(ii) Explain nucleophilic substitution in allylic and vinylic substrates. Explain with suitable examples. 8

**OR**

(b) Explain $SN^1$ and $SN^2$ reactions with examples and draw the energy profile diagrams for both the reactions. 8+8 = 16





# 2016
# (January)

*Time : 3 hours*

*Full Marks : 80*

*The figures in the right-hand margin indicate marks.*

*Answer from both the Sections as per direction.*

## (BASIC ORGANIC CHEMISTRY – I)

### Section – A

1. Answer any **four** of the following : 4×4 = 16

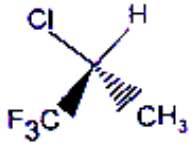
(a) What is the difference between crown ether and cryptands ? Explain with suitable examples.

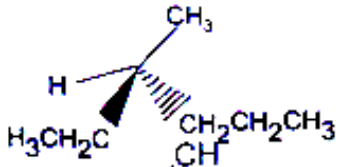
(b) Give three points of differences between Inductive effect and Resonance effect.

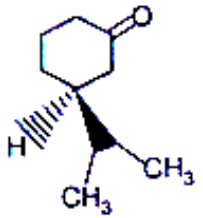
(c) What is Taft equation ? Explain it.

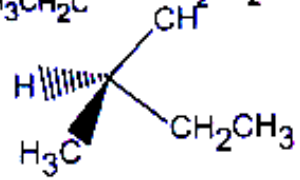
(d) Define and illustrate the terms distereoselectivity and enantioselectivity with examples.

(e) Assign R or S configuration to the following compounds :

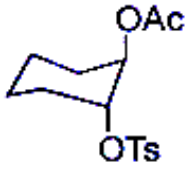
(i) 

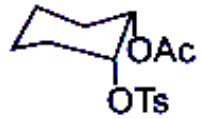
(ii) 

(iii) 

(iv) 

(f) Explain why trans isomer (I) undergoes acetolysis 670 times faster than *cis* isomer (II) and that the product has the same *cis* stereochemistry in both the cases ?

(I) 

(II) 

**OR**

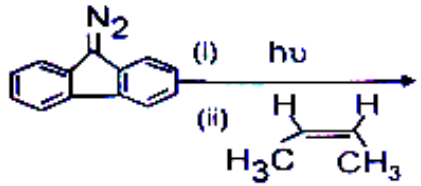
2. Answer **all** questions from the following : 2×8 = 16

(a) Which of the followings is not aromatic and why ?

(i) (ii) (iii) (iv)



(b) Write the product of the following reaction :



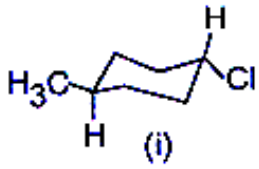
(c) What is the significance of σ and ρ values in Hammett equation ?

(d) The pKa value of p-chlorobenzoic acid is 3.98 and that of benzoic acid is 4.19. Calculate σ for p-chlorobenzoic acid.

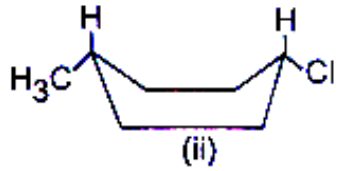
(e) Give an example of stereospecific reaction.

(f) Explain why 1-bromotriptycene is inert to nucleophilic substitution by both $SN^1$ and $SN^2$ mechanisms ?

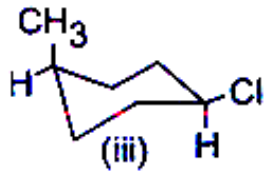
(g) Which of the following is the most stable conformation of 1-chloro-4-methylcyclohexane and why ?



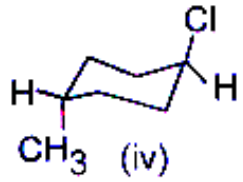
(i)



(ii)

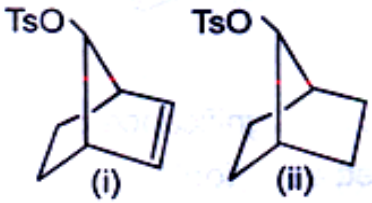


(iii)



(iv)

(h) The acetolysis of 7-norbornenyl tosylate (I) is $10^{11}$ times faster than the saturated analogue, 7-norbornyl tosylate (II). Explain it.




## Section – B

Answer **all** questions :

3. (a) (i) How will you distinguish between singlet and triplet carbenes based on their stability and stereochemical behaviour in addition reactions ? 8

(ii) Define the term Catenanes. Give method of preparation of catenanes. 8

**OR**

(b) (i) Explain the structure and stability and formation of carbon free radicals. 8

(ii) Draw the structure of cyclooctatetrene (14) annulene and (18) annulene. Explain which one is aromatic/ nonaromatic/antiaromatic. 8



4. (a) (i) Show that Hammett equation represents a linear free energy relationship. 8

(ii) Write notes on hard and soft electrophiles and nucleophiles. 8

**OR**

(b) Write notes on the following : 8+8 = 16

(i) Hammonds Postulates

(ii) Curtin-Hammett principle

5. (a) Discuss optical activity of biphenyls, allenes and spiranes. 16

**OR**

(b) What is asymmetric synthesis ? Describe an asymmetric synthesis using a chiral catalyst and asymmetric synthesis using a chiral substrate. Explain with examples. 16

6. (a) (i) What is NGP ? How C-C single bond can participate in neighbouring group participation reaction ? Explain with examples. 8