

AS-2144

M. Sc (First Semester) Examination, 2013

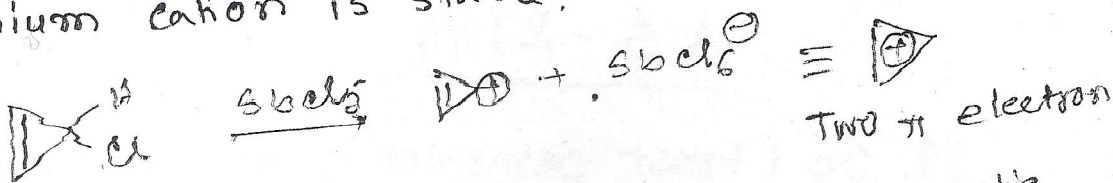
CHEMISTRY

Paper : CMT-103

Organic Chemistry-I

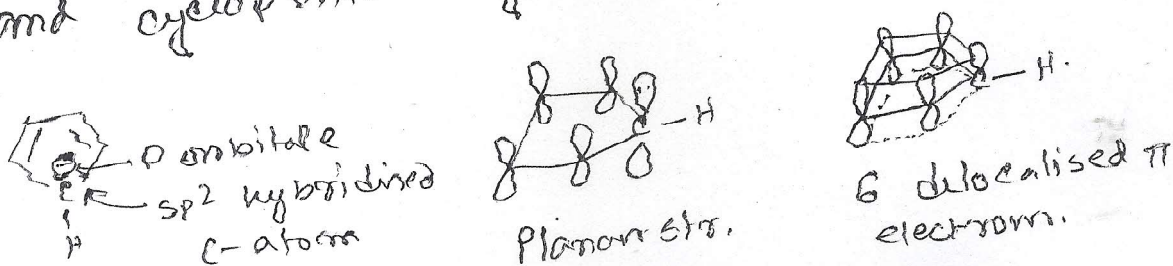
DR. PATHIK MAJI

(143) Give your explanation why cyclopropenium cation is stable.



from a closed shell so it is aromatic.  
 And thus it is stable and obeying the Hückel's rule.

(47). Account for the aromaticity of cyclopentadienyl anion and cyclopentadienyl cation.



It has planar cyclic structure with 6 delocalised  $\pi$  e. Hence Hückel rule tells us that cyclopentadienyl anion is aromatic.

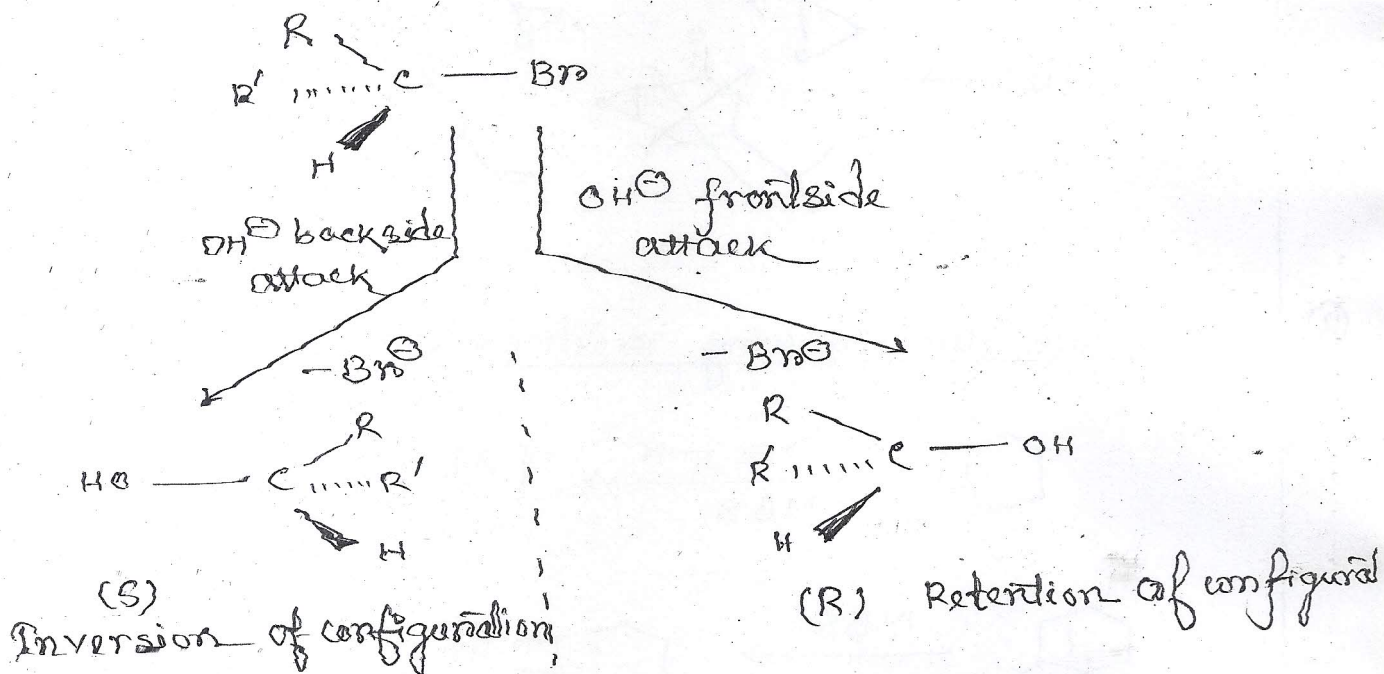


It has planar cyclic structure with 4 delocalised  $\pi$  e. Hence Hückel rule tells us that cyclopentadienyl cation is not aromatic.

1/13

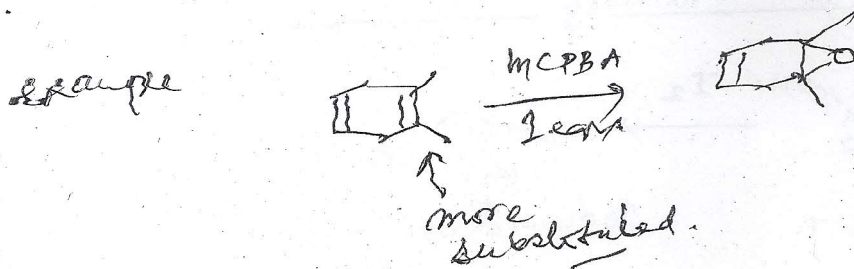
Discuss the stereochemistry of  $S_N2$  reaction.

As in a  $S_N2$  reaction the nucleophile attacks the C-site from back side from which the 'L' group departs. Inversion of configuration of C-site is observed. A  $S_N2$  reaction is a stereospecific reaction.



More substituted = alkene epoxidise faster. Explain.

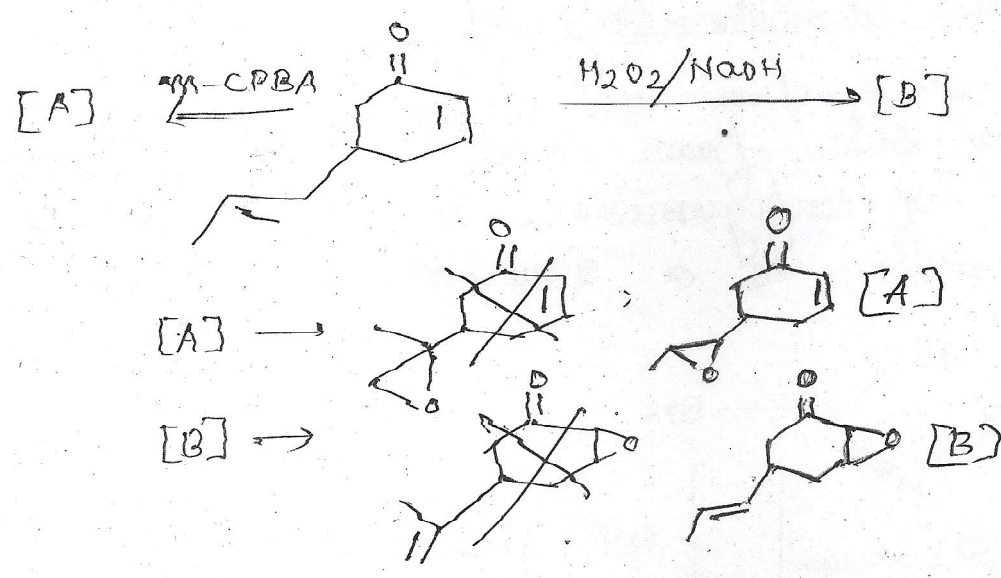
More substituted (=) bond will form epoxide faster. This is due to the fact that the presence of electron donating groups increases the electron density of alkene (i.e., alkene becomes more nucleophilic in nature). The same electron donating group raises the energy of the HOMO of a double bond makes it more nucleophilic.



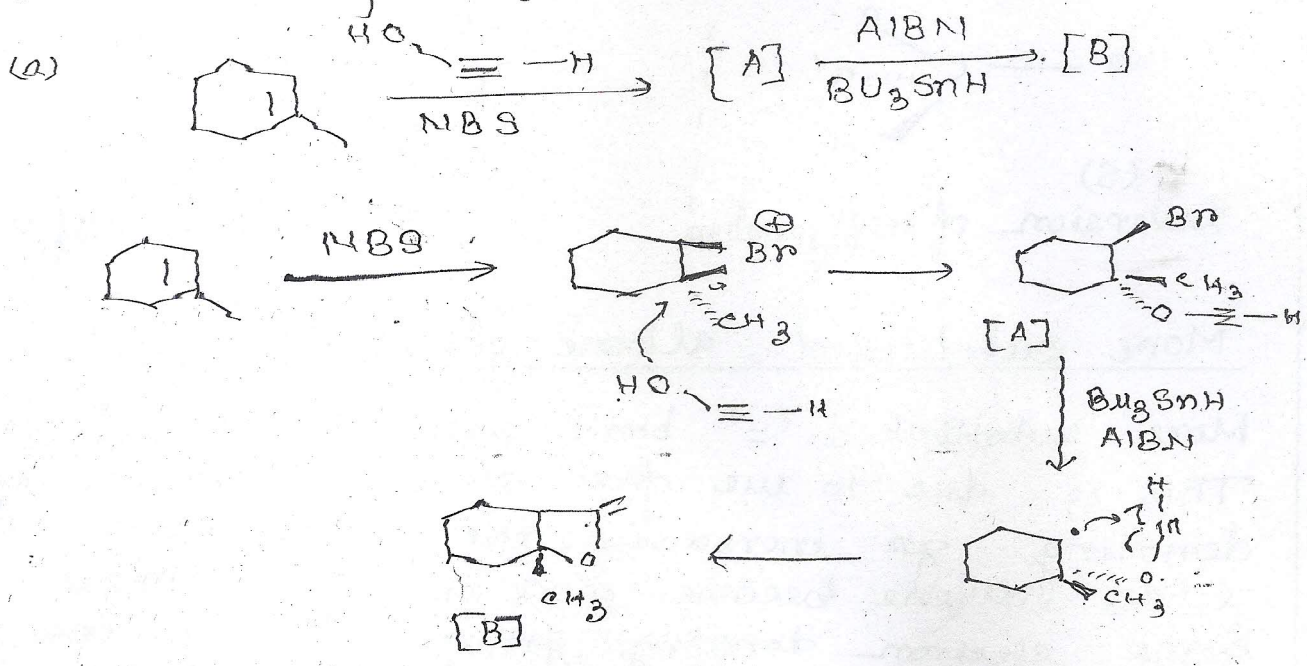


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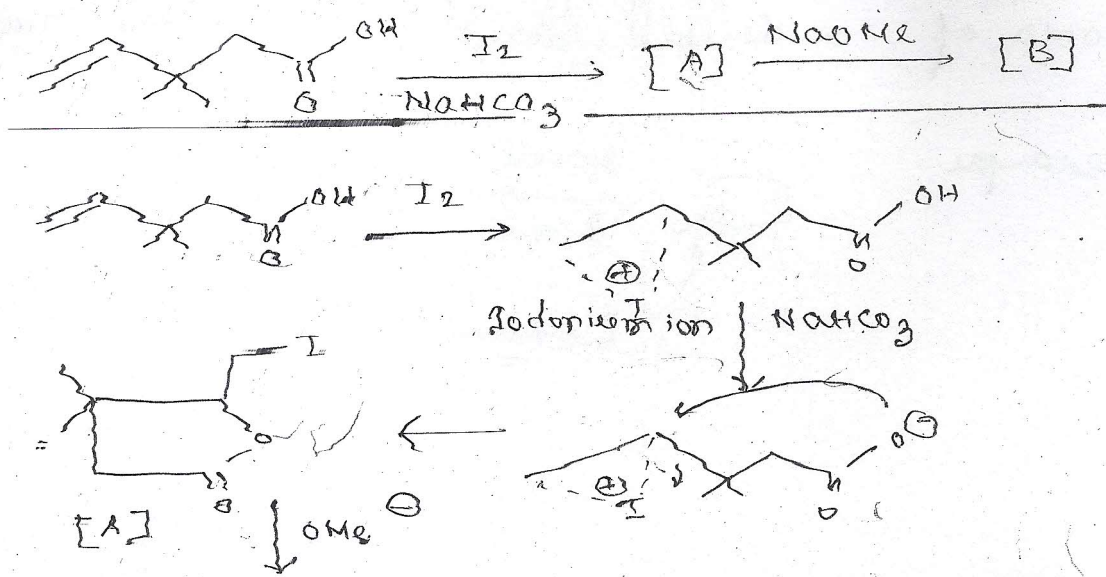
(iii)



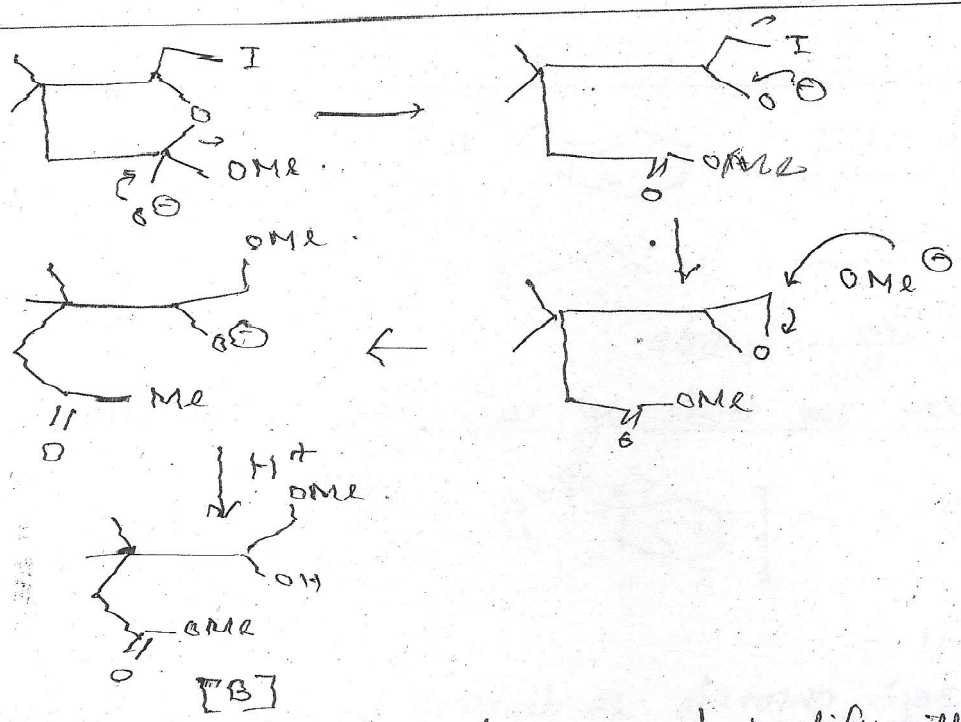
2) Complete the following reactions with mechanism:



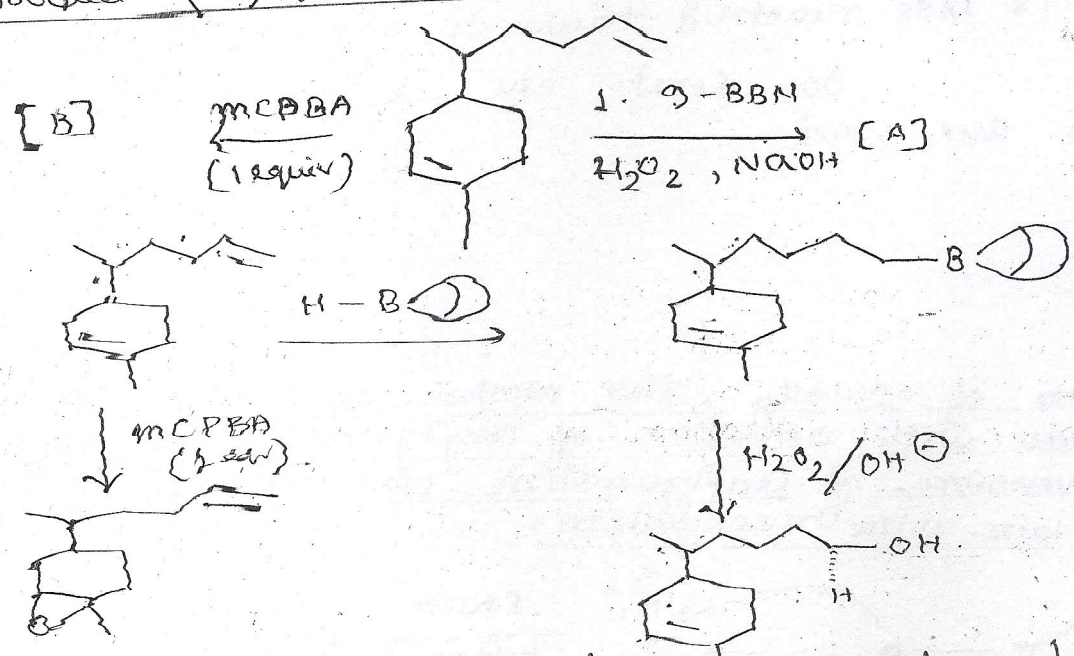
(ii)



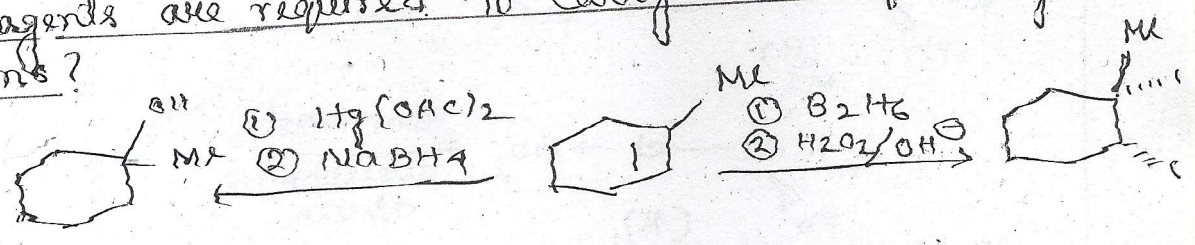




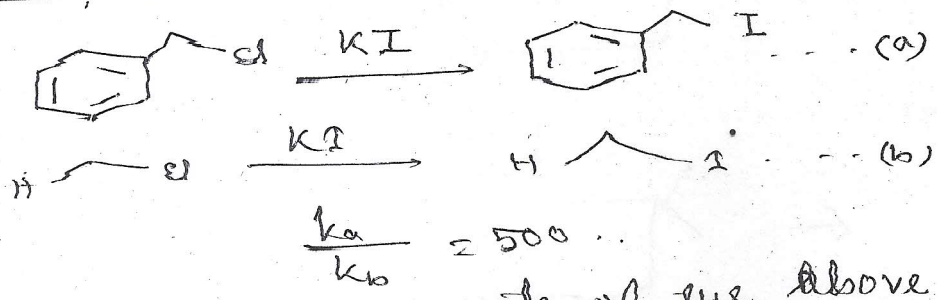
3) Complete the transformations and justify the formation of product (s) product :



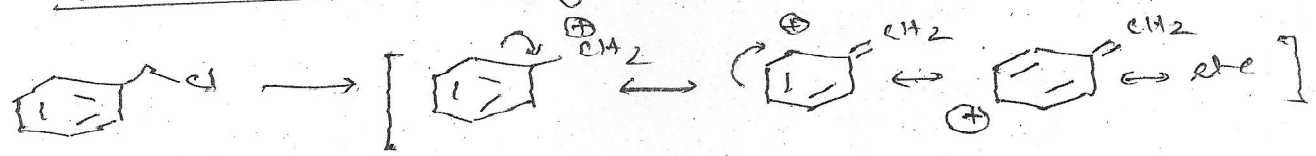
4) What reagents are required to carry out the following transformations?



(c)



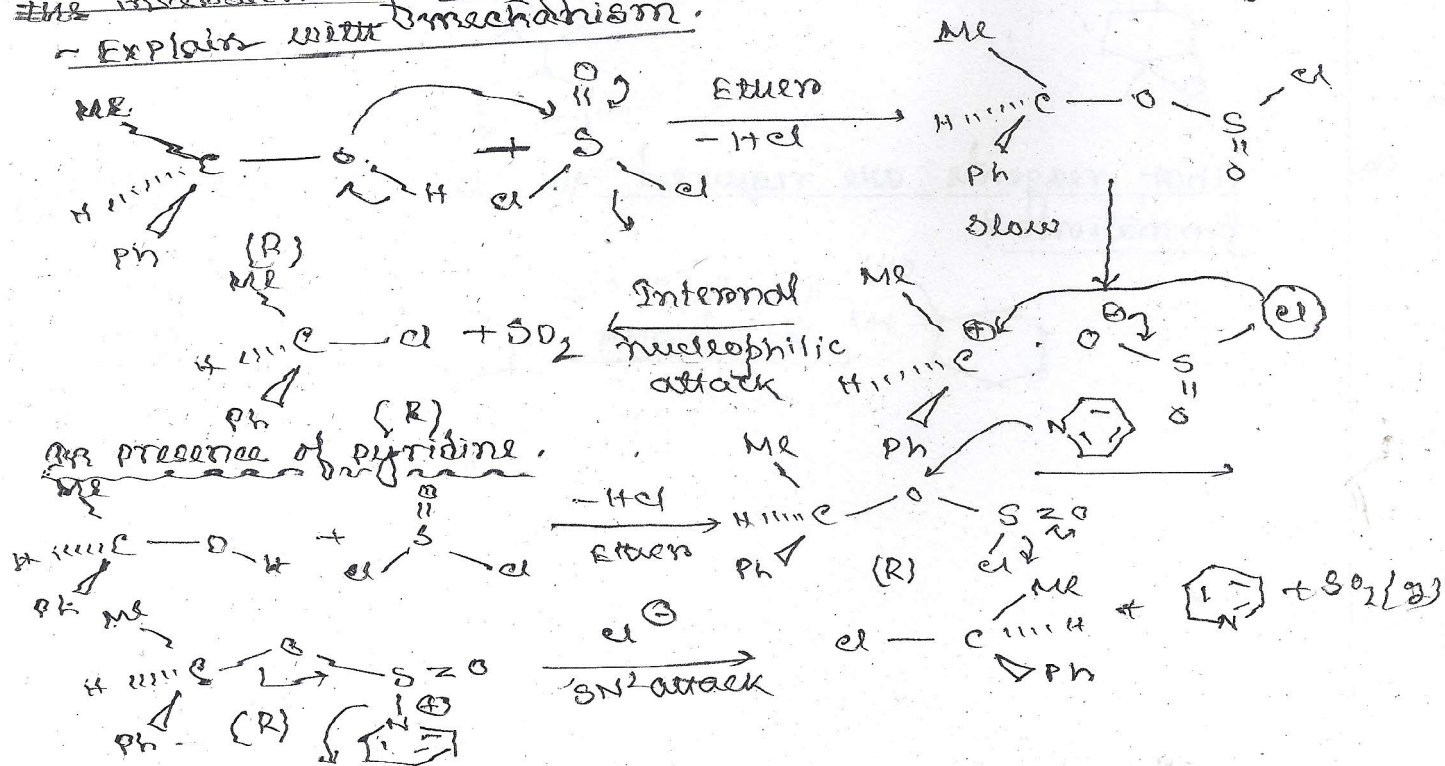
Explain the rate of the above reactions.



benzyl chloride is better substrate for  $S_N1$  reaction because of the resonance stabilisation.  $n$ -ethyl chloride is not resonance stabilised so it is less reactive towards  $S_N1$  reaction. So, first one is more faster in rate than the second.

(b)

Reaction of optically active alcohol with  $SOCl_2$  produces alkyl chloride with retention of configuration in ethers however the inversion of configuration was observed in pyridine. Explain with mechanism.





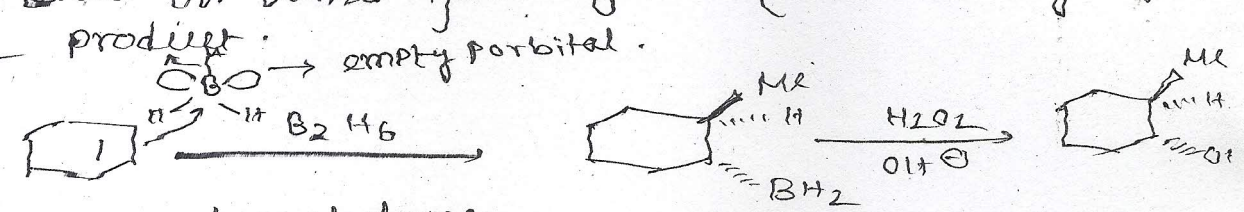
When (R) 1-phenyl ethanol and thionyl-chloride react in presence of a base e.g. pyridine (S)-1-phenyl ethyl chloride is obtained. i.e., inversion of configuration occurs.

Inversion result because pyridine reacts with the alkyl chlorosulphite to give (A) before anything further can take place. The  $Cl^-$  freed in the reaction is an effective nucleophile which attacks from the back side of the  $C-O$  bond in a normal  $SN_2$  reaction leading to inversion of configuration.

Hydroboration reaction is regioselective taking suitable e.g.

Hydroboration reaction is regioselective in nature. 'B' atom add to the '1' atom of alkene which contains more H atom or less substituent and H atom add to the more substituent end of the alkene. This is due to the fact that B is larger in size than H. So it prefers to add to the terminal end. The electronic reason for such kind of addition is that B is less electronegative than H atom. So, +ve part (B) is added to carbon atom contains more H atom by Markovnikov rule.

Some side Addition of H and B takes place from the same side or same face of alkene resulting syn addition product.



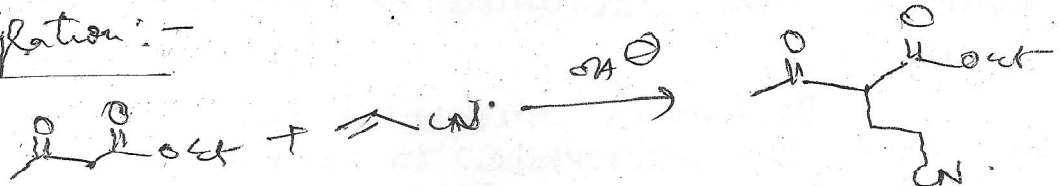
The alkene pushes electrons into the 'B' empty p orbital while the H<sup>+</sup> transfers into the alkene.

Syn add<sup>n</sup>  
regioselective add<sup>n</sup>.



⑥

Cyanosulfonation:-



- Introduction of  $\text{-CN}$  group is known as cyanosulfonation.
- Can be done by addition of acylonitrile to active methylene compounds.

① vi) Write down the expression of Taft equation and indicate meaning of each term within it.

considering the polar effect only on substituent R in the ester hydrolysis.

$$\log \left[ \frac{k_R}{k_0} \right]_{\text{Base}} - \log \left[ \frac{k_R}{k_0} \right]_{\text{acid}} = \rho^* \sigma_R^*$$

where  $\rho^*$  is the reaction constant with polar effect  $\rho^*$  was calculated by subtracting the  $\rho$  value for acid catalysed hydrolysis of benzoate esters from the  $\rho$  value of base catalysed hydrolysis of the same esters.

① (vii) What is substituent constant ( $\sigma_x$ )? How it could be obtained with the help of pKa value?

$$\sigma_x = \log \frac{k_x}{k_H}$$

Knowing  $k_H$  &  $k_x$  for a variety of differently x-substituted benzoic acids it is then possible to define a quantity.

$$\log \frac{k_x}{k_H} = \rho \sigma_x$$

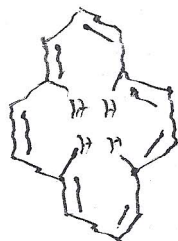
$$\sigma_x = \log k_x - \log k_H$$

$$\Rightarrow \sigma_x = -pK_a(x) + pK_a(H)$$

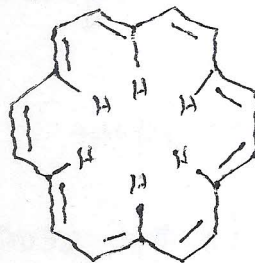
$$\Rightarrow \sigma_x = pK_a(H) - pK_a(x)$$

8

(4)(a) Draw the structure of [14]annulene and [18]annulene? Give your explanation why [18]annulene is more stable than [14]annulene although both are having  $(4m+2)$   $\pi$  electron.



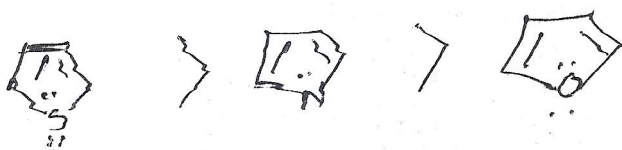
[14]annulene



[18]annulene

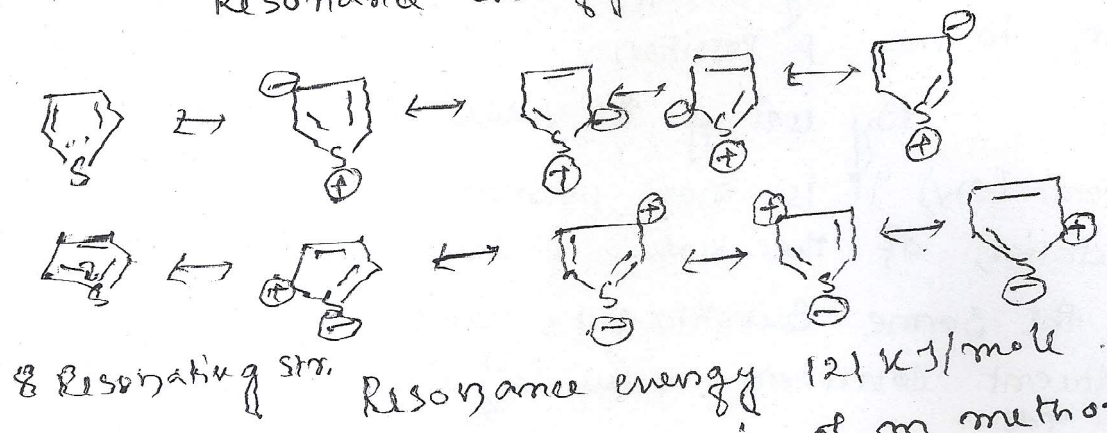
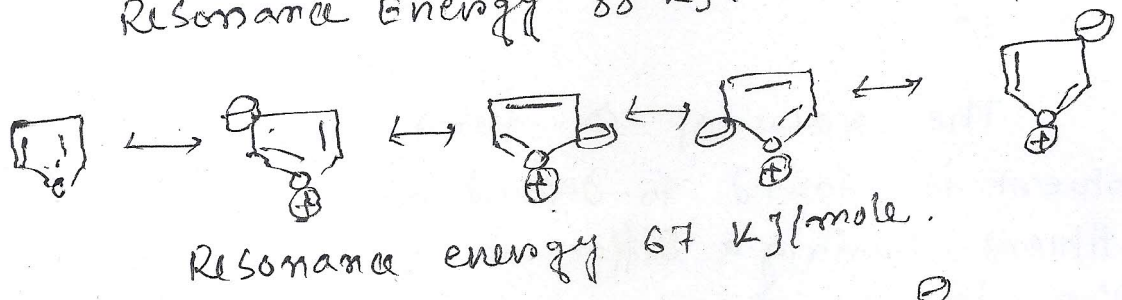
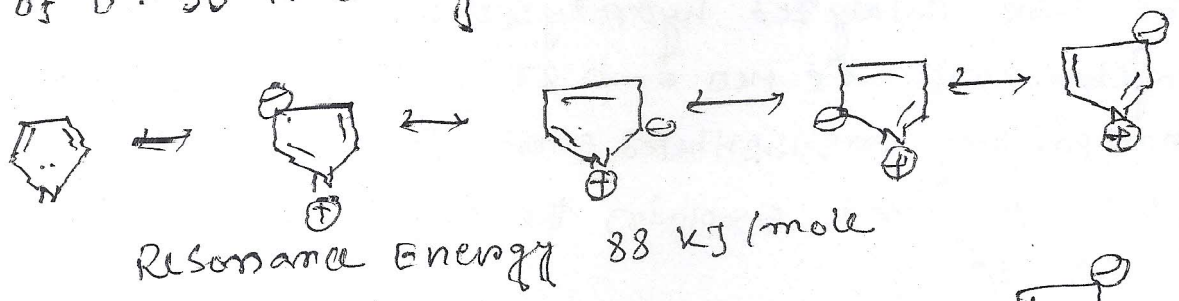
These two are ordinary aromatic, but have some alkene characters because the internally substituted H atoms inside the ring exerts steric repulsion and thus the system deviates from planarity. And the rep<sup>n</sup> in [14]annulene is greater so the [18]-annulene is more stable than [14]annulene.

(b) Write down the descending order of aromaticity in the given heterocyclic compounds with explanation:  
 (i) Pyrrole (ii) Furan (iii) Thiophene (draw the resonance structure and indicate the resonance stability in each case)

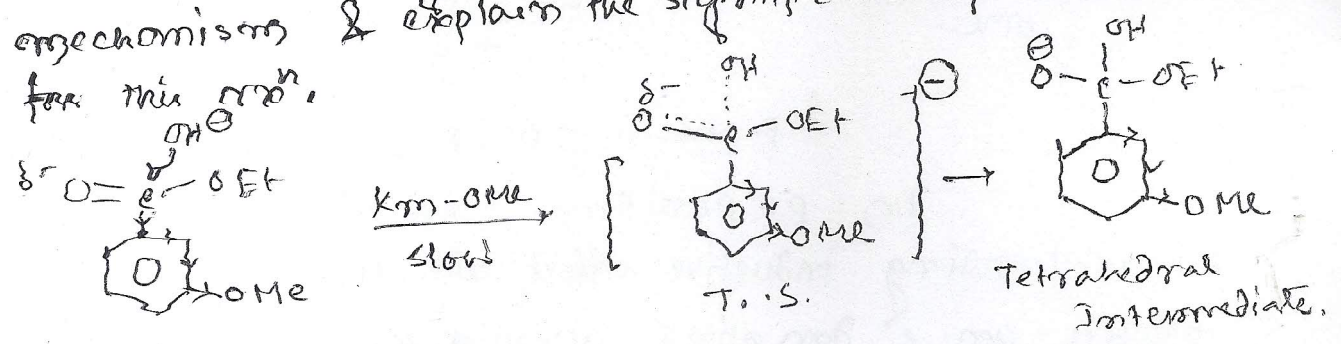




In thiophene aromaticity is more due to S is 3rd period element vacant d orbital as well as low electronegativity so it easily donate lone pair in the ring i.e d orbital participation is occur.  
 In case of pyrrole N is less e.n compare to that of O. so N easily donate lone pair of electron.



(5) (a) why base catalysed hydrolysis of m methoxy ethylbenzoate ( $\sigma_{m-MeO} = +0.12$ ) is faster than the corresponding unsubstituted ester? Draw the mechanism & explain the significance of  $\sigma$  value for this rxn.



$$\sigma_{m-MeO} = 0.12$$

$$k_{m-MeO} > k_H$$

(16)

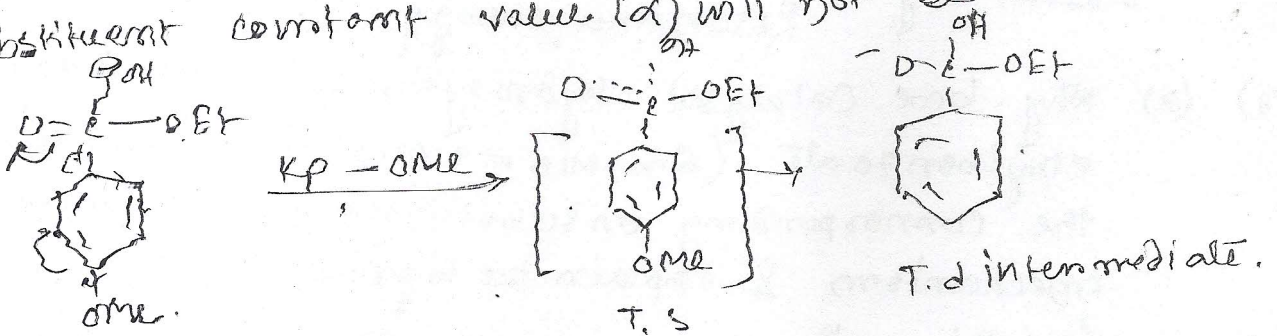
In the m-position the electronegative oxygen atom of the MeO gr exerts an electron withdrawing inductive effect ( $\sigma_{m-MeO} = 0.12$ ). The T.S will be more stabilized than an unsubstituted ester. Thus ester hydrolysis is faster than the corresponding unsubstituted ester.

(b). why base catalyzed hydrolysis of p-methoxy ethylbenzoate  $\sigma_{p-MeO} = -0.27$  is slower than the corresponding unsubstituted ester? Draw the mechanism of the rxn and explain the significance of  $\sigma$  value for this rxn.

The value of  $\sigma$  for a particular substituent is found to depend on the location of the substituent, having a different value in the m-position to the p-position.

By using the value of substituent constant ( $\sigma$ ) it is now possible to use them for the calculation of the value of the  $k$  the reaction constant.

For the same substituents at the p-position the substituent constant value ( $\sigma$ ) will not be same.



$\sigma_{p-OMe} = -0.27$  i.e.  $k_{12} > k_{p-OMe}$ .

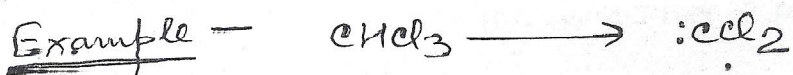
In p-position MeO will still exerts an e withdrawing inductive effect but undergo its e pairs exerts an e donating mesomeric effect on the ring carbon atom to which COOEt gr attached.



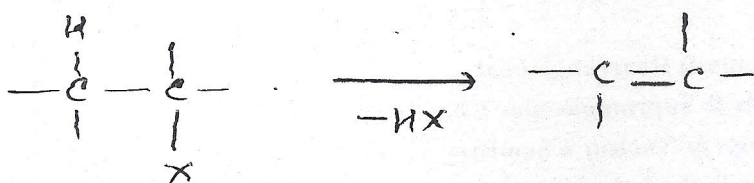
⑤ The latter effect is greater b/w these two. Because it involves more readily polarisable  $\pi$  e system and the overall result is therefore net e donation ( $\rho_{p-MeO} = -0.27$ ). Thus T.S will be more unstable compared with unsubstituted ester. Hence p-MeO ester hydrolysis proceeds more slowly than the unsubstituted analog.



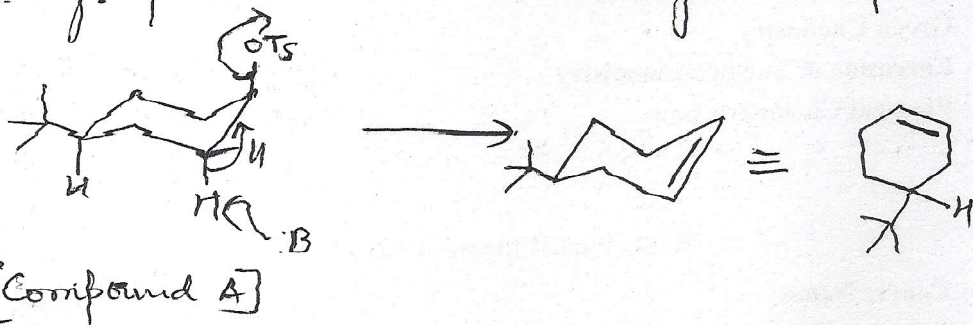
Answer 1 (viii) — When the loss of both the groups occurs from the same carbon atom, the elimination is called as  $\alpha$ -elimination reaction or, 1,1-elimination.



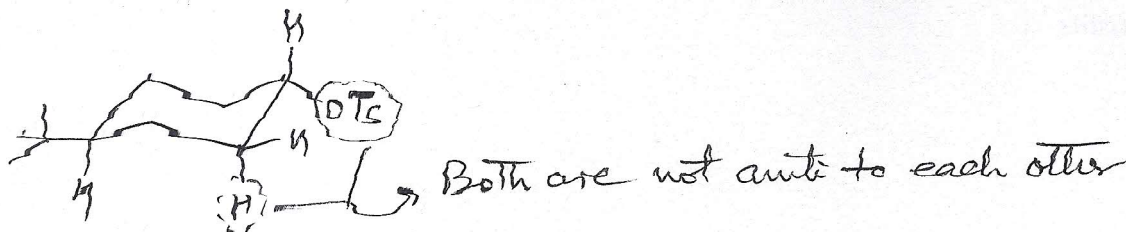
$\beta$ -elimination is the most common reaction and also called as 1,2-elimination reaction. It involves the loss of two groups or substituents from vicinal atoms resulting in the formation of a double or triple bond.



Answer (ix) In both the compounds A and B, flipping of the cyclohexane ring is prevented by bulky *t*-butyl group present at equatorial position. In compound A, leaving group OTs is situated anti-parallel to the adjacent H atom which results in readily elimination of both the group i.e. H and OTs leading corresponding alkene.



On the other hand, compound B lacks this geometrical requirement and hence does not undergo  $\text{E}_2$  reaction under moderate condition.



9. Course structure for M. Sc. (Applied Chemistry):

M. Sc. Part-I (Semester I):

Course Code	Course Name	L-T-P	Credits
APCL-101	Essential Organic Concepts	3-1-0	4
APCL-102	Bonding & Catalysis	3-1-0	4
APCL-103	Thermodynamics & Solid State Chemistry	3-1-0	4
APCL-104	Photochemistry	4-0-0	4
APCP-101	Organic Chemistry Lab	0-0-10	5
Total Credits			21

M. Sc. Part-I (Semester II):

Course Code	Course Name	L-T-P	Credits
APCL-105	Reactions, Reagents & Rearrangement	3-1-0	4
APCL-106	Transition Metals & Supramolecular Chemistry	3-1-0	4
APCL-107	Reaction Dynamics & Nuclear Chemistry	3-1-0	4
APCL-108	Natural Products & Biomolecules	3-1-0	4
APCP-102	Inorganic Chemistry Lab	0-0-9	5
Total Credits			21

M. Sc. Part-II (Semester III):

Course Code	Course Name	L-T-P	Credits
APCL-109A	Material Chemistry	3-1-0	4
APCL-109B	Advanced Analytical Instrumentation		
APCL-109C	Environmental Chemistry		
APCL-109D	Medicinal Chemistry		
APCL-110	Spectroscopic Techniques - I	3-1-0	4
APCL-111	Green Chemistry	3-1-0	4
APCL-112	Corrosion & Surface Chemistry	3-1-0	4
APCP-103	Physical Chemistry Lab	0-0-10	5
Total Credits			21

M. Sc. Part-II (Semester IV):

Course Code	Course Name	L-T-P	Credits
APCL-113A	Polymer Chemistry	3-1-0	4
APCL-113B	Sensor Technology		
APCL-113C	Nano Chemistry		
APCL-113D	Advance Synthetic Approach		
APCL-114	Spectroscopic Techniques - II	3-1-0	4
APCB-115	Investigation Projects		15
Total Credits			23



Q7

S	M	T	W	T	F	S
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

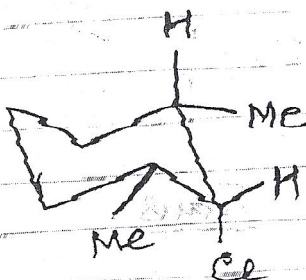
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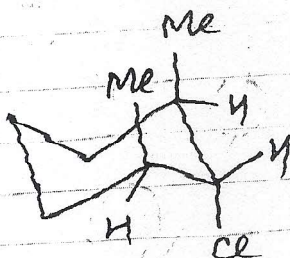
Week-26 (178-187)

Q7

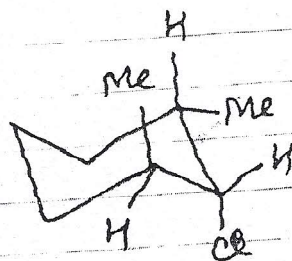
It has three possible diastereomers -



A

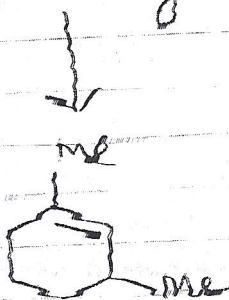


B

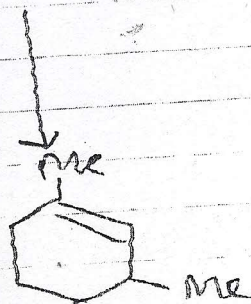


C

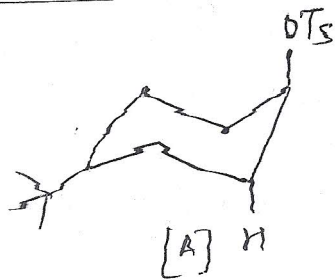
Both A and C can achieve anti-coplanarity and undergo  $E_2$  reaction giving 1,3-dimethylcyclohexene. But B can not react because both vicinal hydrogens are equatorial and are cis and therefore anti-coplanarity can't be achieved.



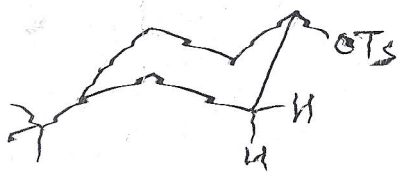
No  $E_2$  Reaction



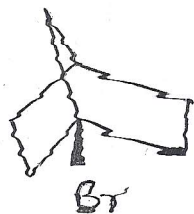


Answer:

Compound A will undergo readily  $E_2$  elimination. This is because, both the eliminating groups have anti-coplanarity arrangement or trans-diaxial arrangement.



Compound B does not have anti-coplanarity between both the eliminating group i.e. OTs and H hence it will either do not undergo  $E_2$  elimination or very slow  $E_2$  reaction will be possible.



This is bicyclic system and the rigidity of the bicyclic system prevents Br and an adjacent H atom from even being anti-coplanar. Therefore, in this case, syn-coplanarity prevails and this is the mode of  $E_2$  reaction. In these bicyclic systems, coplanarity can only be achieved in the T.S. leading to cis elimination rather than trans.

#### Reference Books

1. K. Nakamashi. *Natural Products Chemistry*, Vols. I and II, Academic Press, New York and London (1974).
2. M. Harmata. *Strategies and Tactics in Organic Synthesis* 4 & 5, Academic Press (2004).
3. Bugas, H. & Penny, C. *Bioorganic Chemistry: A Chemical Approach to Enzyme Action*, Springer Verlag (1998).
4. *The Chemistry of Alkaloids* - S.W. Pelletier.
5. *Terpenoids Volume I and II* - P. De Mayo.
6. *Styrids* - Fieser and Fieser.
7. *Introduction to the Chemistry and Biochemistry of fatty acids and their Glycerides* - F.D. Gunstone, Chapman and Hall, London (1986).
8. *Introduction to Nucleic acids* - Harber, Domagle and Muller

#### INORGANIC CHEMISTRY LAB - (APCL-102)

1. Separation and Determination of two metal ions involving volumetric and gravimetric methods from the following:  
 $\text{Fe}+\text{Ni}$ ,  $\text{Zn}+\text{Cu}$ ,  $\text{Cu}+\text{Fe}$ ,  $\text{Zn}+\text{Ni}$ .
2. Preparation of complexes:  $\text{Hg}[\text{Co}(\text{SCN})_4]$ ,  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  and  $[\text{Cu}(\text{H}_2\text{O})_5]2 \cdot \text{H}_2\text{O}$ .
3. Determination of composition of a complex (colorimetric method)- Demonstration. Quantitative estimation involving volumetric (redox and complexometry), gravimetric and spectrophotometric methods of constituents in three component mixtures and alloys
4. Preparation and Characterization of the following compounds :
  - Reinecke salt
  - Tris(oxalate) manganese(III)
  - Tetrapyridine silver(I) peroxodisulphate
  - Tris(acetylacetonato) iron(III)
  - Bis(N,N-diethyldithiocarbamate)nitrosyliron(I)
  - Optical isomers of tris(ethylenediamine)cobalt(III) chloride
  - Linkage isomers of nitro and nitropentamminecobalt(III) chloride
  - Ferrocene or dibenzene chromium
  - Hydrido chlorocarbonyl tris(triphenylphosphine)ruthenium(II)
  - Tris(2,2'-bipyridine)ruthenium(II) perchlorate
  - $\{(\text{p-cymene})\text{RuCl}_2\}_2$
  - Tris(acetylacetonato)manganese(III)

#### Reference Books

1. J. Bassett, R. C. Denney, G.H. Jeffery & J. Mendham. *Vogel's Text Book of Quantitative Analysis* (4th edn.), English Language Book Society (1978).
2. U. W. Willard, L. L. Merril & J. A. Dean. *Instrumental Methods of Analysis* (4th edn.), East-West Press (1974).
3. G. W. Parshall (Ed. in Chief). *Inorganic Synthesis*, Vol. 15, McGraw Hill, p. 48 (1974).
4. *A text book of macro and semimicro qualitative inorganic analysis-A. I. Vogel*, 4<sup>th</sup> Edition, Orient Langman.
5. J. Mendham, R. C. Denney, J. B. Barnes & M. Thomas. *Vogel's Textbook of Quantitative Chemical Analysis*, Peterson Education (2000).
6. G. Marr & B. W. Rockett. *Practical Inorganic Chemistry*, Van Nostrand (1972).
7. E. Pizz & H. Smithe, *Practical Inorganic Chemistry* (2nd edn.), Chapman & Hill (1974)

### M. Sc. Part - II (Semester - III)

#### MATERIAL CHEMISTRY (APCL 109A)

##### Unit - I: Ceramic powder synthesis

Solid state reaction method, Chemical routes: coprecipitation, spray drying, freeze drying, sol-gel method, hydrothermal and combustion.

10 HRS