Total No. of printed pages = 10

3(Sem 2) CHM M2

2015 CHEMISTRY (Major) Paper : 2.2 Full Marks – 60 Time – 2½ hours

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

- 1. (a) What do you mean by syn-clinal and anticlinal conformations ? $1 \times 7 = 7$
 - (b) Draw the most stable conformer of 1, 2difluoroethane.
 - (c) How will you prepare Gilman's Reagent for the synthesis of alkane ?
 - (d) Arrange the stabilities of conjugated diene, isolated diene and cumulated diene in decreasing order.

- (e) Arrange the following derivative of carboxylic acid in order of reactivity with nucleophiles. (increasing order)
 RCONH₂, RCOCl, (RCO)₂O, RCOOR[']
- (f) $CH_3 CH_2 CH_2 NH_2$ boils at 49°C whereas $(CH_3)_3N$ boils at 3°C. Explain.
- (g) Nitroalkanes and nitroarenes are good solvents for polar compounds. Explain.
- 2. Answer any four questions : $2 \times 4=8$
 - (a) Draw the corresponding Newman and Saw horse projection of the following molecule.



(b) Assign R or S designation with IUPAC nomenclature of the following molecule.



- (c) Draw the different conformations of cyclohexane and also draw the potential energy curve for the different conformers.
- (d) Identify the faces present in E and Z, but-2-ene with a suitable reaction.
- (e) What do you mean by Re and Si-face ? Give an example.
- (f) Find the topicity of the hydrogens in



- 3. Answer any *three* questions : $5 \times 3 = 15$
 - (a) What is ortho-effect ? Explain on this basis why nearly all ortho substituted benzoic acids are stronger acid than benzoic acid. 2+3=5
 - (b) What is ipso attack ? Explain with an example. Write the product of the following reaction 2+2+1=5

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- (c) Write the products in each case and give mechanism. $1\frac{1}{2}+1\frac{1}{2}+2=5$
 - (i) Cis-2-butene $\frac{BR_2}{CCl_4}$

(ii) trans-2-butene
$$\frac{\text{OsO}_4, \text{Py}}{\text{NaHSO}_3/\text{H}_2\text{O}}$$

(iii)
$$\operatorname{RCH}_2\operatorname{NO}_2 + \operatorname{R'CHO} \xrightarrow{\operatorname{KOH}, \operatorname{H}_2\operatorname{O}} \rightarrow$$

- (d) How will you prepare cinnamic acid from benzaldehyde by Perkin Reaction ? Write mechanism. How will you prove that only α hydrogen atoms of the anhydride are involved during the condensation reaction. 1+3+1=5
- (e) In the following reaction find the products. 1+4=5



The rate of the reaction does not charge appreciably with change in the nature of G, except when G = Fluorine. Explain.

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- 4. Answer any *three* questions : $10 \times 3=30$
 - (a) (i) What happens when an allene $CH_2 = C=CH_2$ is treated with dil. H_2SO_4 ? Give reaction. 2
 - (ii) Cyclopentadiene has an active hydrogen. To show this give a reaction. 2
 - (iii) How will you prepare an alkane by Hunsdiecker reaction ? Give probable mechanism.
 - (iv) What do you mean by transesterification reaction? Give one example.

1+1=2

- (v) Carbonic acid (pKa=6) is stronger acid than phenol (pKa=9.95). Explain. 1
- (b) (i) In Rosenmund reduction of RCOCl to RCHO the catalyst $Pd/BaSO_4$, H_2 is used along with small amount of sulphur or quinoline. Explain. 2
 - (ii) What happens when propionaldehyde is treated with Al(OEt)₃? What is the name of the reaction ?

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(iii) Complete the following reactions: 2



 (iv) Arrange the following group in increasing activating order towards electrophilic reagent with explanation.

 $\stackrel{\oplus}{\mathrm{NR}}$ $\stackrel{(=)}{\mathrm{NH}}$ $\stackrel{(=)}{\mathrm{NH}}$ $\stackrel{(=)}{\mathrm{NHCOCH}}$

- (v) Formaldehyde undergoes Cannizzaro reaction, but acetaldehyde does not. Explain.
- (c) (i) How will you protect $a NH_2$ group in aniline during nitration ? 1
 - (ii) Convert the following :

2



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(iii) Arrange the following in increasig order of basicity : 1



(iv) Write the products with mechanism and name the following reactions : $2 \times 3=6$

(i) Ph CHO + Br CH₂CO₂
$$\varepsilon t \xrightarrow{Zn} H_3O^+$$

(ii)
$$CH_3 \rightarrow O - CHO + CH_2(CO_2 \varepsilon t)_2$$

$$\frac{Me_2 NH_2}{MeCOO^-}$$

- (d) (i) What do you mean by Kinetic Isotope effect ? How this effect can be applied as evidence for Areniumion mechanism in ArSE, reaction ? $1\frac{1}{2}+1\frac{1}{2}=3$
 - (ii) Benzene does not decolorise bromine water. Explain. 2
 - (iii) Friedel Crafts acylation of aniline is difficult. Briefly explain. 2

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- (iv) How will you explain that electrophilic substitution in anthracene takes place almost exclusively at 9 or 10 position. 3
- (e) (i) What are the different steps involved in the intermediate complex mechanism of nucleophilic aromatic substitution reaction? What are the evidences in support of this mechanism ? 2+2=4
 - (ii) Write down the mechanism of ArSN reaction involving benzyne intermediate. 3
 - (iii) How will you trap a benzyne intermediate? 2
 - (iv) Write the product of the following reaction :



(8)

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(f) Identify the products in the following reactions :

CHO $(CH_3)_2 C = O \xrightarrow{KNH_2} A \xrightarrow{NaBH_4} B$

 $\overset{\text{NO}_2}{\checkmark} + \overset{\text{Sn}}{\xrightarrow{\text{ConcHCl}}} C \xrightarrow{\text{n-pentyl}} D \xrightarrow{\text{H}_3\text{PO}_2} E$

$$\bigcirc H + H_2 O \longleftrightarrow F \xrightarrow{FeCl} G$$

$$CH_{3}CH = CH_{2} \xrightarrow{H^{+}, CO} H \xrightarrow{RNH_{2}} I$$





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(i)

(9)

[Turn over

6

- (ii) Benzene is not used as a solvent for the Friedel Crafts alkylation of chlorobenzene. Explain.
- (iii) Between phenol and benzylalcohol which one is stronger acid ? Give reason. 2

