2013

CHEMISTRY

(Major)

Paper : 2.2

(Organic Chemistry)

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions : 1×7=7

(a) Write IUPAC name of

(b) Give an example, where S_N1 reaction does not follow the first-order kinetics.

(c) What is partial rate factor?

(d) What does the term 'topocity' signify?

(e) Why only α-H atoms in saturated carbonyl compounds take part in the aldol condensation?

(f) What are homotopic ligands?

(g) Arrange the following hydrocarbons in order of their increasing acid strengths :

CH_3-CH_3, $CH\equiv CH$, $CH_2=CH_2$

2. Answer the following questions : 2×4=8

(a) Discuss the relative stabilities of different conformations of cyclohexane.

(b) What is the requirement for showing prochirality?

(c) Give two examples of molecules containing enantiotropic H-atoms.

(d) How are the H-atoms at a prochiral centre distinguished from one another?

3. Answer any *three* questions : 5×3=15

(a) (i) Explain why chlorine (—Cl) in chlorobenzene is an *o*, *p*-director, but a deactivator at the same time. 2

(ii) How will you trap a benzyne intermediate? 1

(iii) Write down the mechanism of Chichibabin reaction of pyridine. 2

(b) Give an example of Ar S_N1 reaction. What is the mechanism involved? What are the evidences in support of this mechanism? 1+2+2=5

(c) (i) Explain why substitution via benzyne mechanism is not possible when the adjacent positions of the leaving group are blocked. 3

(ii) Aniline is more reactive than acetanilide towards electrophilic substitution. Why? 2

(d) (i) How will you prepare *meta*-nitrotoluene from benzene? 2

(ii) What is o/p ratio? What are the factors influencing o/p ratio? 1+2=3

4. Answer any *three* questions : 10×3=30

(a) (i) Propose a mechanism of the following reaction :

$$RCO\overset{\ominus}{O} \xrightarrow{\text{Electrolysis}} R—R$$

What are the evidences in support of the proposed mechanism?

1½+1½=3

(ii) Starting from benzene diazonium chloride, synthesise nitrobenzene. 2

(iii) When excess alcohol vapours are passed over conc. H_2SO_4 at 130 °C–140 °C, an ether is formed. What is the mechanism involved in this reaction? 2

(iv) How can you distinguish between 1°-, 2°- and 3°-amines by Hofmann mustard oil test? 3

(b) (i) Show, mechanistically, that a 1°-alcohol can be selectively converted into an aldehyde by Swern oxidation. 3

(ii) Convert CH_3Br into C_3H_8 involving Corey-House synthesis. 2

(iii) Discuss the mechanism of Tollens' reaction. 3

(iv) The rate of hydrolysis of $(CH_3)_3CBr$ in 50% aqueous methanol is thousand times faster than that in pure methanol. Explain. 2

(c) (i) Glycolization of olefins can be stereospecifically controlled to yield either *cis*- or *trans*-1, 2-glycol. Explain. 3

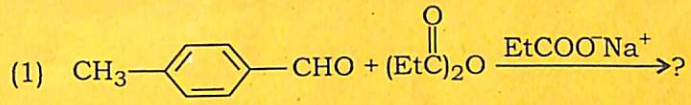
(ii) Distinguish between Hofmann's rule and Saytzeff rule. 3

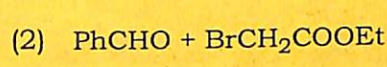
(iii) An organic compound *A* with molecular formula, $C_5H_{12}O$ reacts with sodium metal to produce H_2 gas. Compound *A* reacts with Lucas reagent (anhydrous $ZnCl_2$ + conc. HCl) and produces turbidity immediately. When vapours of compound *A* are passed over alumina (Al_2O_3), it is converted into compound *B*. Compound *B*, on ozonolysis, forms compounds *C* and *D*. Compounds *C* and *D* give coloured p.p.t. with Brady's reagent. Compound *C* forms silver mirror with Tollens' reagent, while compound *D* does not respond to this test. Identify compounds *A* to *D* and write all the chemical equations involved. 4

Or

What is Wittig reaction? What is its mechanism? Give its one synthetic application. 1+2+1=4

(d) (i) What are the products of the following condensation reactions? Name the condensation reaction in each case : 2+2=4

(1) 

(2) 

(ii) When toluene is treated with DCl at −78 °C, no deuterium is exchanged and the solution does not conduct electricity. What is the structure of the complex? 2

(iii) What is Nef reaction? Explain its mechanism. 2

(iv) *o*-nitrobenzaldehyde undergoes the benzoin condensation, but *p*-nitrobenzaldehyde does not. Why? 2

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