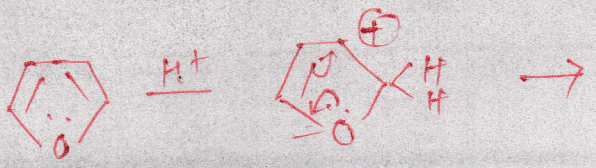


2015

CHEMISTRY

(Major)

Paper : 5.3

Full Marks : 60

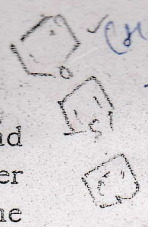
Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions (any *seven*) : 1×7=7

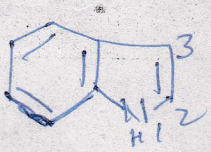
(a) Give the product of the following reaction :

$$CH_3—CH=CH—COOH \xrightarrow[2)\ H_3O^+]{1)\ LiAlH_4,\ Ether}$$



(b) Which among furan, pyrrole and thiopene 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 :

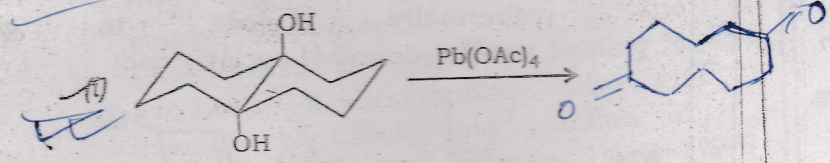
$$PhCH{=}CHCH_2\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{I}$$

(g) Why does pyridine not undergo Friedel-Crafts reaction?

(h) Why is catalytic reduction of thiophene difficult? Because it made the catalyst poisonous

2. Answer the following questions (any *four*) : 2×4=8

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

(i) 

(ii) $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{Lindlar's catalyst}]{H_2}$

(Continued)

(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?

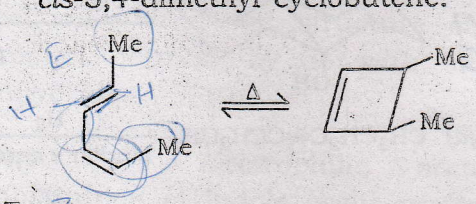
(d) Which one is more acidic—ethanethiol or ethanol and why? How can one distinguish ethanethiol from ethanol?

(e) Why is cope rearrangement called [3,3] sigmatropic shift?

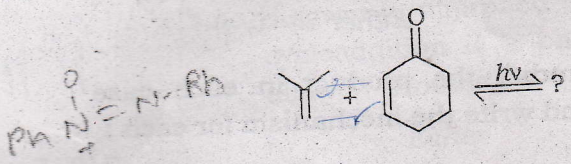
3. Answer any *three* of the following questions [any *one* from *(a)* and *(b)*, any *two* from *(c)*, *(d)* and *(e)*] : 5×3=15

(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)* α, β-unsaturated acid? 1+1+1+1+1=5

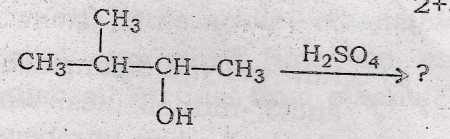
(e) What are the IUPAC names of pyrrole, furan and pyridine? Write down the steps involved in the Bischler-Napieralski reaction leading to synthesis of isoquinoline. Give an example of Chichibabin reaction of pyridine. 1½+2+1½=5

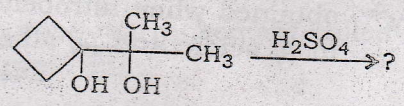
(Continued)

4. Answer the following questions :

Either

(a) (i) Predict the product in each case and write the mechanism for each : 2+3=5

(1) 

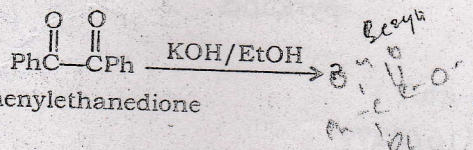
(2) 

(ii) (1) Explain why reaction of naphthalene with conc. H_2SO_4 at 40 °C yields naphthalene-1-sulphonic acid whereas at 160 °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

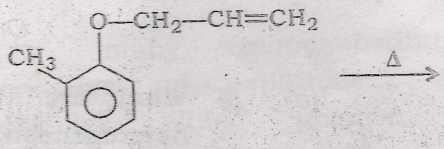


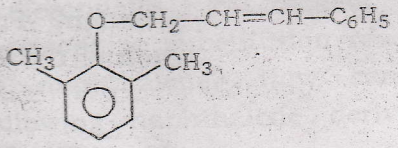
Diphenylethanedione

(ii) Show by symmetry correlation diagram approach that [2+2] cycloaddition is a photochemically allowed process. 5

Either

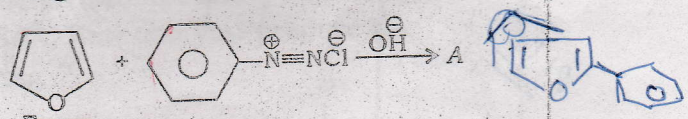
(c) (i) Complete the following reactions :

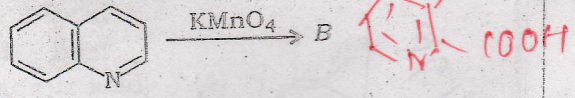
(1) 

(2) 

Account for the product obtained in each case. 2½+2½=5

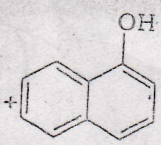
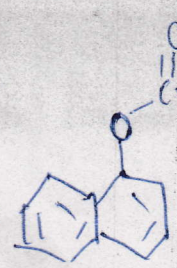
(ii) Identify *A*, *B*, *C*, *D* and *E* in the following reactions : 1×5=5

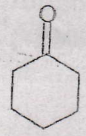
(1) 

(2) 

(3) $CH_3NO_2 \xrightarrow{Cl_2/NaOH} C$

(Continued)

(4) $CH_3-N=C=O$ +  → D 

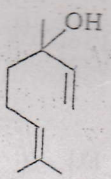
(5)  $\xrightarrow{CrO_3}$ E

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

(1) $PhCH{=}CHCO_2CH_2Ph \xrightarrow[H_2]{[Ph_3P]_3RhCl}$?

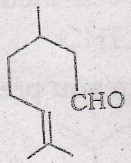
(2) $PhCH_2OH \xrightarrow[25\,^\circ C,\ 3\ atm]{H_2\text{-}Pd}$?

(3)  $\xrightarrow[C_6H_6]{H_2;\ (Ph_3P)_3RhCl}$?

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

product in the following reactions : 3+1+1=5

(1) $CH_3COCH_3 + SeO_2 \longrightarrow ?$

(2)  $\xrightarrow[2)\ H_2O_2]{1)\ O_3,\ AcOH} ?$

Either

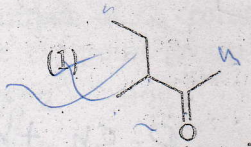
(e) (i) How many monosubstituted derivatives of naphthalene are possible? Which position is preferentially attacked in electrophilic substitution reactions of naphthalene? How can the following naphthalene derivatives be prepared? 1+1+3=5

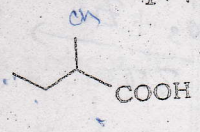
(1) 2-naphthylamine

(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

(1) 

(2) 

(3) Adipic acid

(4) 

(No mechanism needed)

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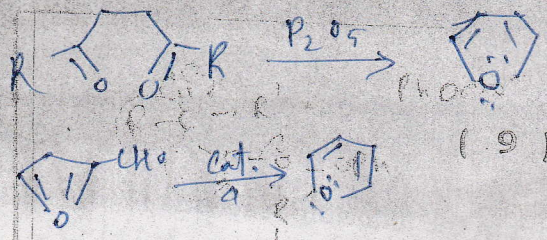

(9)

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