

MODEL ANSWERS

BSc. Chemistry (Hon's) V Semester, 2013

Organic Chemistry

Section A (SAT Questions):-

1 i) Write down the entropy changes for the given reaction and explain why ΔG value is more negative in the exothermic reaction? $A \rightleftharpoons B + C$

Ans:- Entropy change for the given reaction is -

$$\boxed{\Delta S = +ve}$$

ΔG value is more negative in the exothermic reaction because:- $\Delta G = \Delta H - T\Delta S$

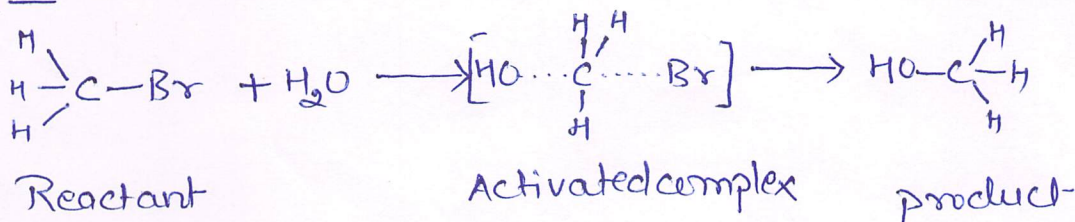
& $\Delta H = -ve$ ($\because H_R > H_P$), $\Delta S = +ve$ for exothermic reaction.

$$\therefore \boxed{\Delta G = -ve}$$

ii) What is activated complex? Draw the activated complex for the alkaline hydrolysis of bromomethane.

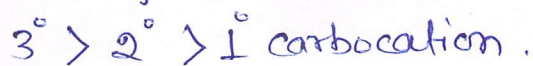
Ans:- An activated complex is a transition state, that is formed during the conversion of reactants into products.

Activated complex for the alkaline hydrolysis of bromomethane is:-



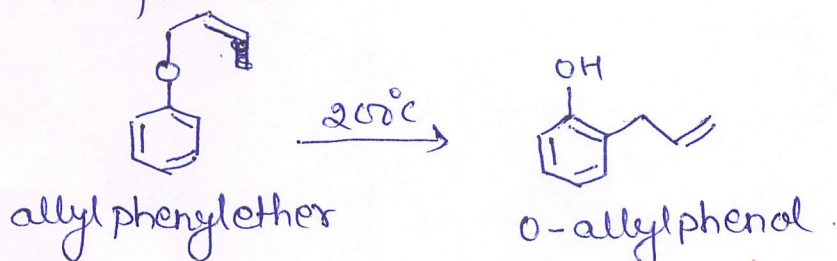
iii.) What is the order of stability of 1° , 2° , and 3° carbocation?

Ans:- Order of stability of carbocation is -



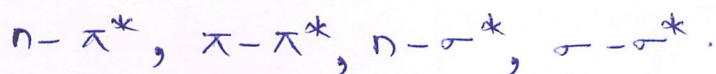
iv.) What happens when allyl phenyl ether is heated at 200°C ?

Ans:- When allyl phenyl ether is heated at 200°C then Ortho-allyl phenol is formed.



v.) What are the different excitations in a carbonyl compound?

Ans:- Different excitations possible in a carbonyl compound are -



vi.) What is the basic difference between Norrish Type I & II?

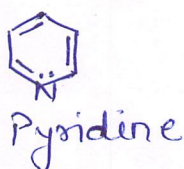
Norrish Type-I	Norrish Type-II
1.) In Norrish Type-I reaction decarbonylation takes place.	1.) In Norrish Type-II reaction decarbonylation does not take place.
2.) In Norrish Type-I reaction α -cleavage takes place.	2.) In Norrish type-II reaction γ -H abstraction followed by β -cleavage takes place.

vii.) What are heterocyclic compounds? Give an example.

Ans:- Heterocyclic compound are cyclic compound with a ring containing carbon and other element (like O, N, S, P, Si).

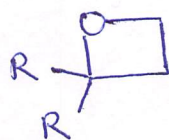
These compounds are very stable in nature, containing conjugated double bond and exhibited aromatic character.

eg:-



viii) Write the structure of oxetan and imidazole.

Ans:- Oxetan :-



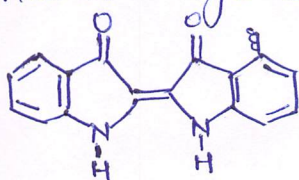
imidazole :-



ix) Give the structure and names of natural dyes.

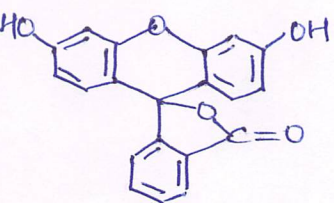
Ans:- Example of natural dye - Indigotin

Structure -

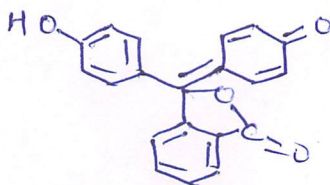


x) Structural changes are taking place in fluorescein dye on changing the pH of the solution.

Ans:-



Acidic pH



Basic pH.

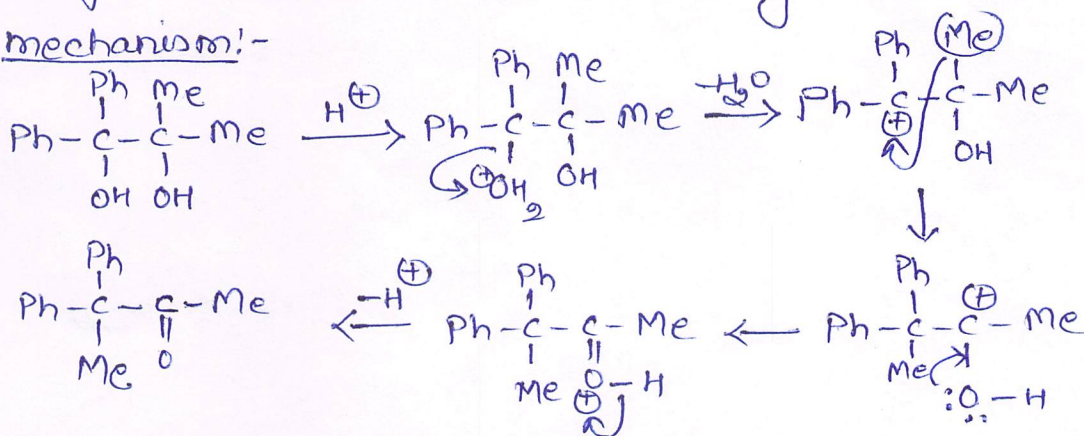
Section B (LAT Questions) :-

Q) How does crossover experiment help in establishing the mechanism of a reaction? Illustrate your answer with suitable example.

Ans:- Cross-over experiment helps to explain that in rearrangement reaction, intramolecular shift takes place or intermolecular shift takes place. In this way it helps in establishing the mechanism of a reaction.

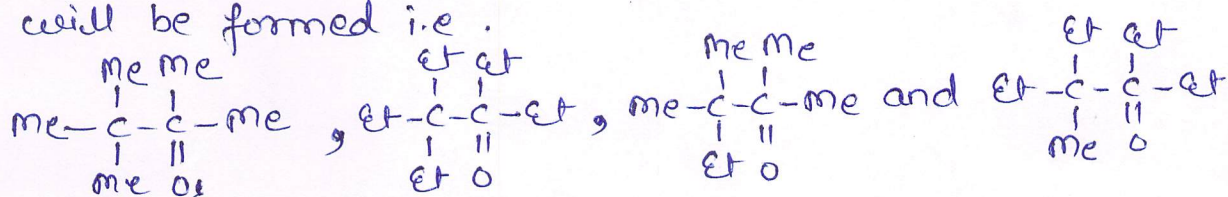
for eg:- Pinacol - Pinacolone rearrangement :-

Mechanism :-

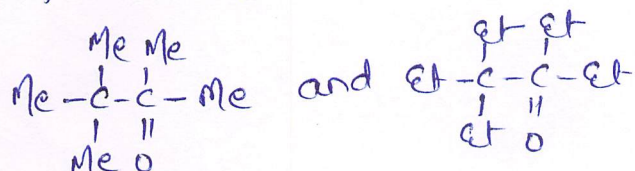


Intra- or inter molecular nature of a rearrangement can often be demonstrated by carrying out the reaction on a mixture of two different reactant i.e. $\text{Me}-\overset{\text{Me}}{\underset{\text{OH}}{\text{C}}}-\overset{\text{Me}}{\underset{\text{OH}}{\text{C}}}-\text{Me}$ and $\text{Et}-\overset{\text{Et}}{\underset{\text{OH}}{\text{C}}}-\overset{\text{Et}}{\underset{\text{OH}}{\text{C}}}-\text{Et}$ and then analysing the product.

Case I: If intermolecular shift takes place then four products will be formed i.e.



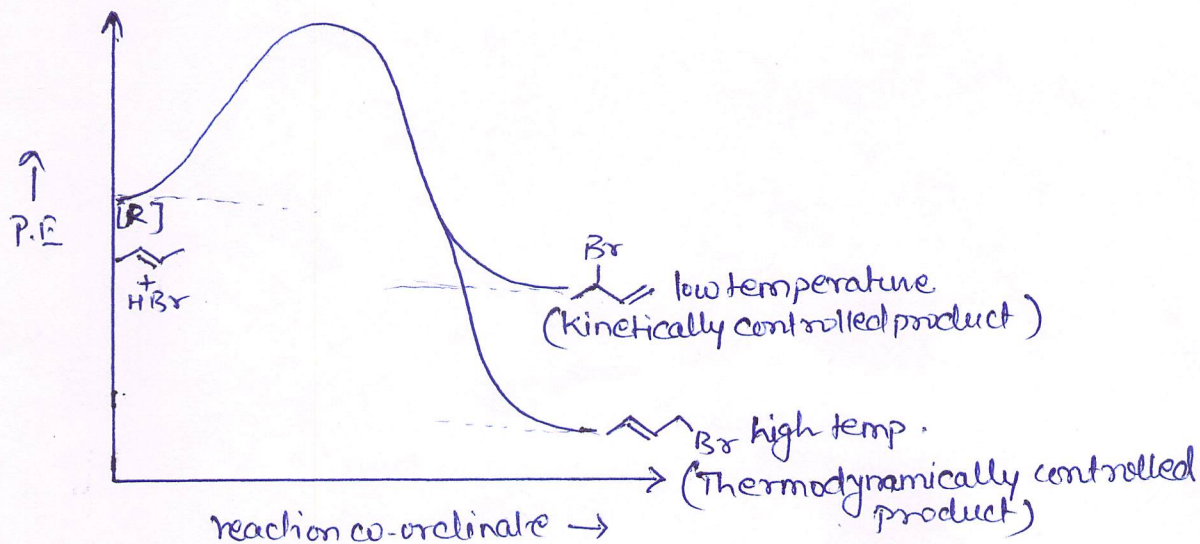
Case II: If intramolecular shift takes place then only two products will form i.e.,



And experimentally we obtain only two products that means intramolecular shift takes in pinacol-pinacolone type rearrangement.

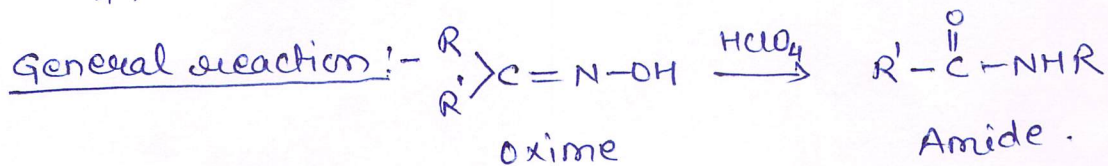
3.) Explain with energy profile diagram the addition of HBr to 1,4-butadiene at lower temperature produced 3-bromobut-1-ene as the major product whereas at higher temperature produced 1-bromobut-2-ene as the major product.

Ans:- Energy Profile diagram:-



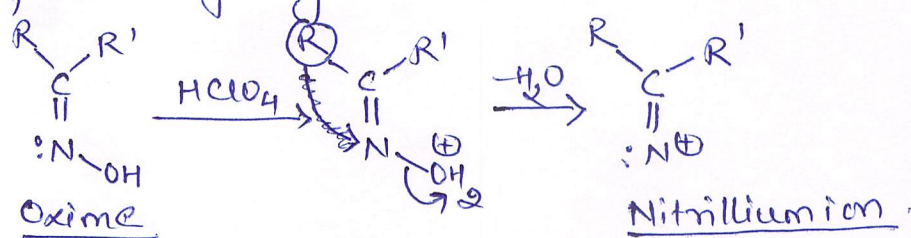
4) Write a short-note on Beckmann rearrangement.

Ans:- When oximes are treated with conc. H_2SO_4 or PCl_5 or H_3PO_4 or $HClO_4$, then amides are formed via Nitrilium ion intermediate.

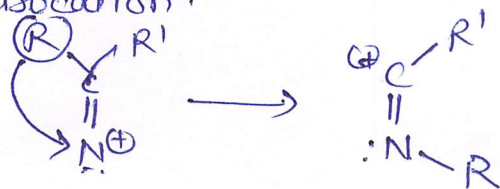


Mechanism:-

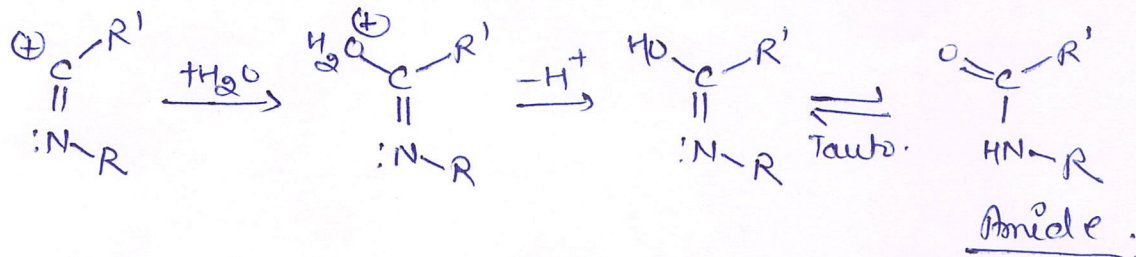
Step 1:- Protonation of -OH groups followed by the elimination of water giving a nitrilium ion.



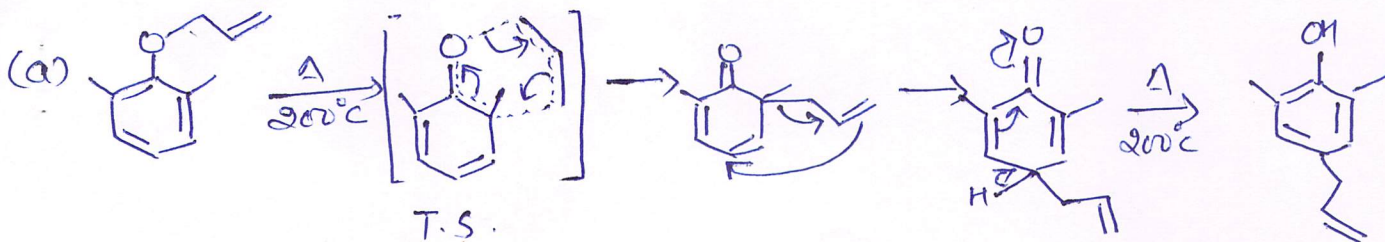
Step 2:- Migration of -R group which is anti -OH group, producing a carbocation.

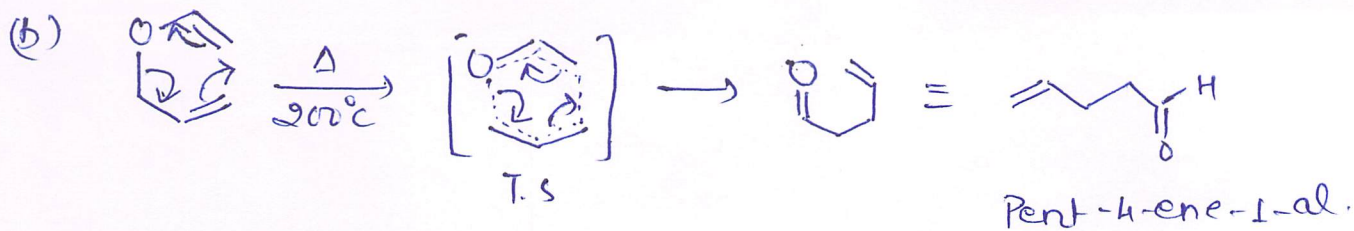


Step 3:- Addition of H_2O to carbocation followed by tautomerism, then amides are formed.

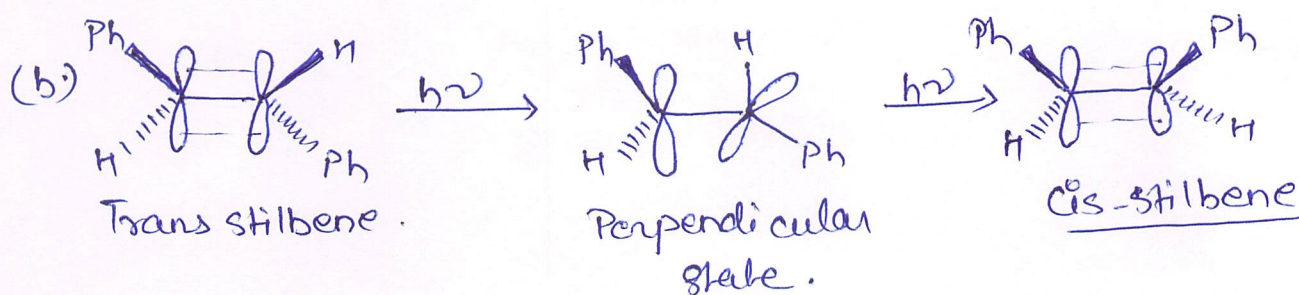
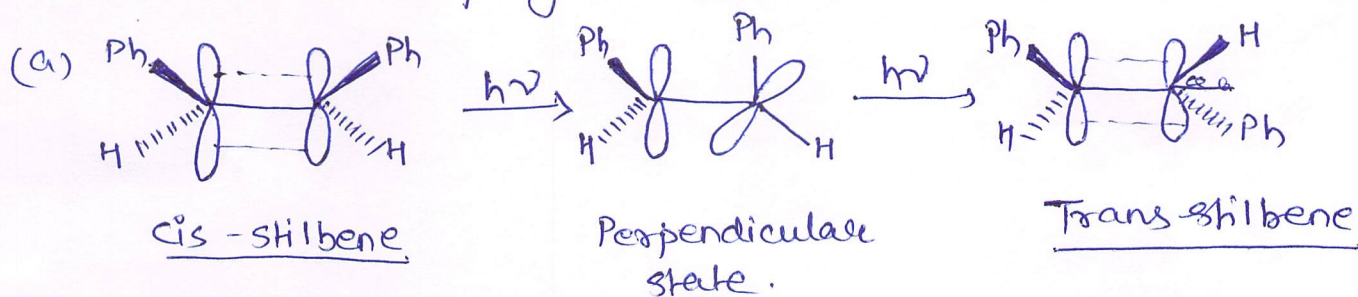


5) Complete the following reaction with mechanism.





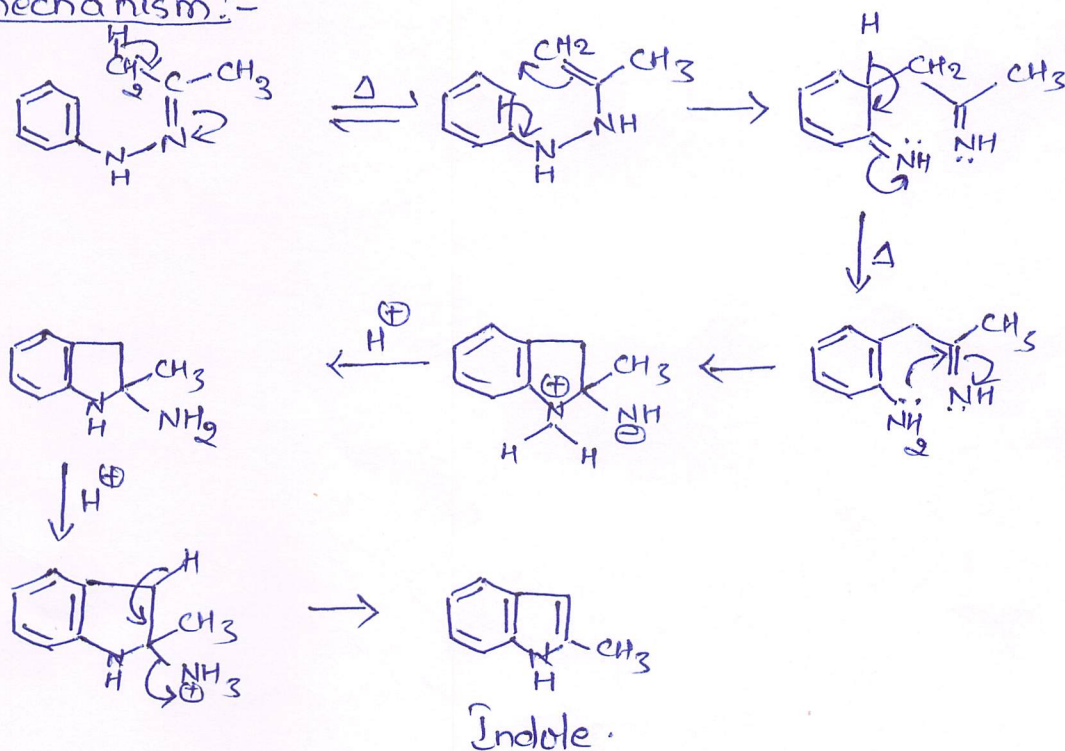
6.) Explain the results obtained for irradiating Cis-Trans stilbene separately by UV.



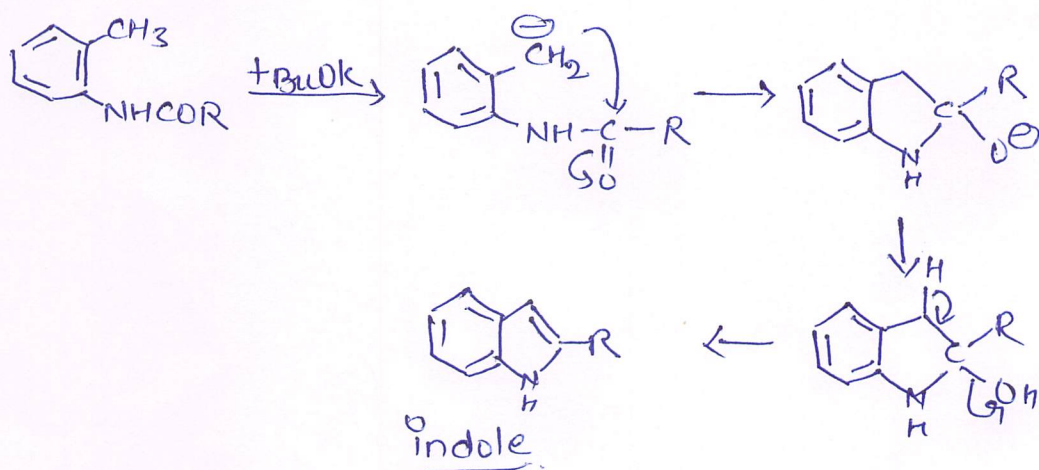
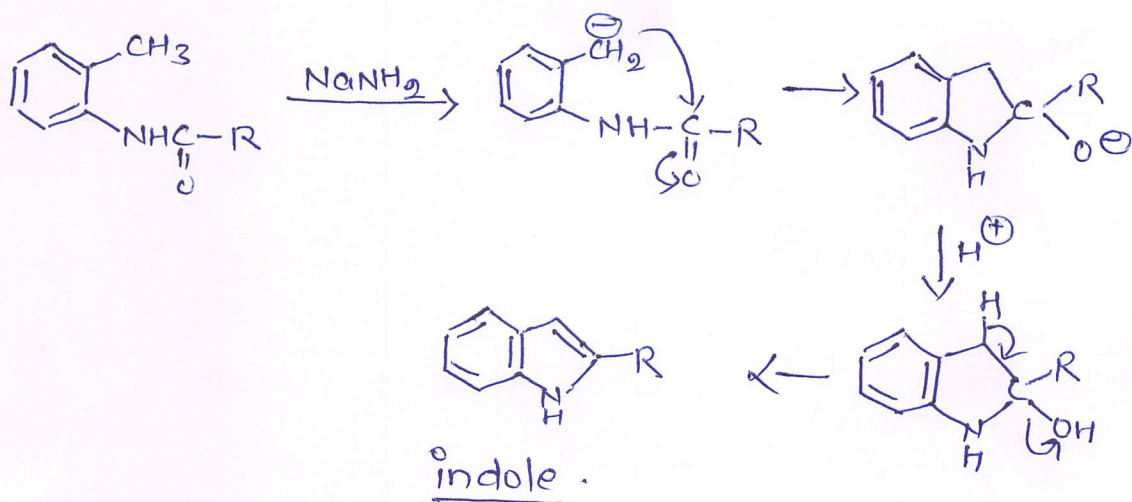
7.)(a) Explain in details the mechanism of Fischer's indole synthesis.

Ans:- When phenylhydrazone derivative of an aldehyde or ketone is heated with $ZnCl_2$, then indole is formed.

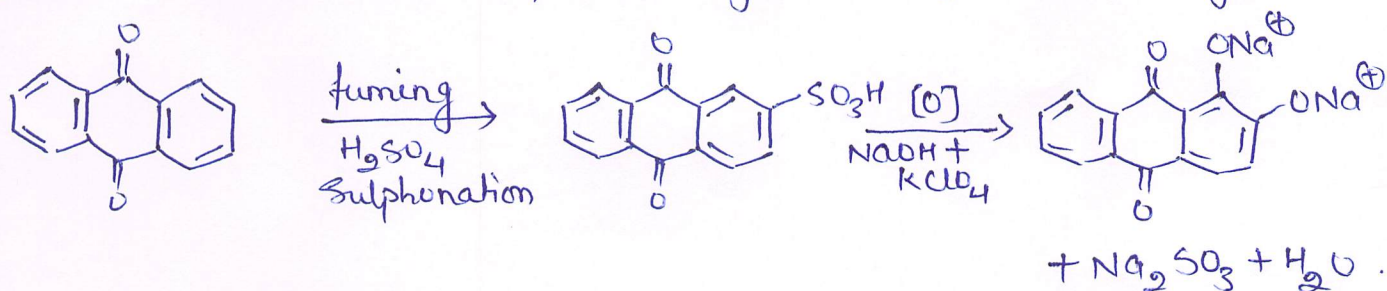
mechanism:-



(b) Complete the following reactions below :-



8) (a) Give one method for the synthesis of Alizarin dye.



Here, KClO_4 act as an oxidising agent (source for 'O' atom) and oxidise 2-hydroxyanthraquinone to 1,2-dihydroxyanthraquinone.

(b) Explain Bathochromic shift .

Ans:- The groups that brings about the deepening of colour are also called Bathochromic group.

Absorption at longer wavelength gives deep colour, so the presence of Bathochromic group in a molecule shifts the absorption of colours towards red also called Red shift or Bathochromic Shift.