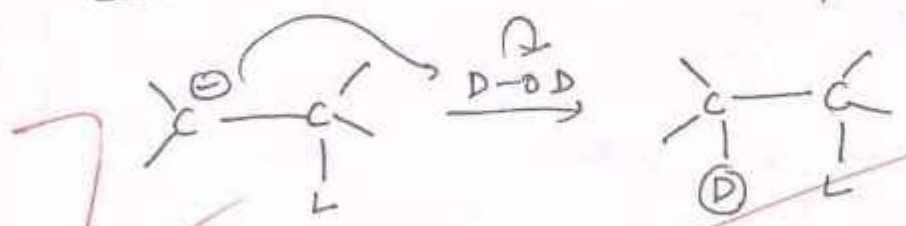
Both E_2 and E_{1cb} reaction are bimolecular. Thus rate of reaction ~~can't~~ (rate law) can't distinguish between E_2 and E_{1cb} . Isotopic effect is used for this purpose.

A) Deuterium incorporation

For E_{1cb}



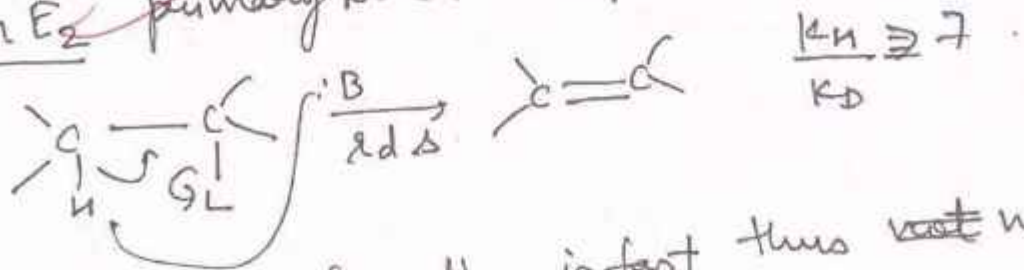
If D_2O is used instead of H_2O , deuterium incorporation takes place



This is due to formation of carbanion

But in E_2 no deuterium incorporation takes place

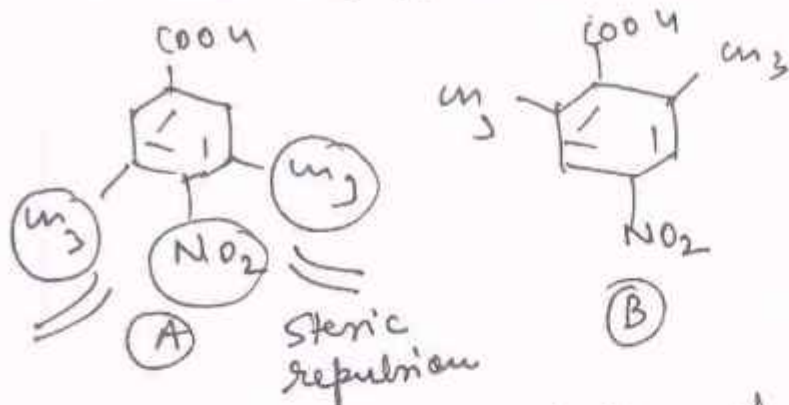
(B) In E_2 primary kinetic isotopic effect is observed.



In E_{1cb} carbanion formation is fast thus ~~not~~ no primary kinetic isotopic effect.

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8(a)(i) Out of 3,5-dimethyl-4-nitrobenzoic acid and 2,6-dimethyl-4-nitrobenzoic acid, which one is more acidic and why? (5)



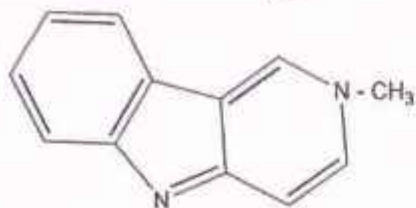
Due to steric inhibition of resonance, in (A) NO_2 becomes out of plane of benzoic acid and thus does not exert $-R$ effect which has the potential to increase acidic strength.

In B $-\text{NO}_2$ is in plane of benzoic acid thus increases acidic strength.

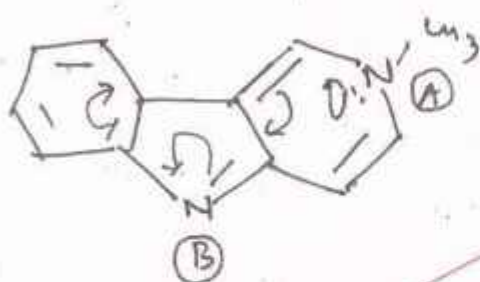
Thus, 2,6 dimethyl 4-nitrobenzoic Acid is more acidic.

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(ii) The compound shown is a somewhat stronger base than ammonia. Which nitrogen do you think is protonated when it is treated with an acid? Write a structural formula for the species that results. (5)

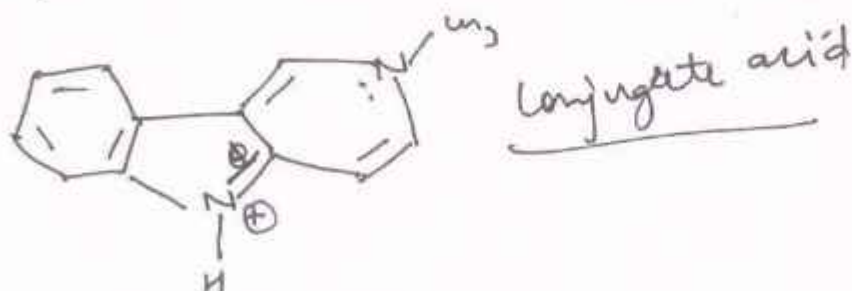


5-Methyl- γ -carboline
 pK_a of conjugate acid = 10.5



lone pair of A is involved in conjugation with the middle ring thus less available for attack.

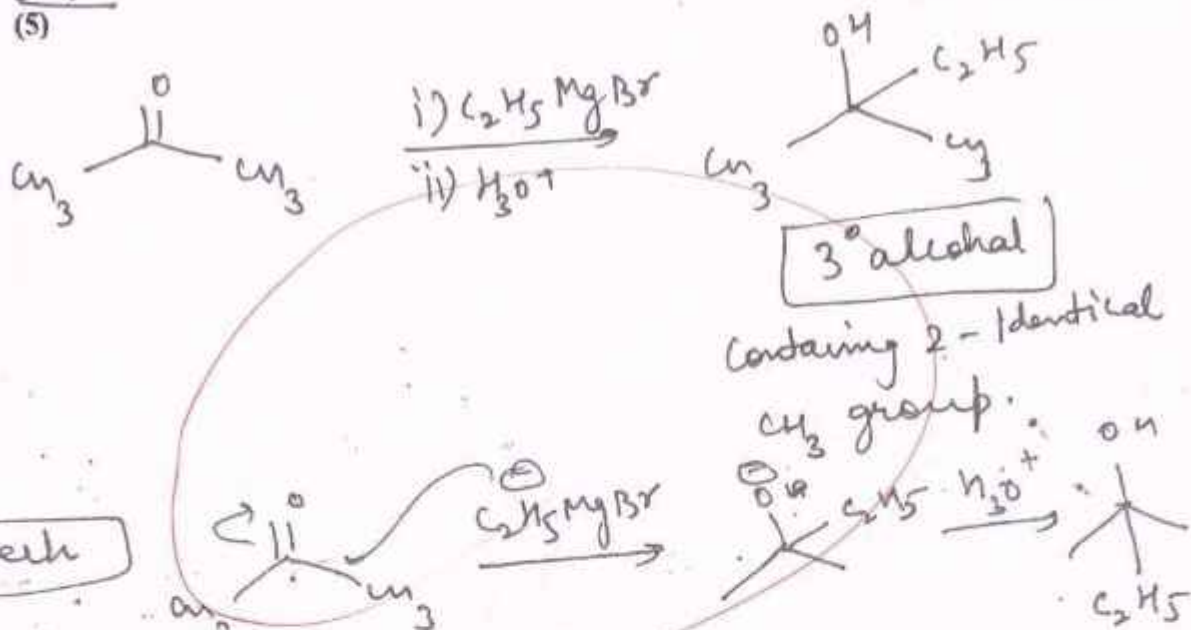
Thus, ~~the~~ B is more basic than A due to readily available lone pair and thus is protonated when treated with Acid.



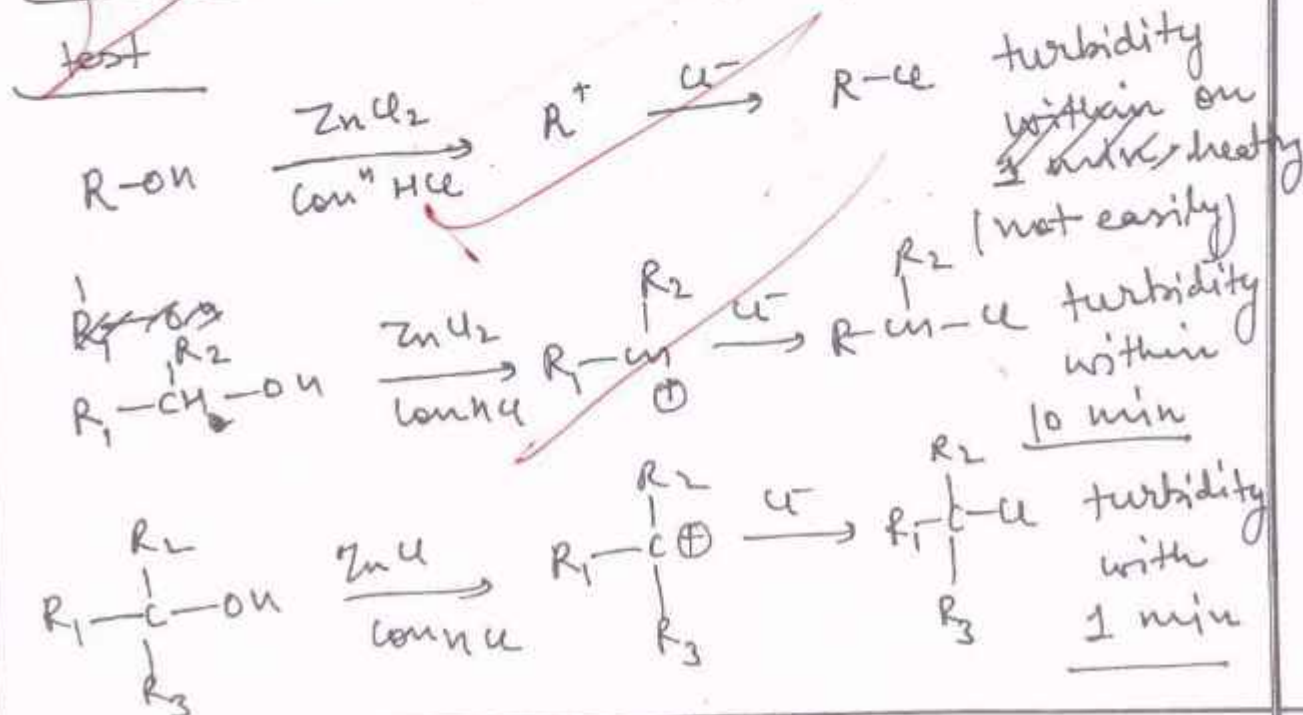
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(b) (i) Write a method of preparation of a tertiary alcohol containing two identical alkyl groups. Write one method for distinguishing primary, secondary and tertiary alcohols.

(5)

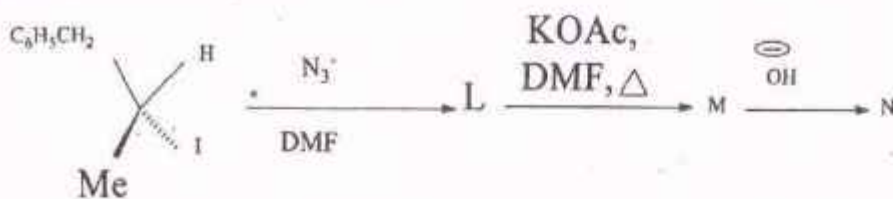


~~1°, 2°, 3° alcohol can be distinguished by Lucas~~

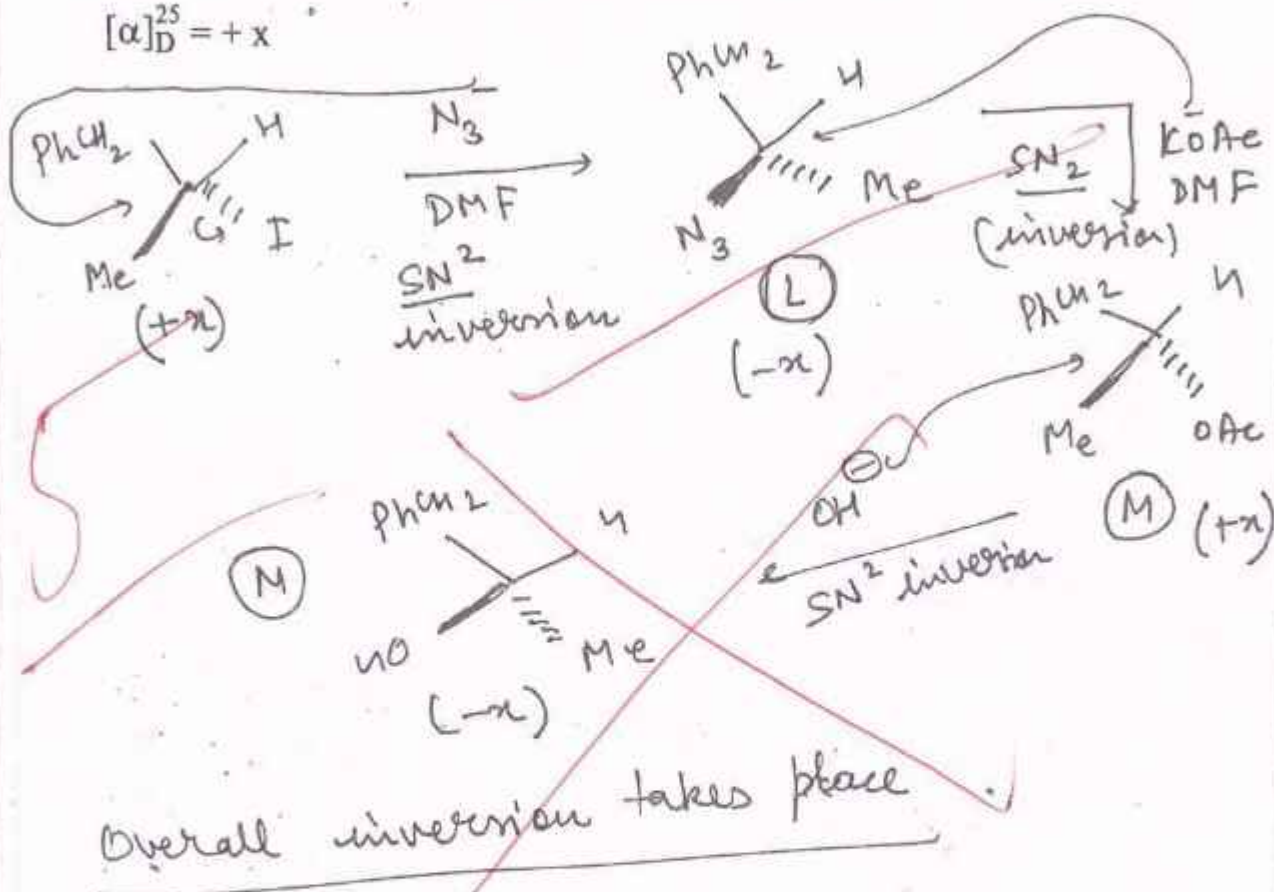


DIAS

(ii) Write the stereo structures of L to N comment on the specific rotation of N. Specific rotation of the starting iodide is +x. (10)



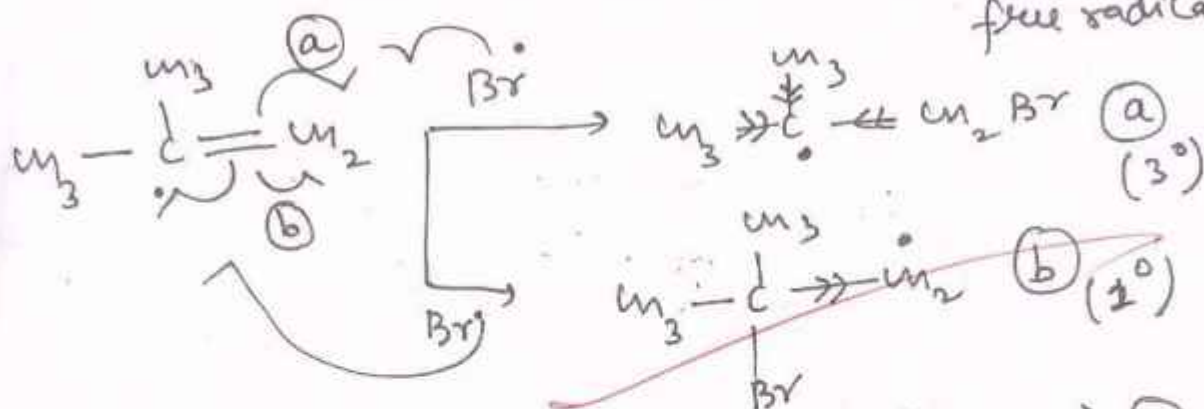
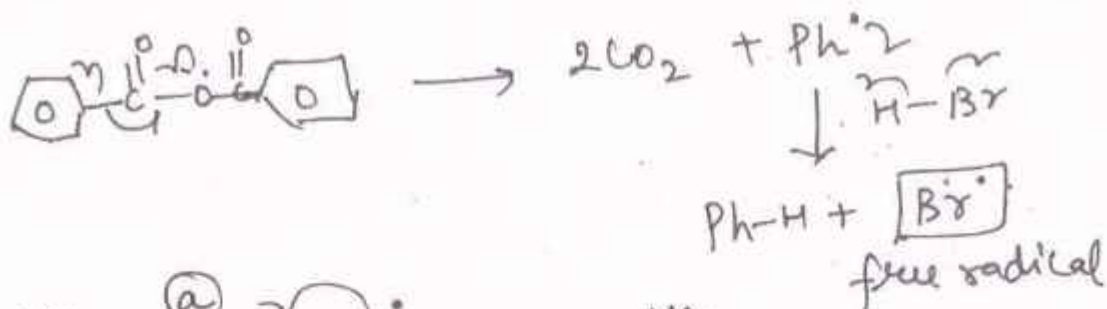
$[\alpha]_D^{25} = +x$



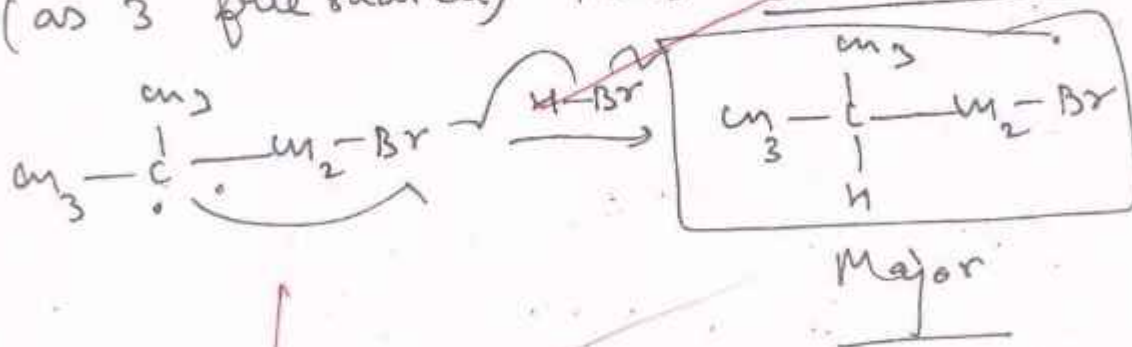
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(c) (i) Isobutene is treated with conc. HBr in the presence of dibenzoyl peroxide in acetonitrile solution. Formulate the reaction and give explanation for the formation of the product.

(5)

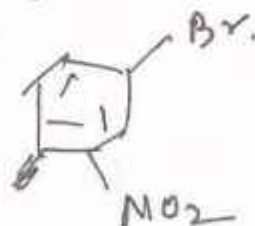
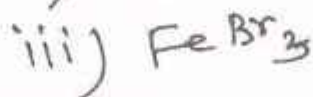
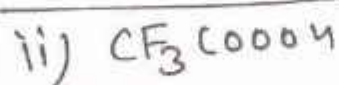
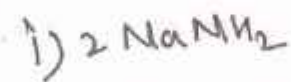
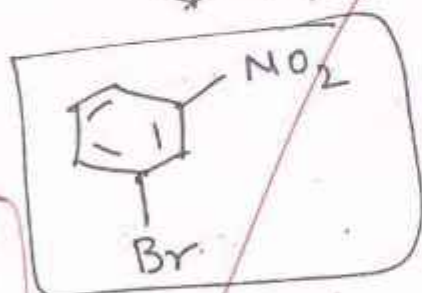
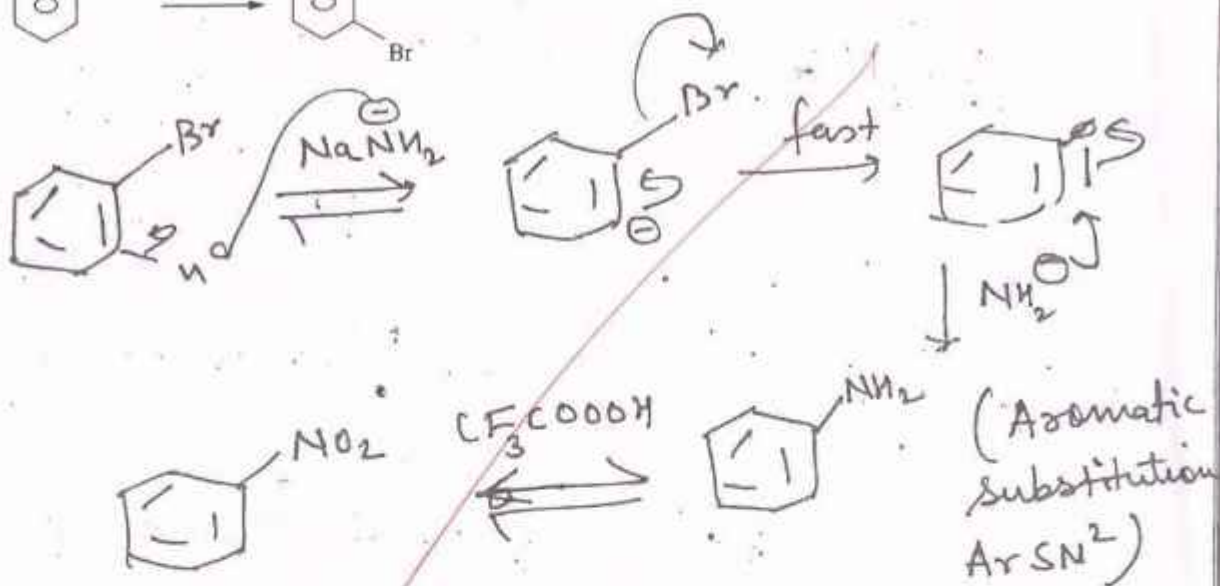


since free radical is more stable in (a) (as 3° free radical) thus (a) is formed



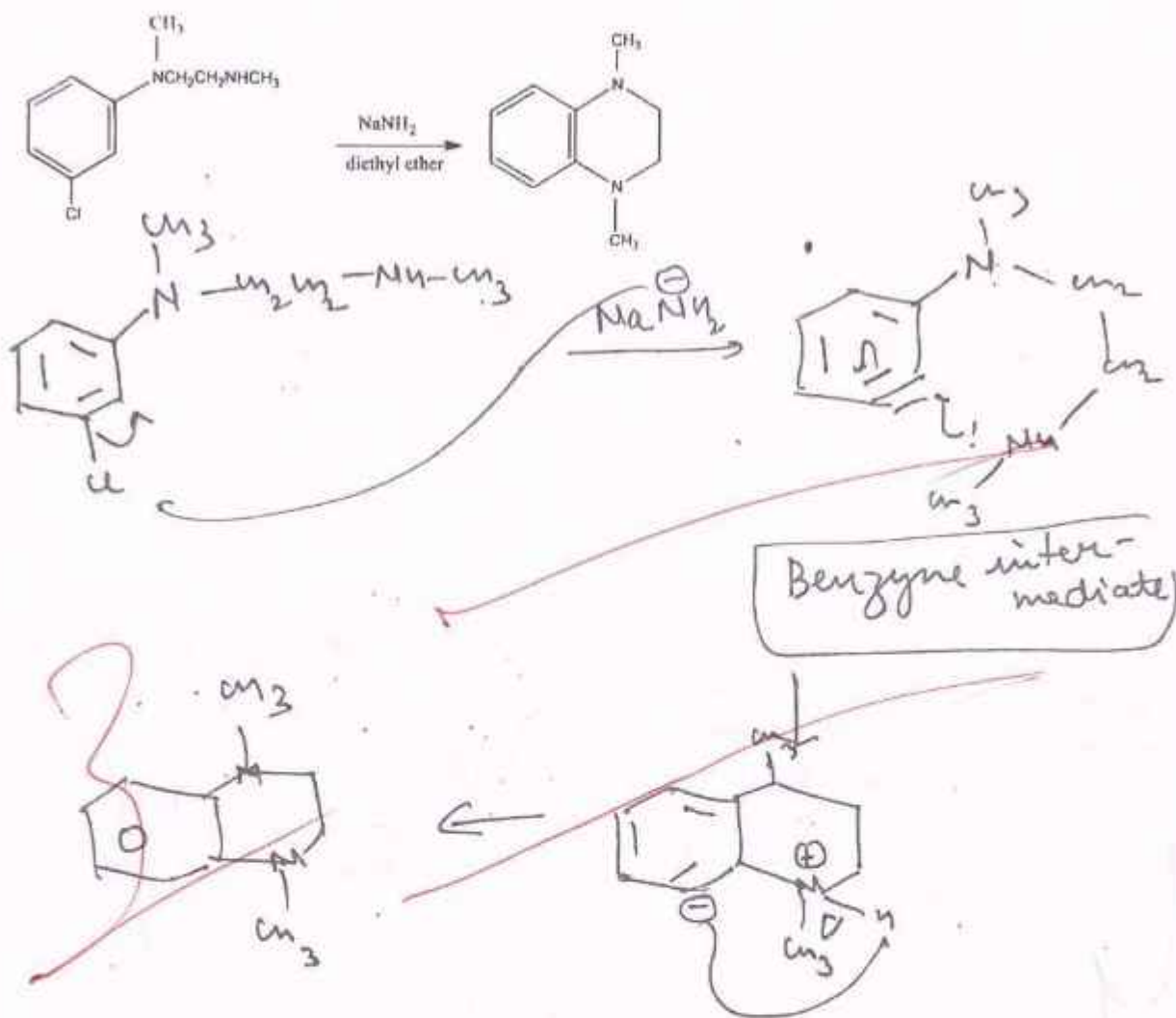
DIAS

(ii) Carry out the following transformation: (5)



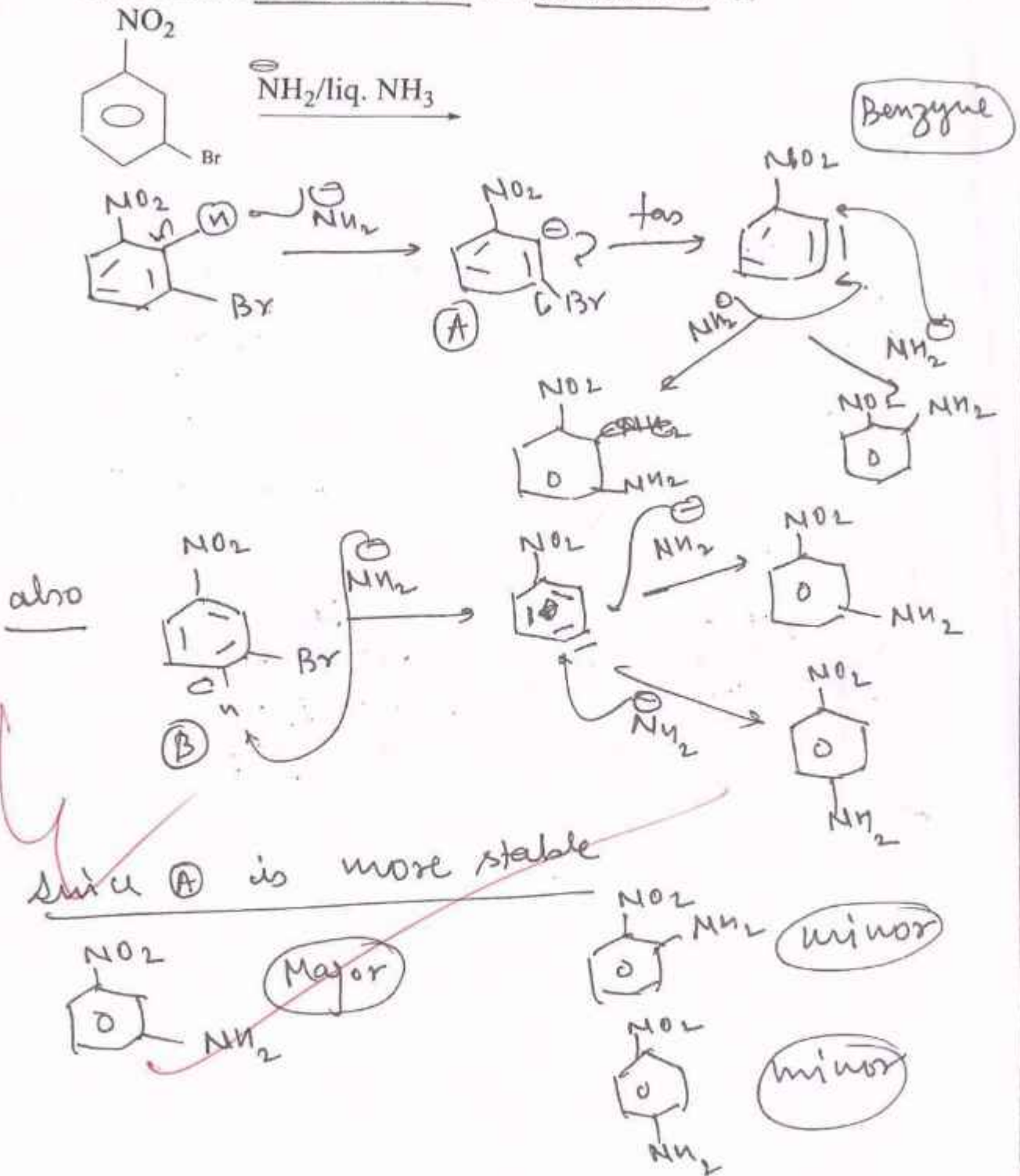
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(iii) How this product is formed give mechanism. (5)



DIAS

(d)(i) Predict the product(s) with mechanism and justify your answer. (5)



DIAS

(ii) Define a region specific reaction. How will you convert aniline into p-phenylene diamine? (5)

Region specific reactions are those which take place at a particular reaction center specifically in case of choice.

