2014

CHEMISTRY

(Major)

Paper : 2.2

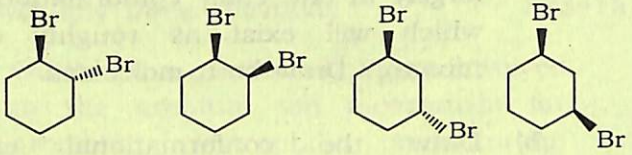
Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer all questions : 1×7=7

(a) Which of the following molecules have two axial bromines in at least one of the chair conformations? 1



(b) Draw the most stable conformation of 2-fluoroethanol. 1

(c) Arrange the following alkenes in order of decreasing reactivity towards peroxy acid : 1

(d) What functional group transformation takes place during saponification? Write the reaction. 1

(e) Which of the following should have higher boiling point? Explain briefly. 1

1,5-pentanediol or 1-pentanol

(f) While carrying out substitution reactions on alcohols, they are usually allowed to react with TsCl. Why? 1

(g) Why is cyclopropane more reactive than propane? 1

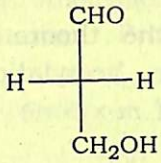
2. Answer any *four* questions : 2×4=8

(a) Of *cis*- and *trans*-1,2-diisopropyl-cyclohexane, which molecule will exist largely in one chair conformation and which will exist as roughly equal mixture? Draw both molecules. 1+1

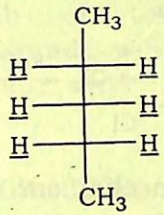
(b) Draw the conformational energy diagram of *n*-butane, showing the conformations at the energy maxima and minima. 2

(c) Define homotopic ligands and stereoheterotopic ligands. 1+1

(d) Assign pro-*R* and pro-*S* designations to the enantiotopic ligands in the following molecule : 2



(e) Identify the underlined atoms as homotopic, enantiotopic and diastereotopic (whichever is applicable). 2



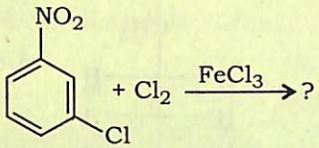
3. Answer any *three* questions : 5×3=15

(a) Outline the mechanistic steps involved in the arenium ion mechanism for aromatic electrophilic substitution. Draw the energy profile diagram for the proposed mechanism. Give one evidence in support of the proposed mechanism. 3+1+1

(b) Define partial rate factor. Why is it important? For acetylation of toluene,

the partial rate factors are for the *ortho*-position $o_f^{Me} = 4 \cdot 5$, for the *meta* $m_f^{Me} = 4 \cdot 8$ and for the *para* $p_f^{Me} = 7 \cdot 49$. Calculate the theoretical partial rate factors for acetylation at different positions of *m*-xylene 1+1+3

(c) Explain why chlorine is *ortho*- and *para*-directing but deactivating. Complete the following reaction and state the effect associated with it : 3+1+1



(d) The S_N1 mechanism is important for aromatic diazonium salts. Write the mechanism. Provide two evidences in support of the mechanism. Why is this mechanism observed rarely for aryl halides and sulphonates? 2+2+1

(e) What products are expected to be formed when isomeric dichlorobenzenes viz. 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene were each allowed to react with potassium amide? Provide an explanation for the products obtained. 2+3

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

(a) *(i)* How can you convert cyclohexene to 3-bromocyclohexene? Propose a mechanism. Provide one evidence to support the proposed mechanism. 1+3+1

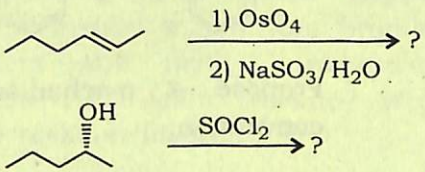
(ii) Give a method for preparation of lithium dialkylcuprate. What would happen if 1-bromobutane is allowed to react with lithium dimethyl-cuprete? 1+2

(iii) Which of the following two compounds will react faster with HCl and why? 1+1

$H_3CCH{=}CHCH_3$ *Or* $H_3CC(CH_3){=}CH_2$

(b) *(i)* How can you convert an alkene to *trans*-vicinal diol? Propose a mechanism for the reaction. 2+3

(ii) Write the major product for the following reactions (take care of the stereochemistry) : 1½+1½



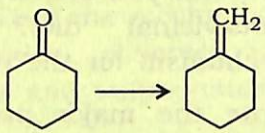
(iii) Distinguish between ethanol and phenol. 2

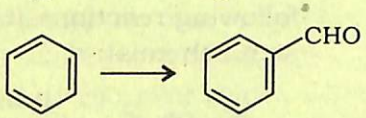
(c) (i) Explain the mechanism involved in Knoevenagel reaction. 4

(ii) How can you distinguish between a primary aliphatic amine and a primary aromatic amine? Write the appropriate reaction. 1+2

(iii) How can you convert propanoic acid to 2-aminopropanoic acid? Write the reaction. The 2-aminopropanoic acid obtained can be either racemic or optically active. In the reaction you have written, what is the nature of 2-aminopropanoic acid? 2+1

(d) (i) How can you bring about the following conversions (any *one*)?

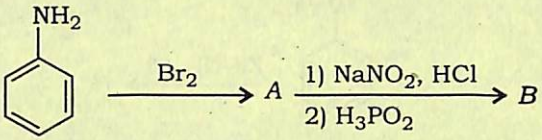




Propose a mechanism for the conversion. 1+3

(ii) Write the mechanism for acid catalysed conversion of benzoic acid to methylbenzoate. Provide one evidence in support of the proposed mechanism. 3+1

(iii) Identify the products *A* and *B* : 2

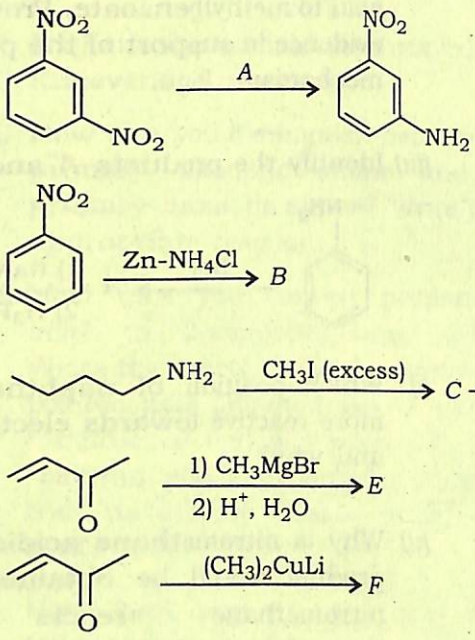


(e) *(i)* Which position of naphthalene is more reactive towards electrophiles and why? 3

(ii) Why is nitromethane acidic? What product would be obtained when nitromethane reacts with benzaldehyde in presence of a hydroxide base? Write the reaction. 1+2

(iii) How are Grignard reagents prepared? Why must they be prepared under anhydrous condition? What would happen when methyl magnesium bromide reacts with methyl propanoate, followed by acidic workup? Write the reaction involved. 1+1+2

(f) (i) In the following reactions, identify *A*, *B*, *C*, *D*, *E* and *F* : 3



(ii) How can you convert 2-phenylpropene to 2-phenyl-1-propanol? 2

(iii) What would happen when butanal reacts with Tollens' reagent? Write the reaction. 2

(iv) Carboxylic amides are less reactive towards nucleophiles compared to ketones. Why? How can you convert benzoic acid to benzamide? 2+1

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