

2015

CHEMISTRY

( Major )

Paper : 5.3

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks  
for the questions*

1. Answer the following questions (any seven) :

1×7=7

- (a) Give the product of the following reaction :



- (b) Which among furan, pyrrole and thiophene undergoes Diels-Alder reaction? Write the structure of the product formed by it with maleic anhydride.
- (c) Why does electrophilic aromatic substitution of indole occur preferably at the 3-position?

- (d) Which bond of phenanthrene is readily attacked by reagents?
- (e) 2-methyl-2-nitropropane does not dissolve in alkali whereas 2-nitropropane dissolves. Why?
- (f) Write the structure of the product when the following compound is treated with Na/Hg :

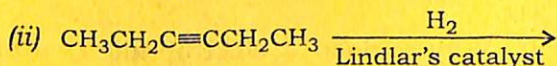
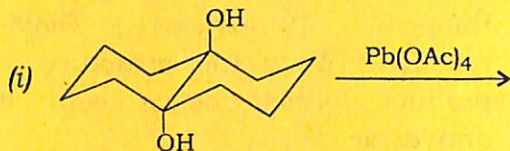


- (g) Why does pyridine not undergo Friedel-Crafts reaction?
- (h) Why is catalytic reduction of thiophene difficult?

2. Answer the following questions (any four) :

2×4=8

- (a) Write the appropriate product for the following reactions :

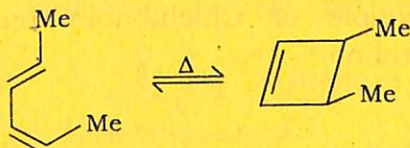




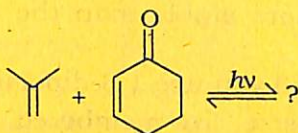
- (b) Draw the tautomers of acetoacetic ester. Identify the stable form and explain why it is more stable than the other form.
- (c) How will you use 1,3-dipolar reagents to synthesize five-membered heterocyclic compounds?
- (d) Which one is more acidic—ethanethiol or ethanol and why? How can one distinguish ethanethiol from ethanol?
- (e) Why is cope rearrangement called [3,3] sigmatropic shift?

3. Answer any *three* of the following questions [any *one* from (a) and (b), any *two* from (c), (d) and (e)] : 5×3=15

- (a) How can you convert propanoic acid to ethanamine, using a reaction that involves isocyanate intermediate? Name the reaction. Write the mechanism of the reaction. 2+1+2=5
- (b) Explain why (2*E*, 4*Z*) hexadiene thermally cyclizes to give *cis*-3,4-dimethyl cyclobutene.



Write the product of the following reaction :



4+1=5

- (c) How will you distinguish between 1°, 2° and 3°-nitroalkanes? What products are obtained when nitrobenzene is reduced in (i) acidic and (ii) alkaline media?

3+2=5

- (d) Explain why methylene group in diethylmalonate is more reactive than methylene group in malonic acid. Starting from diethylmalonate, how can you synthesize (i) a dicarboxylic acid, (ii) a heterocyclic compound, (iii) an alicyclic compound and (iv)  $\alpha$ ,  $\beta$ -unsaturated acid? 1+1+1+1+1=5

- (e) What are the IUPAC names of pyrrole, furan and pyridine? Write down the steps involved in the Bischler-Napieralski reaction leading to synthesis of isoquinoline. Give an example of Chichibabin reaction of pyridine.  $1\frac{1}{2}+2+1\frac{1}{2}=5$

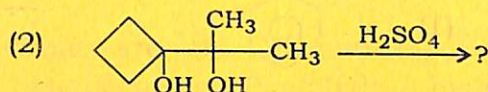
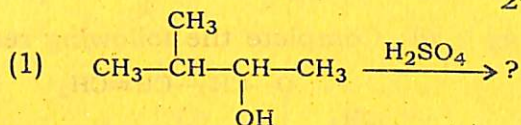


4. Answer the following questions :

*Either*

- (a) (i) Predict the product in each case and write the mechanism for each :

2+3=5



- (ii) (1) Explain why reaction of naphthalene with conc.  $\text{H}_2\text{SO}_4$  at  $40^\circ\text{C}$  yields naphthalene-1-sulphonic acid whereas at  $160^\circ\text{C}$  naphthalene-2-sulphonic acid is the major product. 3

- (2) Convert nitrobenzene to 1,3-dichlorobenzene (give equations). 2

*Or*

- (b) (i) Give the product of the following reaction, name the rearrangement and propose a mechanism : 1+1+3=5



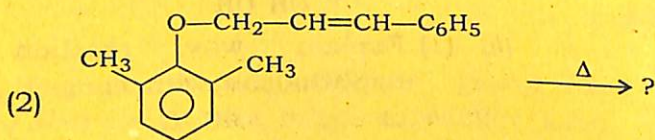
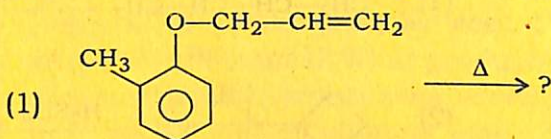
Diphenylethanedione

- (ii) Show by symmetry correlation diagram approach that [2+2] cycloaddition is a photochemically allowed process.

5

Either

- (c) (i) Complete the following reactions :

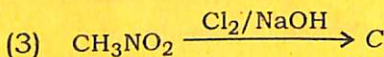
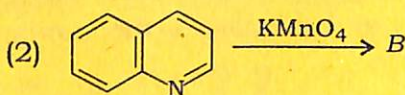
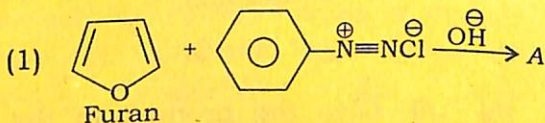


Account for the product obtained in each case.

$$2\frac{1}{2} + 2\frac{1}{2} = 5$$

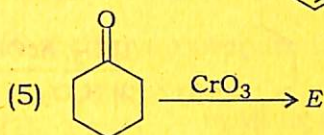
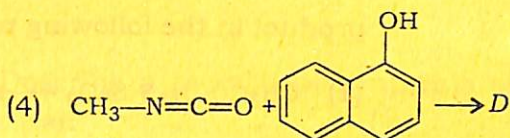
- (ii) Identify A, B, C, D and E in the following reactions :

$$1 \times 5 = 5$$





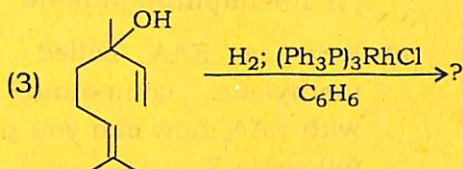
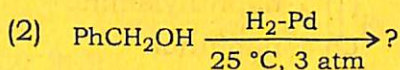
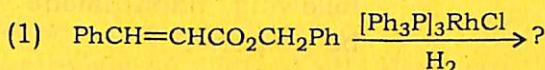
( 7 )



Or

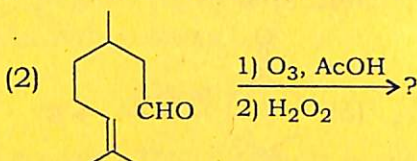
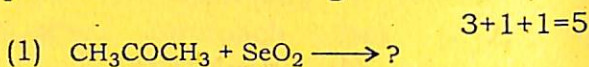
- (d) (i) What are the disadvantages of heterogeneous catalytic hydrogenation? Predict the product in each of the following reactions :

$$2+1+1+1=5$$



- (ii) Describe the mechanism involved in the oxidation of 1,2-diols with lead tetraacetate. Identify the

product in the following reactions :



*Either*

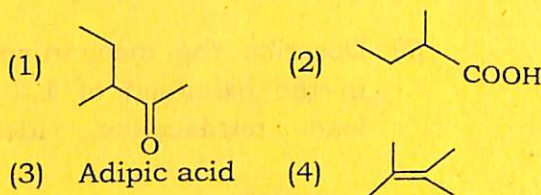
- (e) (i) How many monosubstituted derivatives of naphthalene are possible? Which position is preferentially attacked in electrophilic substitution reactions of naphthalene? How can the following naphthalene derivatives be prepared? 1+1+3=5

(1) 2-naphthylamine

(2) 1-naphthol

(3) 1,4-naphthaquinone

- (ii) Why is EAA called an active methylene compound? Starting with EAA, how can you prepare the following? 1+4=5



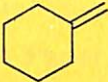
(No mechanism needed)



Or

(f) (i) Describe a method of synthesis of furan. 3

(ii) How can you prepare the following? 2

(1)  by Wittig reaction

(2) PhCOOMe by Baeyer-Villiger reaction

(iii) Why does Hofmann elimination of a quaternary ammonium salt give thermodynamically less stable alkene as the predominant product? 2

(iv) Write one general method of synthesis of thiols, RSH. How can RSH be converted to (1) RSSR and (2) RSR? 1+1+1=3

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