

(7 pages)

DECEMBER 2015

P/ID 40127/PCHG

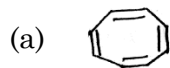
Time : Three hours

Maximum : 100 marks

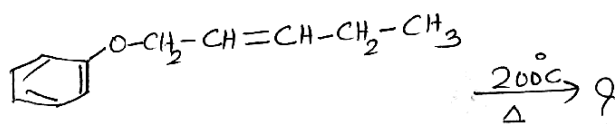
PART A — (10 × 2 = 20 marks)

Answer ALL questions.

1. How would you distinguish cyclohexanone from 2-cyclohexenone spectroscopically?
2. An organic compound of molecular formula C_9H_{12} gives two singlets at $\delta 2.27(9H)$ and $6.7(3H)$ respectively in the 1H nmr spectra. Assign the structure to this compound.
3. Tropylium cation is stable. Explain.
4. Classify the following compounds as aromatic, non-aromatic and antiaromatic.



5. What is hypsochromic shift? Explain with an example.
6. What happens when trans-3,4-dimethylcyclobutene is heated?
7. Complete the following reaction and explain



8. How is 2,5-dimethylthiazole prepared?
9. Draw the structure of uracil where does it occur?
10. Write down the structure of tautomers of guanine.

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

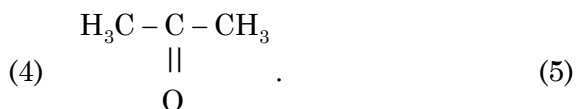
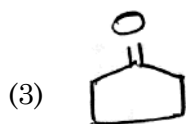
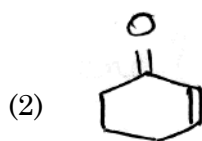
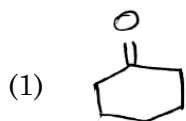
11. (a) (i) State and explain the octant rule with a suitable example. (8)
- (ii) Draw the off resonance decoupled ^{13}C spectrum of 1-chloropropane and explain. (6)

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- (iii) The mass spectrum of an organic compound gave base peak at $\frac{m}{e} 43$, a strong peak at $\frac{m}{e} 42$, two strong peaks at $\frac{m}{e} 122$ and 124 and a very weak peak at $\frac{m}{e} 93$. Identify the compound. (6)

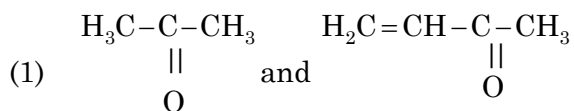
Or

- (b) (i) Give the approximate positions of characteristic carbonyl absorption bands in the IR spectrum of the following compounds.



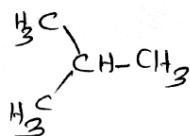
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- (ii) What do you understand by $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions? Illustrate your answer with suitable examples. (5)
- (iii) Two isomeric compounds A and B have molecular formula C_2H_4Cl . Compound A gives on 1H nmr signal (singlet at δ 3.7) where as B gives two signals (a doublet at δ 2.1 and a quartet at δ 5.8). Deduce the structure of A and B. (5)
- (iv) How are the following pairs of compounds distinguished?



by UV spectroscopy.

- (2) $H_3C-CH_2-CH_2-CH_3$ and



by mass spectroscopy. (5)

12. (a) (i) Cyclopentadiene, inspite of being a hydrocarbon, is an unusually strong acid ($K_a = 10^{-15}$). Explain. (5)
- (ii) What are diatropic molecules? Give examples. How can diatropy be determined from nmr spectrum? (8)

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[P.T.O.]

(iii) Phenalene is acidic and readily reacts with potassiummethoxide. Explain. (7)

Or

(b) (i) What are aromatic, non-aromatic and antiaromatic compounds? Give two examples for each class. (8)

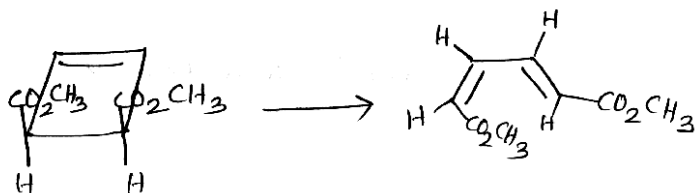
(ii) Discuss the aromaticity in heterocyclic compounds. (6)

(iii) What is ferrocene? Give its structure. Explain its stability. (6)

13. (a) (i) Discuss the radiative and radiationless processes undergone by an excited molecule using the Jablonski diagram. (10)

(ii) What is di- π -methane rearrangement? Explain with a suitable example. (5)

(iii) Consider the following conversion.

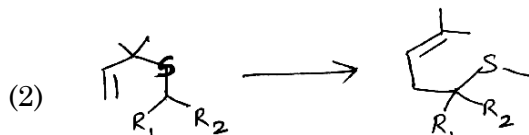
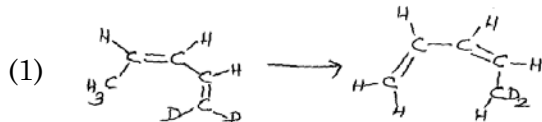


Explain how it happens and predict whether it is thermally or photochemically allowed. (5)

Or

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- (b) (i) With a suitable example explain the photoisomerization reaction. (8)
- (ii) Classify the following as sigmatropic reaction of the order $[i, j]$ (6)



- (iii) Draw the structure of bullvalene and explain how it could exist in more than 1.2-million tautomeric forms. (6)

14. (a) (i) Outline the synthesis of imidazole. (5)
- (ii) How is adenine obtained from 2,6,8-trichloropurine? (5)
- (iii) What happens when flavone is boiled with Conc. KOH solution? (5)
- (iv) Prove that vitamin A1 has half the β -carotene structure. (5)

Or

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- (b) (i) Describe the preparation of oxazole. (5)
- (ii) How is cytosine synthesised? (5)
- (iii) Outline the synthesis of flavone from o-hydroxyacetophenone. (5)
- (iv) How is cholesterol converted to progesterone? (5)
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