

2017

CHEMISTRY

( Major )

Paper : 2:2

( Organic Chemistry )

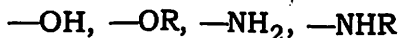
Full Marks : 60

Time : 3 hours

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

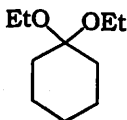
1. Answer the following questions : 1×7=7

(a) Arrange the following in order of decreasing electron releasing ability :



(b) Define specific rotation.

(c) Which compounds are used to make the following acetal?

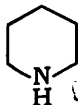


(d) How can you protect a carbonyl group?

(e) What are the topicsities of the hydrogen atom of the —CH<sub>2</sub>— group and faces of  $\text{>C=O}$  group in benzyl methyl ketone?

( 2 )

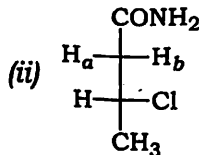
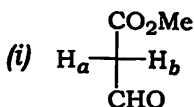
- (f) What would you expect to be the site of  
(i) protonation and (ii) deprotonation if  
the given compound is to be treated  
with an appropriate acid or base?



- (g) How is the octane rating of gasoline  
determined?

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

- (a) Identify homotopic, enantiotopic and  
diastereotopic hydrogens (if any) :



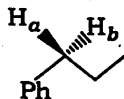
- (b) Calculate the percent of each  
enantiomer of an unknown (X) if the  
specific rotation of (+)-X is  $+110^\circ$  and  
the specific rotation of the mixture is  
 $+30^\circ$ .
- (c) A bromine radical is less reactive and  
more selective than a chlorine radical.  
Explain.
- (d) Draw the *cis*-oid and *trans*-oid  
conformations of 2*E*, 4*E*-hexadiene and  
of 2*E*, 4*Z*-hexadiene.

3. Answer the following questions (any three) :

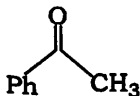
5×3=15

- (a) (i) Draw chair- and boat-forms of cyclohexane in Newman projection. 2
- (ii) Explain why chair-form of cyclohexane is more stable than boat-form. 2
- (iii) Which conformer of *n*-butane is more stable in the gaseous form? 1

- (b) (i) Identify the indicated hydrogens as pro-*R* and pro-*S* : 1



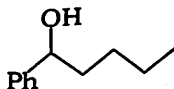
- (ii) Identify which face (front or back) is Re face and Si face : 1



- (iii) Define prostereogenic centre. State whether each carbon atom in chloroethene is prostereogenic or prochiral or both. 1+2

- (c) Account for the observation that NaOH reacts with *p*-bromotoluene to give *m*- and *p*-cresols at 300 °C, while *m*-bromotoluene yields three isomeric cresols. (Use appropriate mechanism) 5

- (d) (i) The drug ferripentol, shown below, is synthesized by the reaction between butylmagnesium bromide and an aldehyde. Draw the structure of the aldehyde and give the mechanism for the reaction : 3



- (ii) Is a Grignard reagent formed when benzyl bromide is heated with magnesium metal in a mixture of diethyl ether and ethanol as the solvent? Explain. 2

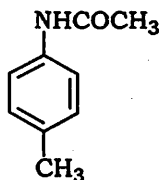
4. Answer the following questions [either (a) or (b) and any two from (c), (d), (e) and (f)] :

10×3=30

- (a) (i) How can you account for the formation of a  $\sigma$ -complex when benzene undergoes electrophilic attack? 2
- (ii) Provide two evidences in support of the arenium ion mechanism. 3
- (iii) A chlorine atom is deactivating but *ortho*- and *para*-directing towards electrophilic aromatic substitution. Explain. 4

- (iv) In a standard nitration reaction with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , the following compound forms a single mono-nitration product. What is its structure?

1



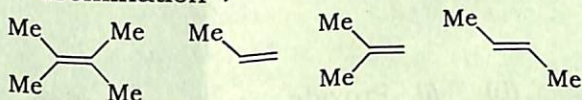
- (b) (i) Provide an explanation for the observation that nucleophilic substitution on 4-bromo-2,6-dimethylnitrobenzene is considerably slower than on 4-bromonitrobenzene.

2

- (ii) The rates of nucleophilic substitution of nitrohalobenzenes depend on the halogen displaced. What is the order of leaving group ability of halogens in such reactions? Provide an explanation. 1+2
- (iii) Give an example each of an ipso substitution and cine substitution. 1+1

(iv) The bromination of toluene by using bromine in aqueous acetic acid takes place 605 times faster than does the same reaction of benzene. The product ratio is 32.9% *ortho*-, 0.3% *meta*- and 66.8% *para*-bromotoluene. Calculate the partial rate factors for the reaction. 3

(c) (i) Arrange the following in order of decreasing reactivity towards bromination : 1



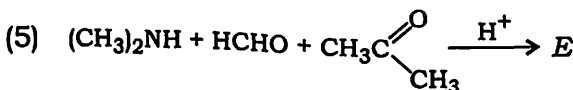
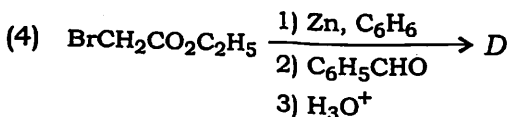
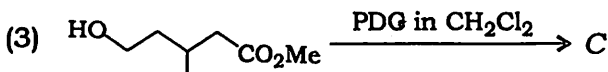
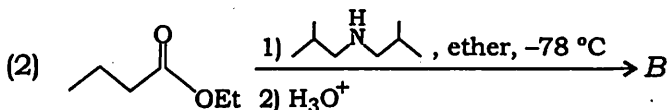
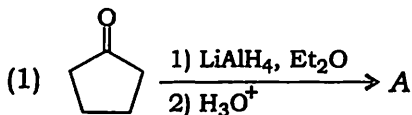
(ii) Show that addition of bromine to alkene is stereospecific. Write the mechanisms involved to justify the same. 4

(iii) How can you carry out the conversion of an olefin to the *cis*-diol and *trans*-diol? Write the appropriate mechanisms. 5

(d) (i) The  $\alpha$ -hydrogen atoms of amides have  $pK_a$  values near 30. Account for the lower acidity of these hydrogen atoms as compared with the  $\alpha$ -hydrogen atoms of esters. 2

(ii) Propose a mechanism for the Claisen condensation reaction. 3

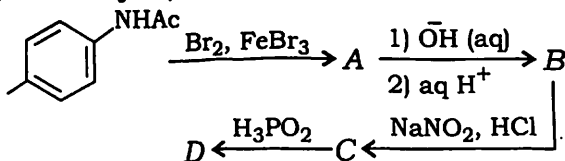
- (iii) Identify the products in the following reactions [only the major product(s) is to be written] : 5



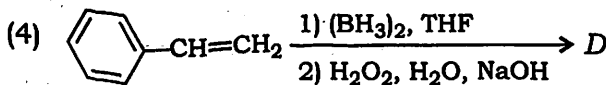
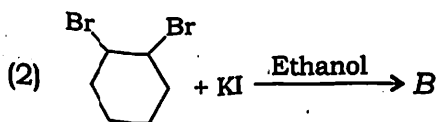
- (e) (i) How can you detect for the presence of nitro- and amino-groups in *m*-nitroaniline? Write the reactions involved. 2

- (ii) Aromatic electrophilic substitution on naphthalene is regioselective. Explain. 4

- (iii) Identify A, B, C and D : 4



- (f) (i) Outline the steps involved in the complete Hofmann degradation of piperidine. 2
- (ii) Write the reaction involved in a Chugaev reaction and propose a mechanism. 3
- (iii) Why is nitromethane acidic? 1
- (iv) Identify the products in the following reactions (major product only) : 4



\*\*\*