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Subject: Chemistry

Year: 2023

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FEDERAL PUBLIC SERVICE COMMISSION
COMPETITIVE EXAMINATION-2023
FOR RECRUITMENT TO POSTS IN BS-17
UNDER THE FEDERAL GOVERNMENT

Roll Number

CHEMISTRY, PAPER-I

TIME ALLOWED: THREE HOURS PART-I(MCQS): MAXIMUM 30 MINUTES	PART-I (MCQS) PART-II	MAXIMUM MARKS = 20 MAXIMUM MARKS = 80
NOTE: (i) Part-II is to be attempted on the separate Answer Book. (ii) Attempt ONLY FOUR questions from PART-II. ALL questions carry EQUAL marks. (iii) All the parts (if any) of each Question must be attempted at one place instead of at different places. (iv) Write Q. No. in the Answer Book in accordance with Q. No. in the Q.Paper. (v) No Page/Space be left blank between the answers. All the blank pages of Answer Book must be crossed. (vi) Extra attempt of any question or any part of the question will not be considered. (vii) Use of calculator is allowed.		

PART-II

- Q.2. (a)** The following reaction occurs via two steps, where the first step is rate-determining step. (12)
Step I $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g})$
Step II $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
i. Write down the rate equation for the above reaction.
ii. Which molecule acts as a catalyst in this reaction? Give a reason.
iii. Which molecule is an intermediate in this reaction and justify it.
- (b)** Describe Arrhenius's equation. (8) (20)
- Q.3. (a)** An explosion is usually considered adiabatic, indicating negligible heat transfer, even though it's rapidly expanding gaseous products are not at the same temperature as the surroundings, and the boundary permits heat transfer. Explain the phenomenon. (10)
- (b)** Draw a working diagram for a reversible heat engine that operates with two isothermal steps and two constant-pressure steps. How many heat reservoirs are needed to operate this engine? (10) (20)
- Q.4. (a)** Describe Schrodinger Wave Equation for a particle in a three-dimensional box. (10)
- (b)** Explain photoelectric effect. (8)
- (c)** What is a wave function? Give Born's interpretation of wave function. (2) (20)
- Q.5. (b)** Describe Nernst's equation. (10)
- (b)** Describe the significance of pH, pK_a , and pK_b . (6)
- (c)** What is the relationship between conductance and Kohlrausch's law? (4) (20)
- Q.6. (a)** Describe three methods of mechanical phase separation. (10)
- (b)** Briefly discuss "The Hard-Soft Acid-Base Principle." (10) (20)
- Q.7. (a)** Compare Valence Bond Theory with Molecular Orbital Theory. (10)
- (b)** What is the oxidation state? Differentiate between the oxidation state and valency/covalency of an element with suitable examples. (6)
- (c)** Write the molecular orbital configuration of the followings: (4) (20)
 O_2^+ , O_2 , O_2^- and O_2^{-2}
- Q.8.** Discuss the following in detail. (5 each) (20)
i. Crystal Field Theory
ii. Hess's Law
iii. Electrophoresis Technique
iv. Freundlich Adsorption Isotherm



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CHEMISTRY, PAPER-II

Roll Number

TIME ALLOWED: THREE HOURS	PART-I (MCQS)	MAXIMUM MARKS = 20
PART-I(MCQS): MAXIMUM 30 MINUTES	PART-II	MAXIMUM MARKS = 80

NOTE: (i) Part-II is to be attempted on the separate Answer Book.
(ii) Attempt ONLY FOUR questions from PART-II. ALL questions carry EQUAL marks.
(iii) All the parts (if any) of each Question must be attempted at one place instead of at different places.
(iv) Candidate must write Q. No. in the Answer Book in accordance with Q. No. in the Q.Paper.
(v) No Page/Space be left blank between the answers. All the blank pages of Answer Book must be crossed.
(vi) Extra attempt of any question or any part of the attempted question will not be considered.
(vii) Use of calculator is allowed.

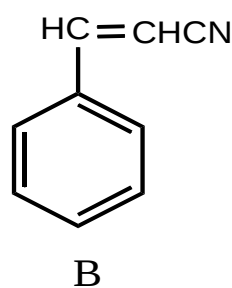
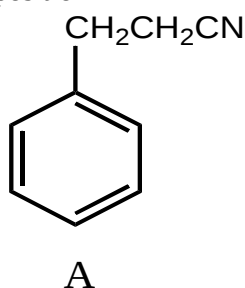
PART-II

- Q. 2. (a)** Arrange the following alkenes in order of their relative stability. How will you proceed to determine the order practically? **(5)**

- i. 1-hexene
- ii. cis-3-hexene
- iii. trans-3-hexene
- (iv) 2-methyl-2-pentene
- (v) 2,3-dimethyl-2-butene

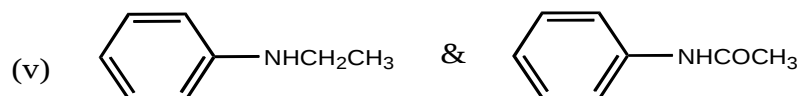
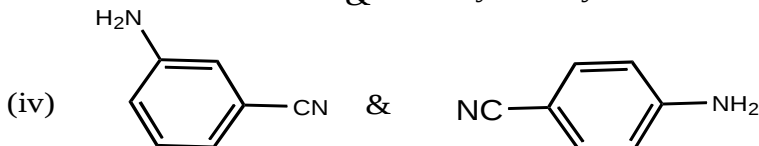
- (b)** Explain why? **(5)**

- (i) Poly substitution is a complicating factor in aromatic alkylation but not in aromatic nitration or halogenation.
- (ii) A undergoes nitration predominantly at the ortho/ para positions but B mainly at meta position



- (c)** Compare the basicity of: **(5)**

- (i) $(\text{CH}_3)_3\text{N}$ & $(\text{CCl}_3)_3\text{N}$
- (ii) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ & $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$
- (iii) Aniline & Cyclohexyl amine



- (d)** Explain why? **(2.5 each) (5) (20)**

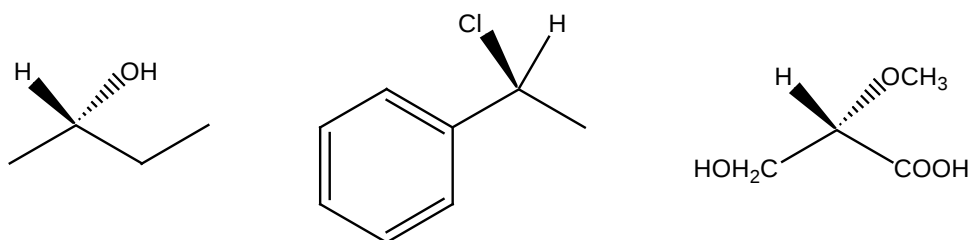
- (i) Tertiary carbocation is more stable than primary.
- (ii) Ethanol has higher boiling point than diethyl ether.

- Q. 3. (a)** Write the structural formula for more stable conformation of each of the following compounds. **(8)**

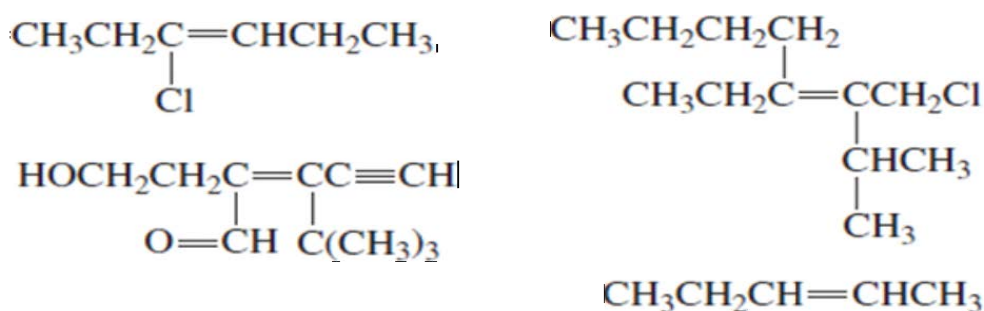
- a) *trans*-1-Fluoro-3-methylcyclohexane,
- b) *cis*-1-Iodo-4-methylcyclohexane
- c) *cis*-1-*tert*-Butyl-4-methylcyclohexane,
- d) *cis*-1,3,5-Trimethylcyclohexane

CHEMISTRY, PAPER-II

- (b) Mention R & S configuration of the following compounds. (5)



- (c) Draw and label the *E* and *Z* isomers for each of the following compounds. (5)



- (d) Draw the structure of (Z)-3-isopropyl-2-heptene. (2) (20)

- Q. 4. (a) In benzaldehyde, two of the ring protons have resonance at 7.87 ppm, and the other three have resonance in the range from 7.5 to 7.6 ppm. Explain. (4each) (20)
- (b) Arrange the following protons in the decreasing order of their δ values in ^1H -NMR and account for your order: Methyl, ethylenic, acetylenic, aryl and aldehydic.
- (c) List the solvents most commonly used in IR spectroscopy. Why water and ethanol are not suitable solvents?
- (d) The UV spectrum of acetone shows absorption maxima at 166, 189, and 279 nm. What type of transition is responsible for each of these bands?
- (e) What types of electronic transitions are possible for each of the following compounds?
- Cyclopentene,
 - Acetaldehyde,
 - Dimethyl ether,
 - Methyl vinyl ether.

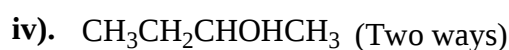
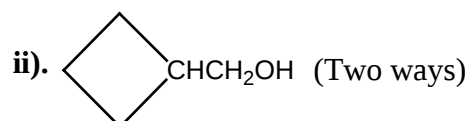
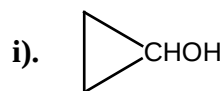
- Q. 5. (a) Write down the reagents, conditions and mechanisms of the following reactions. (10 each) (20)
- Kolbe reaction.
 - Williamson synthesis
 - Dow Process
 - Reimer-Tiemann reaction
 - Bromination of phenol
- (b) Outline all steps involved in the synthesis of the following compounds from benzene or toluene, assuming that the ortho / para mixtures are separable.
- n-Butylbenzene
 - m-Nitrotoluene
 - p- Bromonitrobenzene
 - p- Bromobenzoic acid.
 - 1,2-Dibromo-4-nitrobenzene

- Q. 6. (a) Describe with equations all possible methods that can be used for the preparation of n-hexane. (10)
- (b) Why Corey-House Method is more suitable as compared to Wurtz reaction for the synthesis of alkane. Explain with examples. (5)

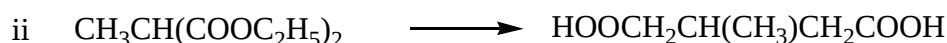
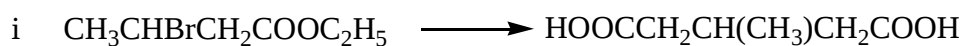
CHEMISTRY, PAPER-II

- (c) Draw the structures of following compounds and label them with IUPAC systematic rules. (5) (20)
- 3-cyclopentylhexane
 - 2-cyclobutyl-3-methylpentane
 - Isopropylcyclodecane
 - 2-methylbicyclo [3.2.0] heptanes
 - 8-methylbicyclo [3.2.1] octane

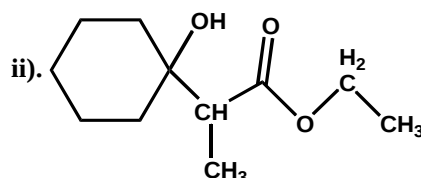
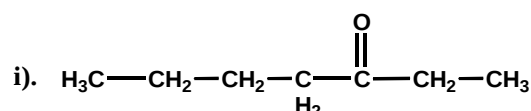
- Q. 7. (a) How can you prepare each of the following substances by a reaction involving Grignard reagent? (5)



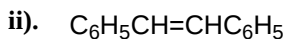
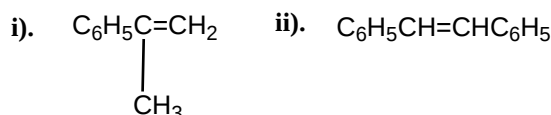
- (b) How will you bring about the following conversions? (5)



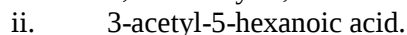
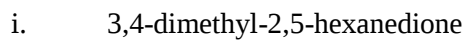
- (c) How would you synthesize each of the following compounds by the Reformatsky reaction? (5)



- (d) How would you synthesize each of the following compounds by the Wittig reaction? (2.5)



- (e) How will you synthesize each of the following substances by an acetoacetic ester synthesis? (2.5) (20)



- Q. 8. (a) Discuss the following topics. (6 each) (12)

- Prostaglandins
- Terpenes

- (b) Name the epimers of d -glucose. (4)

- (c) Clearly represent the most stable conformation of the -pyranose form of each of the following sugars. (4) (20)

- D-Galactose
- D-Mannose
- L-Mannose
- L-Ribose