

3 (Sem-2) CHM M 2

2019

CHEMISTRY

(Major)

Paper : 2.2

(Organic Chemistry)

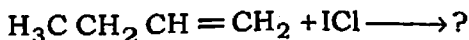
Full Marks : 60

Time : 3 hours

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

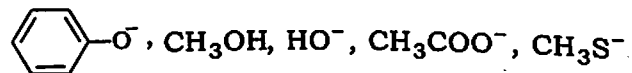
1. Answer any *seven* questions : 1×7=7

- (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-dimethylbenzoic acid, which one is less acidic and why?
- (e) Why are amines generally not prone to substitution reactions?
- (f) Predict the major product :



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



- (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 $-\text{CH}_2$ group and the faces of the carbonyl group in benzyl methyl ketone?

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(3)

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-dimethylbutane. 1

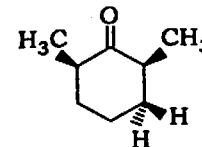
- (ii) Draw and arrange the following conformers of butane in order of increasing energy : 2

Eclipsed, Gauche, Anti

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

- (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. 5

- (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 : 3



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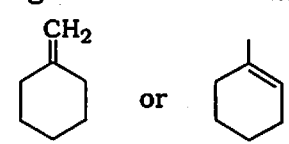
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- (ii) State how you can establish the topicity of groups in a compound. 2
- (d) In aromatic electrophilic substitution, halogens are deactivating but *o*-, *p*-directing. Explain, considering that such a substitution is kinetically controlled. 5
- (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

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(5)

- (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 $\text{S}_{\text{N}}\text{Ar}$ 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
- $$\text{CH}_3\text{CH}_2\text{CH}_2\text{BR}_2 \xrightarrow{\text{HO}^-, \text{H}_2\text{O}_2, \text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{BR}_2(\text{OH})$$

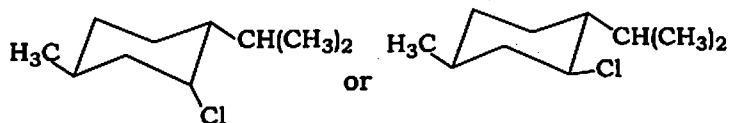
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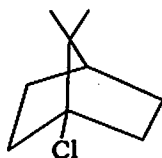
(iii) Suggest a method for conversion of butane-1-amine to but-1-ene. 2

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

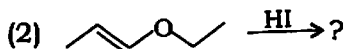
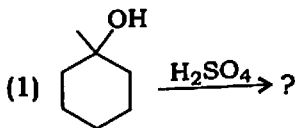


(v) Iodine does not react with ethane even though I₂ is more easily cleaved homolytically than the other halogens. Explain. 2

(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

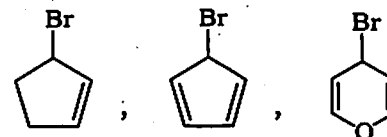


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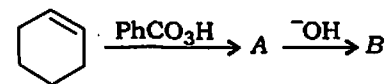
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(iii) Arrange the following compounds in order of decreasing S_N1 reactivity and give a brief explanation : 3

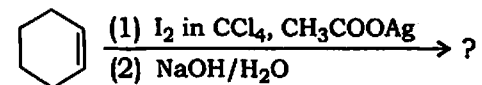


(iv) Identify A and B (including their stereochemistry) : 2



(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

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