

(6 pages)

MAY 2014

P/ID 40127/PCHG

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

All questions carry equal marks.

1. How would you differentiate between $\text{CH}_3 - \text{CO} - \text{CH}_3$ and $\text{CH}_3 - \text{CO} - \text{CH} = \text{CH}_2$ using IR spectroscopy?
2. Which will have higher ϵ_{max} value : biphenyl or 2-methylbiphenyl? Why?
3. Distinguish between circular dichroism and circular birefringence.
4. Which species is the smallest aromatic substance?
5. Which of the following ring compounds obey Huckel's rule – $\text{C}_{10}\text{H}_{10}$, $\text{C}_{12}\text{H}_{12}$, $\text{C}_{12}\text{H}_{12}^{2-}$ and $\text{C}_{12}\text{H}_{12}^{2+}$?

6. Write down the products of the following reaction and rationalise their formation :



7. Mention the Woodward–Hoffman selection rules for electrocyclic reactions of $4n$ and $4n+2$ systems.
8. How will you convert benzophenone into benzopinacol by photochemical method?
9. Give a method of preparation of thiazole.
10. What happens when flavone is treated with KOH?

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

All questions carry equal marks.

11. (a) (i) Sketch and explain the various types of electronic excitations (6)
- (ii) Describe the use of axial haloketone rule in determining the absolute configurations of simple monocyclic ketones. (6)

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- (iii) The vibrational frequency of HBr is 2559 cm^{-1} . Calculate the force constant of the molecule. (8)

Or

- (b) (i) Discuss decoupled and off-resonance decoupled ^{13}C -NMR spectra with two examples. (8)
- (ii) Predict the fragmentation pattern of diphenyl ether. (4)
- (iii) How will you account for the appearance of prominent peaks at M/Z 31, 42 and 70 in the mass spectrum of n-pentanol. (4)
- (iv) State and explain octant rule. (4)
12. (a) Describe the aromaticity of the following compounds :
- (i) Pyrrole
- (ii) Thiophene
- (iii) Furan
- (iv) Pyridine
- (v) Benzene
- (vi) Anthracene

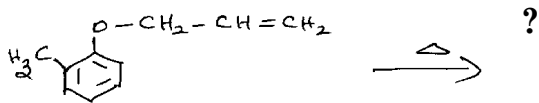
- (vii) Tropylium cation
- (viii) Cycloheptatriene
- (ix) Butadiene
- (x) Cyclopentadienyl anion.

Or

- (b) (i) How can 1, 3, 5, 7 – cyclononatetraene be converted to an aromatic anion? (4)
 - (ii) What are aromatic and anti-aromatic compounds? Is cyclooctatetraene aromatic or antiaromatic? (6)
 - (iii) Draw and explain the aromaticity of azulene and dehydro [14]–annulene. (2 × 5)
13. (a) (i) Illustrate paterno – Buchi reaction with two different examples. (6)
- (ii) Construct an orbital correlation diagram for the con rotation and disrotation interconversion of hexatriene to cyclohexadiene. Analyse the reaction. (8)

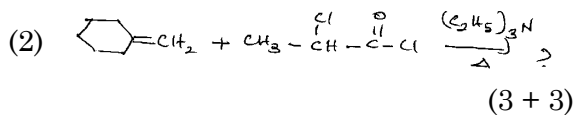
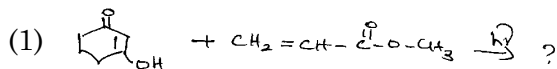
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- (iii) Complete the following reaction and give its mechanism : (6)



Or

- (b) (i) Describe the mechanism of di-pimethane rearrangement. (6)
- (ii) Draw the Jablonski diagram and explain various physical processes based on the diagram. (8)
- (iii) Complete the following reactions and explain their mechanisms.



14. (a) (i) How will you prepare isoflavone from benzyl o-hydroxyphenyl ketone? (5)
- (ii) Elucidate the structure of cholesterol. (15)

Or

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- (b) (i) Describe the synthesis of Vitamin A₁ by wittig method. (6)
- (ii) How will you convert cholesterol into progesterone and esterone? (8)
- (iii) Write one method each for the preparation of uracil and cytosine. (3 + 3)
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