

G

M.Sc. CHEMISTRY
First Semester (Repeat)
ORGANIC CHEMISTRY-I
(MSC - 101)

Duration: 3Hrs.

Full Marks: 70

Part-A (Objective) =20
Part-B (Descriptive) =50

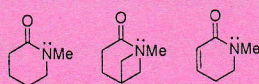
(PART-B: Descriptive)

Duration: 2 hrs. 40 mins.

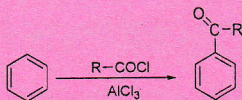
Marks: 50

Answer any four from Question no. 2 to 8
Question no. 1 is compulsory.

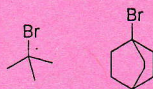
1. (a) Explain why azulene has an unusually high dipole moment. [2×5=10]
(b) Arrange the following amides in the increasing order of basicity with an explanation.



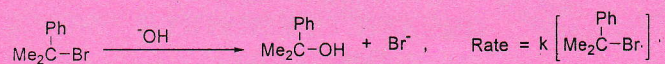
- (c) In case of Friedel Craft's acylation of the following substrate, why does the reaction stop after formation of monoacylation product?



- (d) Explain why nucleophilic displacement in CCOC(Cl)CC by ROH is faster than in CCCCl?
- (e) Discuss how the formation of benzyne intermediate could be proved by trapping experiment.
2. (a) Which of the two carbocations $\text{CH}_2=\text{CH}-\text{CH}_2^+$ and $\text{CH}_3-\text{CH}_2-\text{CH}_2^+$ is more stable and why? [2]
(b) The rate of solvolysis of the following two bromides in 80% ethanol at 25°C is in the ratio 1 : 10^{-6} , give an explanation for that. [3]

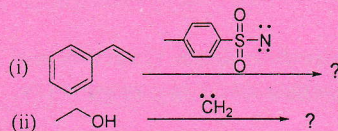


(c) For the hydrolysis of the following compound in the presence of NaOH:



What will be the sign of the reaction constant ρ ? What will be the effect of the electron releasing group in the phenyl ring on the rate of the reaction? [3]

(d) Complete the following reaction— [2]



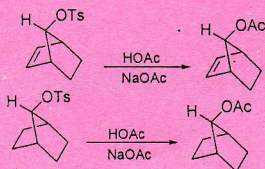
3. (a) Explain how does the rate of a S_N^2 reaction is influenced by polar hydroxylic and polar non- hydroxylic solvents. [2]

(b) Only one bromoether is obtained from the reaction of the following dibromide with methanol. Give the structure of the ether and give reason with mechanism of the reaction. [3]



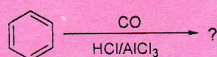
(c) What is an anchimeric assistance (neighbouring group participation) in a S_N^2 reaction? [3]

(d) In the following two reactions, which one will react faster and why? [2]



4. (a) Explain why presence of chlorine as a substituent in benzene, direct the incoming electrophile to *o-p* direction, but at the same time deactivates the benzene ring towards electrophilic substitution. [2.5]

(b) Give the product of the following reaction and suggest a mechanism. [2.5]

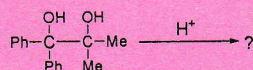


(c) What is an aromatic diazonium ion and how it is formed from an aromatic amine? Why it is stabler than aliphatic diazonium ion? Show the mechanism of diazocoupling reaction of benzene diazonium ion with phenol in a basic medium, (pH \approx 9). [1.5+1+2.5]

5. (a) What is Arndt-Eistert synthesis? Give the mechanism for the following: [3]

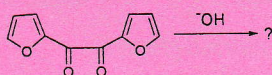


(b) Write down the product with mechanism: [2]



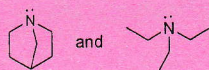
(c) Write a short note on Neber rearrangement. [2.5]

(d) Write down the product with mechanism: [2.5]



6. (a) Define the substituent constant in Hammett equation. Explain why the sign of substituent constant for -NO₂ group is +ve and that for the -OH group is dependant on the position of the substitution. [0.5+1.5+3]

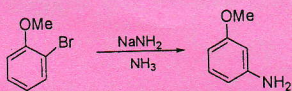
(b) Which of the following is a better nucleophile and why? [2.5]



(c) Why nucleophilic substitution at an aromatic compound is not kinetically favourable? [2.5]

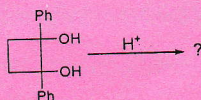
7. (a) Write a short note on cine-substitution. [2]

(b) Explain why *o*-bromo anisole on reaction with sodium amide in liquid ammonia produces only *m*-amino anisole. [3]



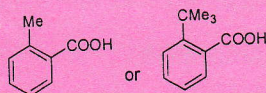
(c) Write a short note on Favorskii rearrangement. [3]

(d) Give the product of the reaction with mechanism: [2]



8. (a) What is Taft's equation? How was the substituent constant in Taft's equation evaluated? [2]

(b) Define ortho effect on acidity of substituted benzoic acid. Which one of the following will be more acidic? [3]



(c) For phthalic acid, $p^{K_{a1}} = 2.98$ while $p^{K_{a2}} = 5.28$, explain this observation. [2]

(d) Write short notes on Beckmann rearrangement. [3]



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Marks – 20

(PART A - Objective Type)

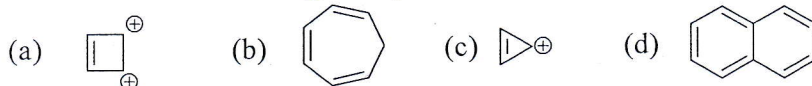
I. Choose the correct answer:

1×20=20

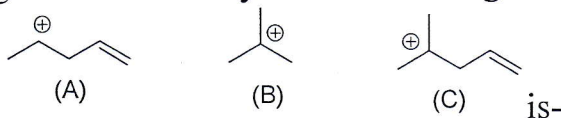
1. Which one of the following factor is responsible for providing stability to Wittig reagent?
(a) Pπ-Pπ bonding (b) dπ-dπ bonding
(c) pπ-dπ bonding (d) Both Pπ-Pπ and dπ-dπ bonding

2. The singlet state of carbene resembles with the structure of –
(a) carbanion (b) free radical
(c) carbocation (d) Aryne

3. Which of the following compound is not aromatic?



4. The decreasing order of stability of the following carbocations

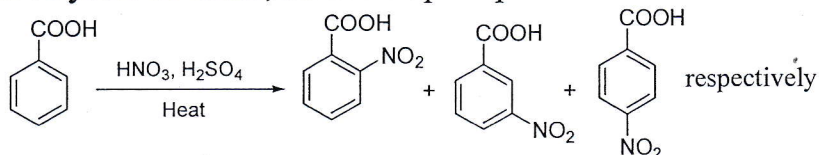


- (a) A>B>C (b) B>A>C (c) C>A>B (d) B>C>A

5. If the rate of solvolysis of methyl benzoate in a given solvent is known and the appropriate reaction and substituent constant are known, the rate of solvolysis of methyl *p*-nitrobenzoate can be calculated by the-

- (a) Hammond equation (b) Kekule equation
(c) Woodward equation (d) Hammett equation

6. The correct % yield of ortho, meta and para products in the following reaction-

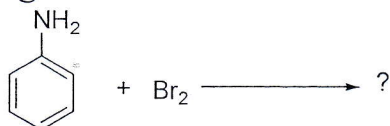


- (a) 18.5%, 80 %, 1.5 % (b) 80 %, 18.5 %, 1.5 %
(c) 1.5%, 80%, 18.5% (d) 18.5%, 1.5%, 80%

7. The total number of deactivating groups from the following groups is-
-NH₃⁺, -OR, -NR₂, -NHCOR, -NR₃⁺, -CF₃, -NO₂

- (a) 3 (b) 4 (c) 1 (d) 5

8. The product of the following reaction is-



- (a) 2,4,6-tribromoaniline (b) bromoaniline
(c) 3-bromoaniline (d) All of these

9. The following reaction proceeds via-

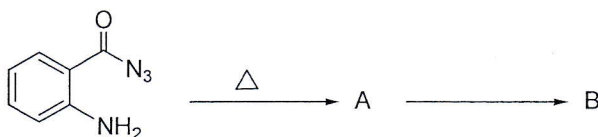


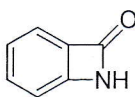
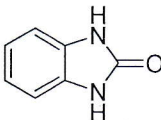
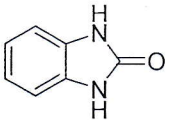
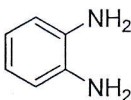
- (a) S_E2 front (b) S_Ei
(c) S_E2 back (d) None of these

10. 1-bromo-2,2-dimethylpropane gives faster S_E2 than S_N2 due to -

- (a) easier front side attack (b) rear side block
(c) +I effect of alkyl group (d) Both (a) and (b)

11. The intermediate A and major product B in the following reaction are



- (a) A is acyl cation; B is  (b) A is acyl cation; B is 
(c) A is isocyanate; B is  (d) A is acyl cation; B is 

12. The Beckmann rearrangement takes place under -

- (a) Acidic (b) Basic
(c) Neutral condition (d) None of these

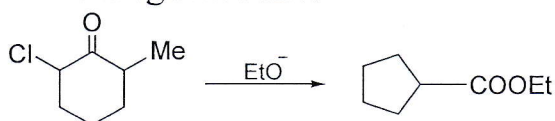
13. The intermediate formed in Neber rearrangement is-

- (a) Azirene (b) Carbene
(c) Carbocation (d) Carbanion

14. The Rearrangement involves electron deficient oxygen is-

- (a) Baeyer-villiger Rearrangement (b) Beckmann Rearrangement
(c) Pinacol Pinacolone Rearrangement (d) Sommelet Hauser Rearrangement

15. The name of the following reaction is -

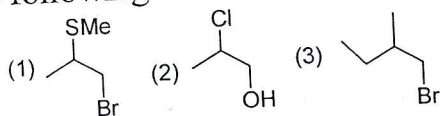


- (a) Favoriskii Rearrangement (b) Wagner Meerwein Rearrangement
(c) Sommelet Hauser Rearrangement (d) Benzil benzilic acid Rearrangement

16. Decreasing order of nucleophilicity of (1) CH_3S^- , (2) CH_3COO^- , (3) $\text{C}_6\text{H}_5\text{O}^-$, is
 (a) $1 > 2 > 3$ (b) $2 > 3 > 1$
 (c) $3 > 2 > 1$ (d) $1 > 3 > 2$
17. Protic polar solvent in the list of solvents (1) CHCl_3 , (2) Et-OH , (3) $\text{CH}_3\text{-COOH}$ and (4) DMF, is
 (a) 2 only (b) 4 only
 (c) 2 and 3 (d) 2, 3 and 4

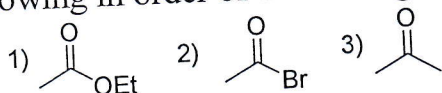
18. For the substitution reaction
 $(R)\text{-2-bromo 3-methyl butane} \xrightarrow{\text{MeOH}} \text{2-methoxy 3-methyl butane}$, the isomer of the product will have the configuration
 (a) (S) only
 (b) Mixture of (R) & (S) with higher % of (S)
 (c) Mixture of (R) & (S) with higher % of (R)
 (d) Mixture of (R) & (S) in ratio 1:1

19. Which of the following substrate/s will exhibit neighboring group participation?



- (a) 1 & 2 only (b) 1 only
 (c) 2 and 3 only (d) all of these

20. List the following in order of decreasing reactivity towards hydrolysis:



- (a) $1 > 2 > 3$ (b) $2 > 3 > 1$
 (c) $2 > 1 > 3$ (d) $1 > 3 > 2$
