Bankim Sardar College

Semester II Examination

B.Sc Hons

Subject- Chemistry, Paper-CC3

Answers of each group should be in separate Answer-Sheet

Group A (F.M-10)

1. **Select the correct answer** 10x1=10

(i) Which of the following is not true about nucleophile?
a) donates an electron pair to an electrophile to form a chemical bond
b) all molecules or ions with a free pair of electrons or at least one pi bond can act as nucleophiles
c) nucleophile are Lewis acids by definition
d) a nucleophile becomes attracted to a full or partial positive charge

(ii) Which halogen nucleophile is weakest in polar, aprotic solvents?
a) Iodide (I^-)
b) Fluoride (F^-)
c) Cholride (Cl^-)
d) Bromide (Br^-)

(iii) Which of the following pairs does not show an acid and its conjugate base?
a) NH_3 and NH_2^-
b) NH_4^+ and NH_3
c) NH_4^+ and NH_2^-
d) H_3PO_4 and $H_2PO_4^-$

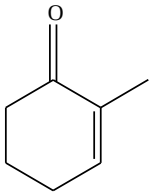
(iv) Which reagent is a good nucleophile?
a) NH_3
b) BH_3
c) Br_2
d) HBr

(v) Which of the following cannot react as a nucleophile?
a) CH_3NH_2
b) $(CH_3)_2NH$
c) $(CH_3)_3N$
d) $(CH_3)_4N^+$

(vi) Which substituted benzoic acid is most acidic?

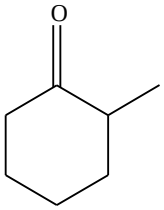
a) *m*-Chloro Benzoic Acid
b) *p*- Chloro Benzoic Acid
c) *m*-Methyl Benzoic Acid
d) *p*-Methyl Benzoic Acid

(vii) How many enolisable H atoms are there in the following compound?



a) 4 b) 5 c) 6 d) 7

(viii) How many tautomers can you draw for the following ketone

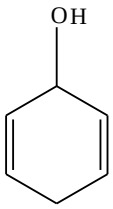


a) 1 b) 2 c) 3 d) 4

(ix) In keto enol form which type of H is must?

a) Alpha b) Beta c) Gamma d) any position of phenol

(x) Which of the following is a tautomer of phenol?

a)


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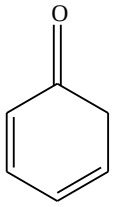

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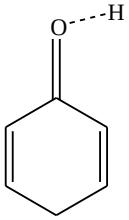

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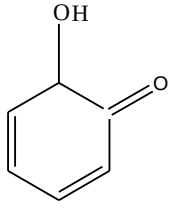


Group B (F.M-30)

2. **(I) Select the correct answer of the following questions** **10x1=10**

(i) When toluene is nitrated by conc. H_2SO_4 and fuming HNO_3 below 50^oC the probable product is

(a) *m*-nitrotoluene (b) *o*-nitrotoluene (c) *o,m*-dinitro toluene (d) none of these

(ii) The melting point of pthalimide which is obtained by condensation of phthalic anhydride and urea is

(a) 200^oC (b) 234^oC (c) 180^oC (d) 155^oC

(iii) Acetanilide is prepared from aniline when it is refluxed with
(a) Glacial acetic acid (b) Acetic Anhydride (c) both of these (d) none of these

(iv) Benzil can be prepared by the oxidation of
(a) Benzene (b) Benoin (c) Benzophenone (d) Benzillic Acid

(v) The solvent used for crystallization of crude Benzil is
(a) Hot Water (b) Cold Water (c) Rectified Spirit (d) 1% HCl

(vi) Select the brominating agent for bromination of Acetanilide which you think is more eco friendly
(a) Br_2/ CCl_4 (b) Br_2/ gl.AcOH (c) KBr/$KBrO_3$ (d) none of these

(vii) Green "Multi-Component-Coupling" reaction of ethyl acetoacetate, formaldehyde and ammonia leads to formation of
(a) Quinoline derivative (b) Pyrrole derivative (c) Indole derivative (d) Pyridine derivative

(viii) The reagent used for oxidative coupling of β-naphthol is
(a) $FeCl_3$ (b) $FeSO_3$ (c) $FeCl_2$ (d) $FeSO_4$

(ix) The mechanism followed by Benzil-Benzillic Acid rearrangement is an example of
(a) Intermolecular Rearrangement (b) Intramolecular Rearrangement
(b) Both of these (d) None of these

(x) Which reagent is used to decolorize the brown colour of MnO_2 formed as a by-product during oxidation of Benzyl Chloride using $KMnO_4$
(a) Na_2SO_3 (b) Na_2SO_4 (c) $NaHSO_3$ (d) NaCl

II. **Answer any five** **5x2=10**

1. Write down the chemical reaction for benzoylation of aniline.
2. Calculate the % of yield of the phthalic acid (3.5 gm) produced by the hydrolysis of phthalimide (5 gm).
3. Show the mechanism of Benzil-Benzillic Acid rearrangement.
4. Describe in 1-2 sentences how the low temperature (0-2^{o}C) of the reaction bath is maintained for nitration of acetanilide in cold condition.
5. Write down the chemical reaction of formation of Dihydropyrimidone derivative by three component coupling. Mention the reaction condition.
6. Show the mechanism of preparation of Diazoaminobenzene from aniline and benzenediazonium chloride at 0-5^{o}C by Diazo Coupling reaction.

III. **Preparation by Hydrolysis of Benzamide**

(a) Write down the procedure of Hydrolysis of Benzamide with showing the chemical reaction involved in it with mechanism. 3+2+2=7

(b) If you start with start with 10 gms of benzamide and get 6 gms of the product calculate the % of yield of the product. 3

Group C (F.M-50)

3. **Answer any ten** 10x2=20

(i) Arrange the following halides in the decreasing order of S_N1 reactivity
(a) $CH_3CH_2CH_2Cl$ (b) $CH_2=CHCH(Cl)CH_3$ (c) $CH_3CH_2CH(Cl)CH_3$

(ii) Arrange the following Compounds in the order of increasing acidity with a brief explanation.
(a) Benzyl Alcohol (b) Benzoic Acid (c) *o*-Cresol (d) Formic Acid

(iii) The correct order of basic strength of the following is with a brief explanation.
(i) Ph-NHCO-CH_3 (ii) Ph-CO-$NHCH_3$(iii) Ph-CO-CH_2-NH_2 (iv) (m-NH_2)-C_6H_4-CO-CH_3

(iv) What is the most stable conformation of ethylene glycol? Why?

(v) Among Ethyl Acetoacetate, Diacetyl acetone and Acetone which one has highest enol content? Why?

(vi) Write down the mechanism of a S_N^1 reaction showing the rate determining step.

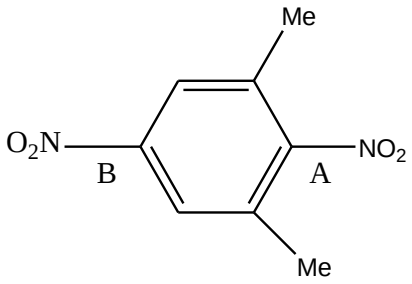
(vii) The S_N2 mechanism for R-X + KOH (aq.) → R-OH + KX
If the alkyl group R has a chiral centre with configuration R what will be the configuration of the product? Why?

(viii) Between the keto form and enol form of one compound which one will be increased if we the increase Solvent Polarity.

(ix) Between the following two oxyanions which one is the better nucleophile and why?
^-OH and ^-OOH

(x) Define bond dissociation energy. Explain how it is related with bond energy by giving an Example.

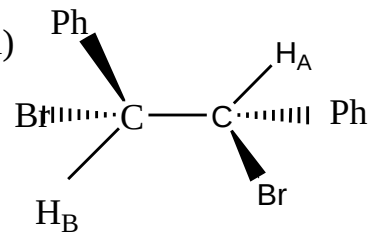
(xi) Bond energy of which bond between bond A (C-N) or bond B (C-N) is greater? Give Reason?



(xii) What is atropisomeism? Give one example.

Answer any five among Q.4-Q-11 **5x6=30**

4. Designate the following H_A and H_B atoms as Homotopic, Enantiotopic and Diastereotopic atoms.

(i)


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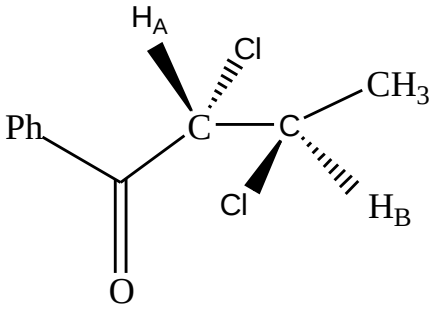

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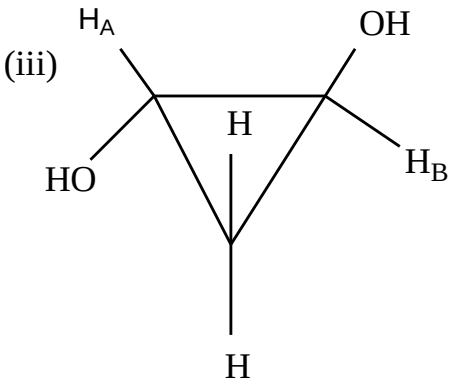
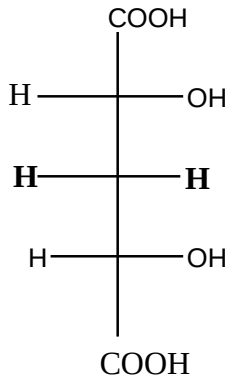


5. Identify the pro-r and pro-s **H** atoms in each of the following molecules.

(i)



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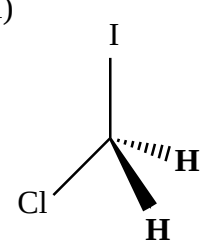

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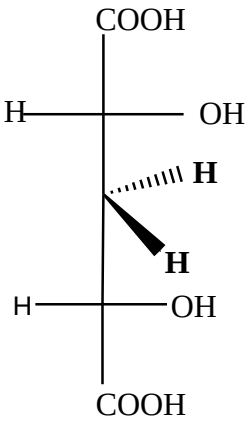
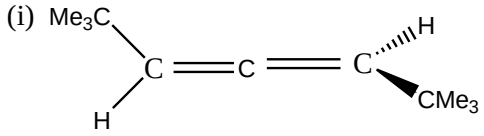


6. What do you mean by prochiral carbon atom? Write down the pro-R configuration of ethyl methyl ketone. If on reduction by sodiumborohydride the H^- approaches from above to the carbonyl carbon of the above mentioned ketone what will be the absolute configuration of the alcohol generated.

7. Write down the absolute configuration of the following compounds.

(i)



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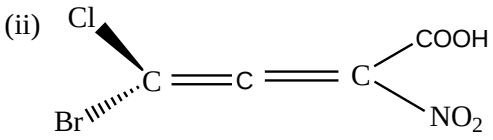

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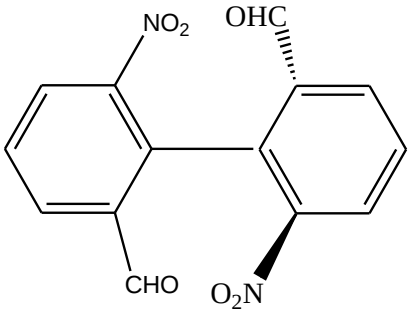

8. Draw the energy profile diagrams arising out of rotation around C-C bond in 2,3 dimethyl butane. Label all maxima and minima with appropriate conformations. Identify the most stable conformation.

9. Draw the Hofmann Saytzeff transition states for E_2 reaction of $Me_2CHCBrMe_2$ in presence of NaOR. Explain how the 1-alkene/2-alkene ratio changes as the size of R increases.

10. Discuss the stereochemistry of de-hydrobromination of meso-1,2-dibromo-1,2-diphenylethane with NaOEt/EtOH and state the products. What is the streoelectronic requirement of an SN^2 mechanism? Can you justify why neopentyl bromide can not undergo an SN^2 displacement?

11. What is tatutomerism? How many types of stepwise mechanisms are possible for prototropic Keto-enol tautomerism? Show any one stepwise mechanistic pathway of keto-enol tautomerism clearly. Also show the possible concerted mechanism of it.