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 anti-clinal conformations ? 1×7=7

(b) Draw the most stable conformer of 1, 2-difluoroethane.

(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.

[Turn over

(e) Arrange the following derivative of carboxylic acid in order of reactivity with nucleophiles. (increasing order)

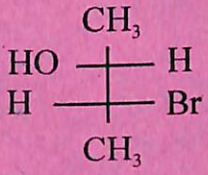
$RCONH_2$, $RCOCl$, $(RCO)_2O$, $RCOOR'$

(f) $CH_3 - CH_2 - CH_2 - NH_2$ boils at 49°C whereas $(CH_3)_3N$ boils at 3°C. Explain.

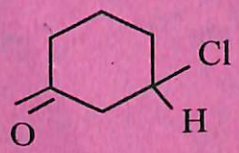
(g) Nitroalkanes and nitroarenes are good solvents for polar compounds. Explain.

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

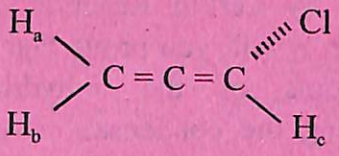


(c) Draw the different conformations of cyclohexane and also draw the potential energy curve for the different conformers.

(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.

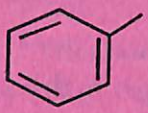
(f) Find the topicity of the hydrogens in



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



$$\frac{Br_2/light}{Or\ NBS}\ ?$$

(c) Write the products in each case and give mechanism. 1½+1½+2=5

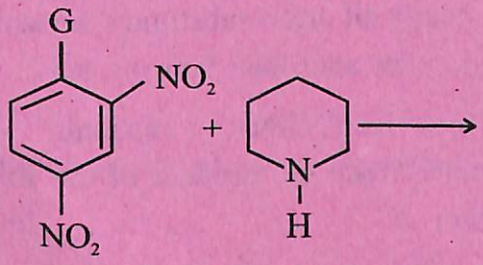
(i) Cis-2-butene $\xrightarrow[CCl_4]{BR_2}$

(ii) trans-2-butene $\xrightarrow[NaHSO_3/H_2O]{OsO_4, Py}$

(iii) $RCH_2NO_2 + R'CHO \xrightarrow{KOH, H_2O}$

(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.

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

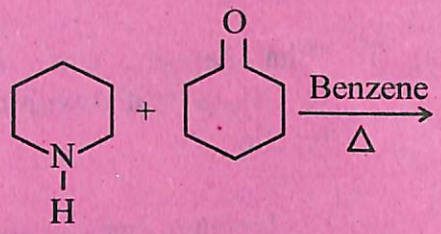
(iv) What do you mean by transesterification reaction ? Give one example. 1+1=2

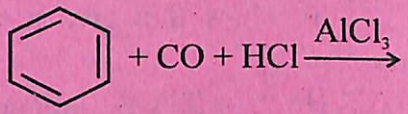
(v) Carbonic acid (pKa=6) is stronger acid than phenol (pKa=9.95). Explain. 1

(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 ? 2

(iii) Complete the following reactions : 2

(a) 

(b) 

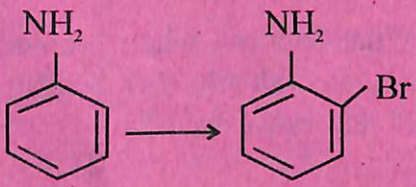
(iv) Arrange the following group in increasing activating order towards electrophilic reagent with explanation. 3

$\overset{\oplus}{N}R_3$, $\overset{(-)}{N}H_2$, $\overset{(-)}{N}HCOCH_3$

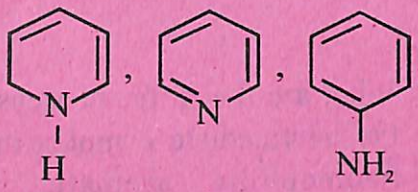
(v) Formaldehyde undergoes Cannizzaro reaction, but acetaldehyde does not. Explain. 1

(c) (i) How will you protect a $-NH_2$ group in aniline during nitration ? 1

(ii) Convert the following : 2



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



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

(i) $\mathrm{Ph\,CHO + Br\,CH_2CO_2\varepsilon t \xrightarrow[H_3O^+]{Zn}}$

(ii) $\mathrm{CH_3-C_6H_4-CHO + CH_2(CO_2\varepsilon t)_2 \xrightarrow[MeCOO^-]{Me_2NH_2}}$

(d) (i) What do you mean by Kinetic Isotope effect ? How this effect can be applied as evidence for Areniumion mechanism in $ArSE_2$ reaction ? 1½+1½=3

(ii) Benzene does not decolorise bromine water. Explain. 2

(iii) Friedel Crafts acylation of aniline is difficult. Briefly explain. 2

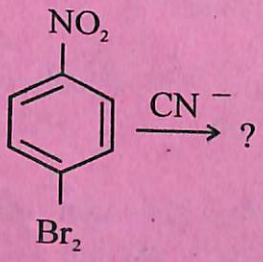
(iv) How will you explain that electrophilic substitution in anthracene takes place almost exclusively at 9 or 10 position. 3

(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

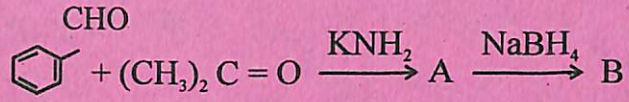
(iii) How will you trap a benzyne intermediate ? 2

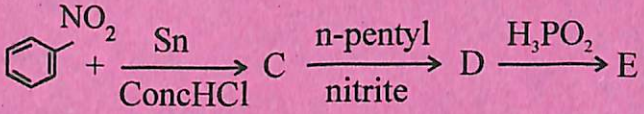
(iv) Write the product of the following reaction : 1

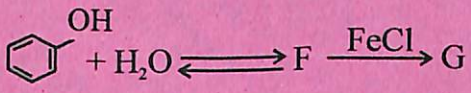


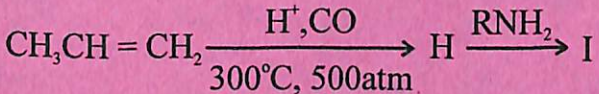
(f) Identify the products in the following reactions : 6

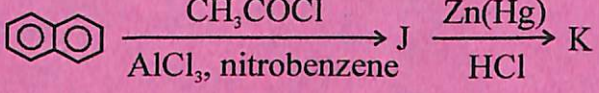
(i)











(ii) Benzene is not used as a solvent for the Friedel Crafts alkylation of chlorobenzene. Explain. 2

(iii) Between phenol and benzylalcohol which one is stronger acid ? Give reason. 2