

M.Sc. Examination 2017
Semester-IV
Chemistry
Course: CH-1021
(Optional : Organic Chemistry)

Time: Three Hours

Full Marks: 40

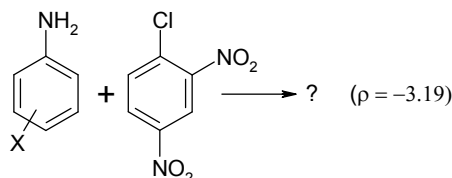
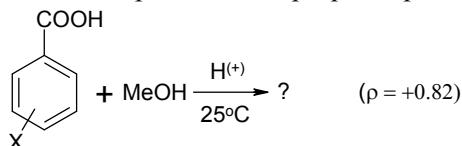
Questions are of equal value or as indicated in the margin.

Answer *any four* questions.

1. a) Using molecular formula and other chemical and/or spectroscopic evidences how could you establish the chemical structure of citral? [M.F. of citral is $C_{10}H_{16}O$] 8
 b) Natural citral is a mixture of the geometrical isomers, citral a and citral b. How do you distinguish these two citrals? 2
2. a) Describe the stereochemistry at C_8 and C_9 position of Cinchona alkaloid. 6
 b) Write down the synthetic pathway of quinine starting from isoquinoline derivative. 4
3. a) Explain why the ρ values in the following set of reactants decreases gradually up to the third member of the series, however the fourth one shows a value somewhat larger. 3

Substrates	ρ value
$X-C_6H_4-COOH$	1.00
$X-C_6H_4-CH_2-COOH$	0.49
$X-C_6H_4-CH_2-CH_2-COOH$	0.21
$X-C_6H_4-CH=CH-COOH$	0.47

- b) Predict the product with proper explanation. 2x2

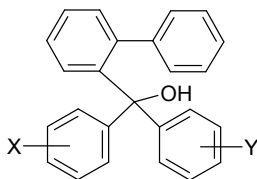


- c) Predict the sign of ρ :
 - i) Ethylation of phenoxide in EtOH at 20°C .
 - ii) Nitration of benzene derivatives. 1.5x2
4. a) The acid catalyzed hydrolysis of Ar-COOMe in aq. MeOH at 25°C shows the ρ value of 0.03. However the reaction in 99.9% H_2SO_4 shows a ρ value of -3.25 . Explain the difference in ρ value in these two cases. 3
 b) When the hydrolysis of Ar-COOEt in 99.9% H_2SO_4 is measured it shows two ρ values, -3.25 and $+2.0$, depending upon the substituent present in the aromatic ring. Explain the deviation. 3

P.T.O.

(2)

- c) Cyclodehydration of the following 2-phenyl-triaryl methanols shows downward deviation in Hammett plot. Explain. 4



5. a) What do you mean by variation principle? How do you utilize this method for evaluating the energies of one electron MOs of bonding and antibonding state of hydrogen molecule ion in terms of Coulomb, resonance and overlap integral? 2+4
b) Show that cyclopropenyl system contains two degenerate orbitals using Hückel approximation. 4
6. a) How do you construct the π -orbitals of 1,3-butadiene molecule from its atomic orbitals using LCAO approach? Show the expression of secular determinant of π -orbitals of this molecule in Hückel framework and calculate the energies of the MOs. 2+4
b) Draw the π -molecular orbitals of benzene and express their energies in terms of Coulomb and resonance integral. Calculate also the resonance energy involved in the system. 3+1
