2019

CHEMISTRY

(Major)

Paper : 2.2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer any *seven* questions : 1×7=7

(a) Why do most of the carboxylic acids exist as dimer?

(b) Why are reductions with $LiAlH_4$ carried out under anhydrous conditions?

(c) Bromination of olefins cannot be carried out in ethanol. Why?

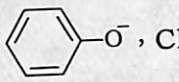
(d) Between benzoic acid and 2,6-dimethyl-benzoic acid, which one is less acidic and why?

(e) Why are amines generally not prone to substitution reactions?

(f) Predict the major product :

$$H_3C\,CH_2\,CH=CH_2 + ICl \longrightarrow ?$$

(g) Arrange the following in order of decreasing nucleophilicity :



, CH_3OH, HO^-, CH_3COO^-, CH_3S^-

(h) Peroxide in ether can be detected using acidified aqueous KI solution. Explain.

2. Answer any *four* questions : 2×4=8

(a) Can tertiary alkyl halides be used in coupling reactions with Gilman reagents? Explain.

(b) What is the product of the reaction of acetamide with ^-OH? The pK_a of NH_3 is 36; the pK_a of H_2O is 15·7.

(c) Arrange the following carbonyl compounds in order of their decreasing reactivity towards nucleophiles and give a plausible explanation for the same :

Cyclohexanone, Cyclopentanone, Cyclopropanone

(d) Aniline on nitration under acidic conditions gives *m*-nitroaniline in good yield. Explain.

(e) What are the topicities of hydrogen atom of the $—CH_2$ group and the faces of the carbonyl group in benzyl methyl ketone?

(Continued)

3. Answer any *two* from *(a)*, *(b)* and *(c)*, and any *one* from *(d)* and *(e)* : 5×3=15

(a) (i) From the perspective of viewing down the $C_2—C_3$ bond, draw the Newman projection of the most stable conformation of 2,3-dimethyl-butane. 1

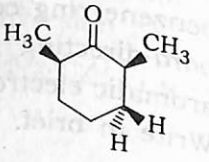
(ii) Draw and arrange the following conformers of butane in order of increasing energy : 2

Eclipsed, Gauche, Anti

(iii) Draw the chair conformer of *trans*-1-ethyl-2-methylcyclohexane and indicate the more stable conformer.

(b) Draw a potential energy diagram showing the conformers of cyclohexane as one chair conformer interconverts to the other. Explain the relative stabilities of all the conformers involved. 2

(c) (i) State whether the compound given below is chiral or achiral. Also indicate the topicities of the CH_3, CH_3 groups; H, H atoms and carbonyl faces : 5



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(Turn Over)

(ii) State how you can establish the topicity of groups in a compound. 2

(d) In aromatic electrophilic substitution, halogens are deactivating but *o*-, *p*-directing. Explain, considering that such a substitution is kinetically controlled. 5

(e) Account for the following : 2+2+1=5

(i) In aromatic electrophilic substitution, CF_3 is *meta*-directing.

(ii) 2,2-dimethylbiphenyl is more difficult to nitrate than biphenyl.

(iii) *t*-butylbenzene gives much less *ortho*-product on nitration as compared to toluene.

4. Answer *either (a) or (b)* and any *two* from *(c), (d), (e)* and *(f)* : 10×3=30

(a) (i) Write the major product obtained when *m*-nitrochlorobenzene is chlorinated. How can you explain the formation of the major product? 2

(ii) What factors govern the product ratios when a monosubstituted benzene ring containing an *ortho*-, *para*-directing group undergoes aromatic electrophilic substitution? Write in brief. 3

(Continued)

(iii) What will happen when bromobenzene and 2-bromo-3-methylanisole are each allowed to react separately with KNH_2 in liquid NH_3? Propose a mechanism to justify the reactions. 5

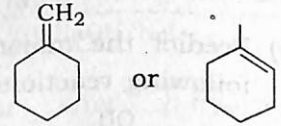
(b) (i) What is called cine-substitution? Give an example. 2

(ii) Provide two evidences in support of S_NAr mechanism. 2

(iii) What happens when 2-chloropyridine reacts with phenol? Propose a mechanism for the reaction. 3

(iv) How would you prepare β-naphthol from naphthalene? What happens when β-naphthol is treated with nitrous acid? 2+1=3

(c) (i) To which of the following compounds is the addition of HBr more regioselective and why? 2



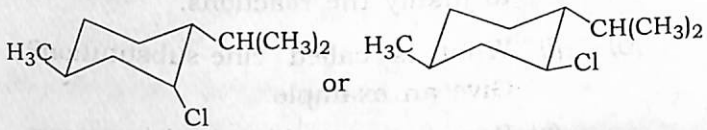
(ii) Propose a mechanism for the following conversion : 2

$$CH_3CH_2CH_2BR_2 \xrightarrow{HO^-, H_2O_2, H_2O} CH_3CH_2CH_2OH + BR_2(OH)$$

(Turn Over)

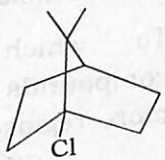
(iii) Suggest a method for conversion of butane-1-amine to but-1-ene. 2

(iv) Out of the following two compounds, which one undergoes E2 elimination faster and why? 2

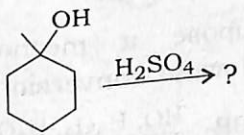


(v) Iodine does not react with ethane even though I_2 is more easily cleaved homolytically than the other halogens. Explain. 2

(d) (i) Explain why the following alkyl halide does not undergo a substitution reaction, regardless of the condition under which the reaction is carried out : 3



(ii) Predict the major product for the following reactions : 2

(1) 

(2) 

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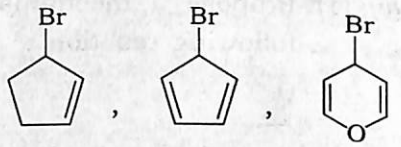
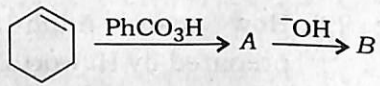
(iii) Arrange the following compounds in order of decreasing S_N1 reactivity and give a brief explanation : 3

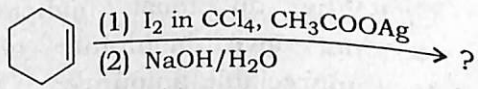


(iv) Identify *A* and *B* (including their stereochemistry) : 2



(e) (i) What will happen when methyl vinyl ketone reacts with diethylmelonate in presence of sodium ethoxide? Propose a mechanism for the reaction. 1+2=3

(ii) Predict the product for the given reaction and propose a mechanism : 3



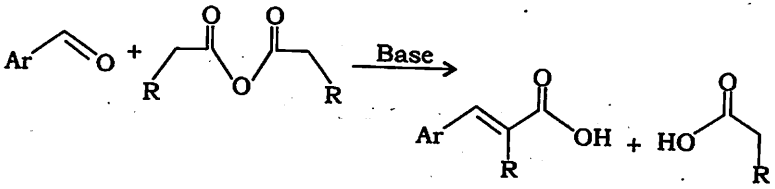
(iii) Explain why *p*-hydroxybenzaldehyde does not undergo Cannizzaro reaction. 2

(iv) Distinguish between nitroethane and 2-nitropropane. 2

(Turn Over)

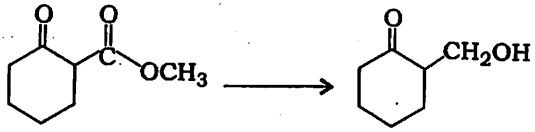
(f) (i) How can you distinguish between β-hydroxy acid and γ-hydroxy acid? 2

(ii) (1) Propose a mechanism for the following reaction : 1½



(2) How can naphthalene be prepared by Haworth synthesis? 1½

(iii) How can you carry out the following conversion? 2



(iv) What is chloromethylation? Give an example. 2

(v) Why do most higher ketones not give bisulphite adduct in appreciable amount? 1

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