Register Number:

Date:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY– I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2018
CH 7218 : ORGANIC CHEMISTRY

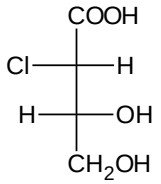
Time- 2 ½ hrs **Max Marks-70**

This paper contains FOUR printed pages and THREE parts

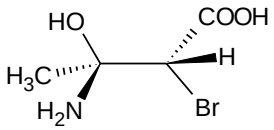
Part A

Answer any SIX questions. **2 x 6 =12**

1. State i) Hammond postulate ii) principle of microscopic reversibility.
2. What is Gatterman-Koch synthesis?
3. What is Chugaev reaction? Give an example
4. Explain chiral helicity with an example.
5. Draw a potential energy diagram to illustrate that E1, E2 and E1cb mechanisms represent variants of a continuum of mechanistic possibilities.
6. Write the $B_{AC}2$mechanism for the hydrolysis of an ester.
7. Write structure **I** in sawhorse formula and structure **II** in Fischer formula.



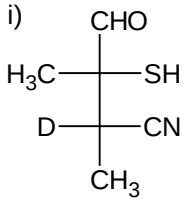
I



II

8. Write the absolute configuration notations for the following.

i)



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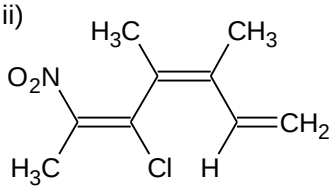


Part B

Answer any FOUR questions. **12 x 4 =48**

9. a) Explain the factors that influence S_N2 reactions. Which of these factors do not influence a S_N1 reaction. Explain.

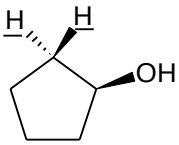
   b) Explain why:

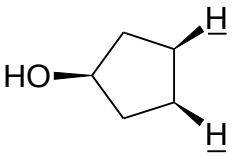
   i) The major product formed when a primary alkyl halide undergoes nucleophilic substitution reaction with AgCN is different from that formed with KCN.

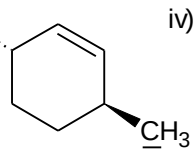
   ii) 1-chloro-2methylcylohexane forms a substitution product in an S_N1 reaction that is different from the substitution product formed in an S_N2 reaction. (6+6)

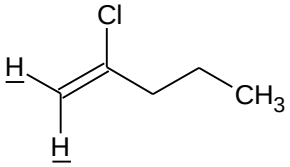
10. With suitable examples, explain the use of (i) isotopic labeling (ii) primary kinetic isotope effects and (iii) secondary kinetic isotope effects iv) characterization of intermediates in deducing the mechanism of a reaction.

11. a) In each of the following, indicate whether the *underlined* groups or atoms are homotopic or heterotopic. For those that are heterotopic, designate them as enantiotopic or diastereotopic. Give the absolute configuration wherever necessary.

i) 

ii) 

iii) 

iv) 

b) Draw the structures of the following:

i) *cis*-decalin.

ii) Least stable chair conformer of *cis*-1,3-diethylcyclohexane.

iii) Newman projection formula of the stable form of 2-bromoethanol.

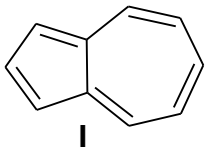
iv) 7,7-dimethylbicyclo[2.2.1]heptane.

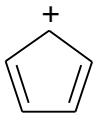
v) Perspective formula of (2*S*,3*R*)-3-chloro-2-pentanol.

vi) Fischer formula of a compound with pseudoasymmetric centre. (6+6)

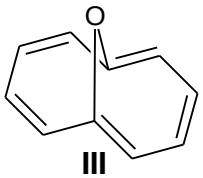
12. a) Discuss benzyne mechanism of nucleophilic substitution on aromatic rings. Give evidences in favour of this mechanism.

b) Use the following list of compounds to answer the questions given below.

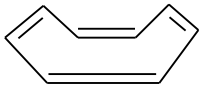

I



II



III


IV

i) Compound I has a dipole moment of 0.8 D. Explain.

ii) Are compounds II and IV aromatic, non-aromatic or antiaromatic. Justify your choice in each case.

iii) Would you expect compound III to undergo electrophilic substitution reaction. Explain.

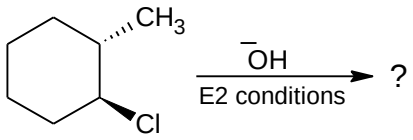
c) Write the general mechanism of S_NAr reaction. Give any two evidences in support of this mechanism. (4+4+4)

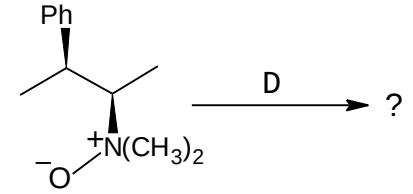
13. a) Write the structure of an optically active derivative of

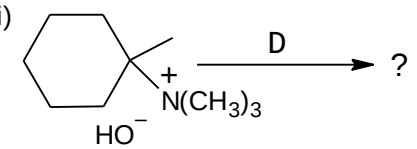
i) a cyclophane ii) a hemispirane iii) a diphenyl compound iv) an allene

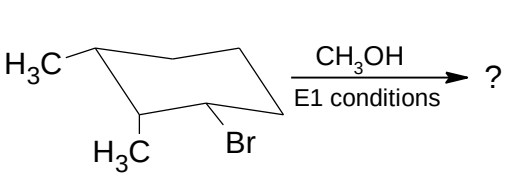
Give the absolute configuration notation in each case.

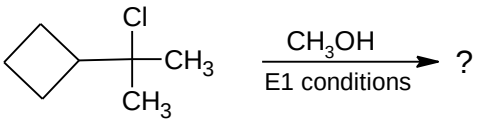
b) Write the major product(s) of the following reactions:

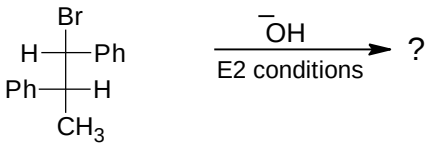
i) 

ii) 

iii) 

iv) 

v) 

vi) 

(6+6)

14. a) Give reasons for the following.

i) The acidity of 2,6-dimethyl-4-nitrophenol is greater than the corresponding 3,5-dimethyl isomer.

ii) Guanidine $(NH_2)_2C=NH$, pKa 13.6, is a very strong base, almost as basic as hydroxide ion.

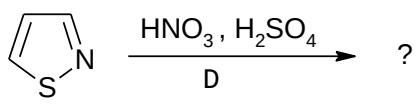
b) Give one method of generation of carbenes. Explain the structure of singlet and triplet carbenes.

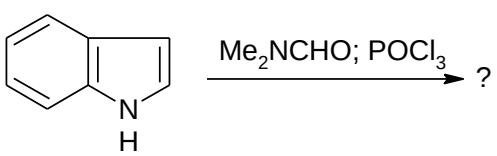
c) With the help of a potential energy diagram, discuss the conformational analysis of n-butane for rotation about the C2-C3 bond in the molecule. (4+3+5)

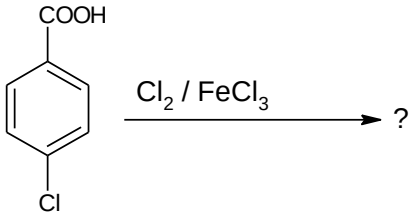
Part C

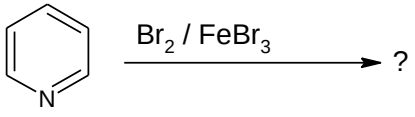
Answer any <u>TWO</u> questions. **5 x 2 =10**

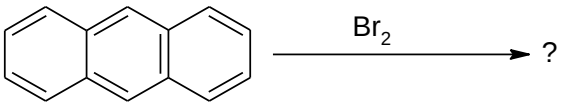
15. Write the major product(s) in the following reactions:

i) 

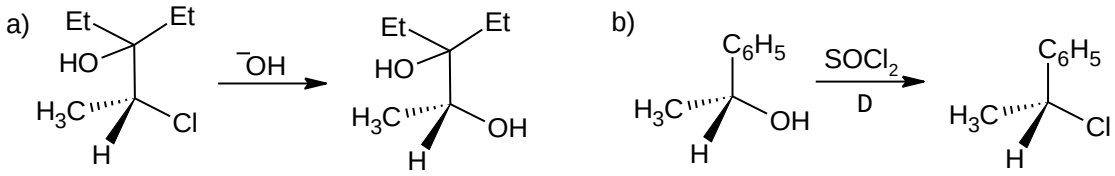
ii) 

iii) 

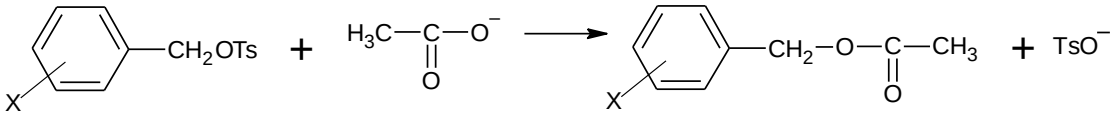
iv) 

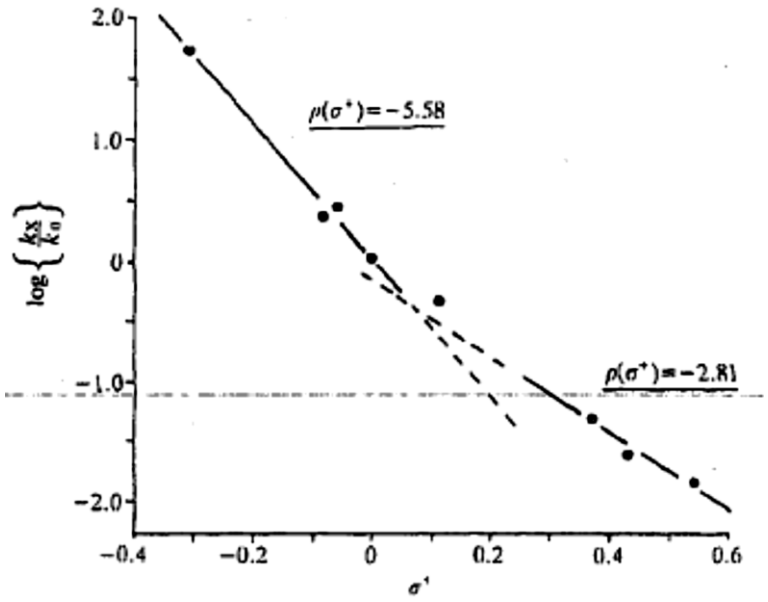
v) 

16. Give an explanation for the following observations:



17. For the following Hammett plot and the reaction shown, two reaction constants are obtained, one for electron donating groups and another for electron withdrawing groups. Explain the magnitude and sign of each of the two reaction constants and provide mechanism/s consistent with these observations.





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