

HAS (main) - 2021

This question paper contains 10 printed pages]

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ASME-21-CHEM-(II)

Roll Number

CHEMISTRY (PAPER-II)

Time Allowed : 3 Hours]

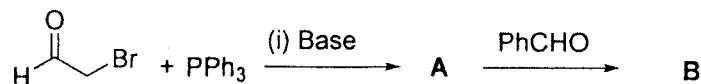
[Maximum Marks : 100

QUESTION PAPER SPECIFIC INSTRUCTIONS

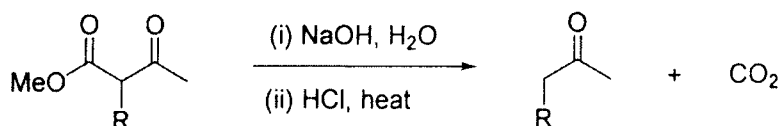
Please read each of the following instructions carefully before attempting questions.

1. There are **EIGHT** questions printed in English.
2. Candidate has to attempt **FIVE** questions in all.
3. Question No. **1** is compulsory. Out of the remaining **SEVEN** questions, **FOUR** are to be attempted.
4. *All* questions carry equal marks. The number of marks carried by a question/part is indicated against it.
5. Write answer in legible handwriting. Each part of the question must be answered in sequence and in the same continuation.
6. Unless otherwise mentioned, symbols and notations carry their usual standard meanings.
7. Assume suitable data, if considered necessary, and indicated the same clearly.
8. Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempt partially. Any page or portion of the page left blank in answer book must be clearly struck off.
9. Re-evaluation/Re-checking of answer book of the candidate is not allowed.

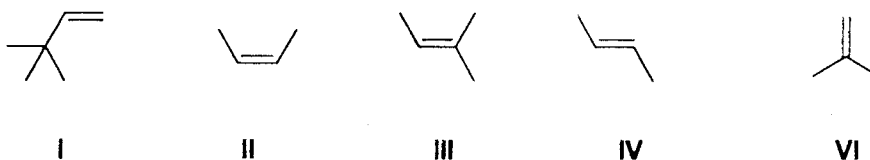
1. (a) An organic compound with molecular formula $C_6H_{12}O$ shows one singlet in 1H -NMR spectrum. Elucidate the structure of the compound ? 4
- (b) Identify the products A and B in the following reaction sequence : 4



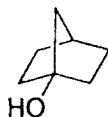
- (c) Write the mechanism of the following reaction : 4



- (d) Arrange the following alkenes towards their rate of bromination in methanol and give reason. 4

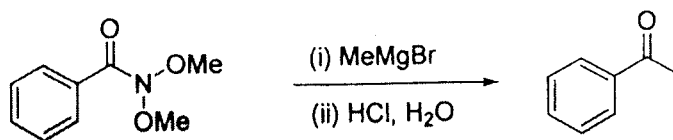


- (e) Why the following compound will not undergo elimination reaction by either an E_1 or E_2 elimination ? 4



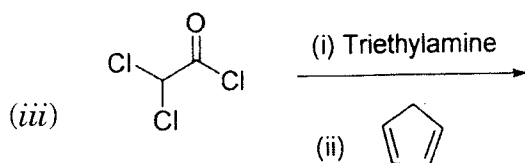
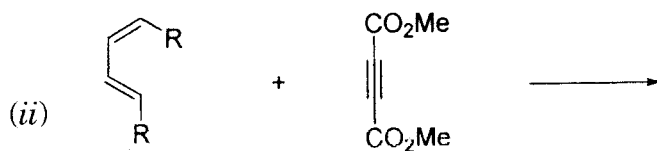
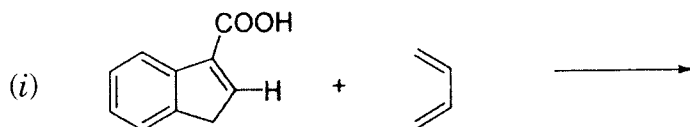
2. (a) Write the mechanism of the following reaction :

5



(b) Write the major product of the following reactions with correct stereochemistry :

6

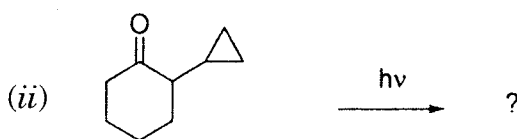
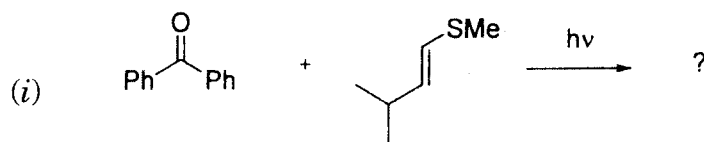


(c) The reaction of (2E, 4Z, 6E)-octa-2,4,6-triene proceeds under thermal condition affords *cis*-5,6-dimethylcyclohexa-1,3-diene. Explain formation of the product by FMO method of electrocyclic reaction.

5

(d) Write the major product formed in the following reactions ?

4



3. (a) Write down the structure of the following polymers and their monomers ?

6

(i) PMMA

(ii) Bakelite

(iii) Buna-s

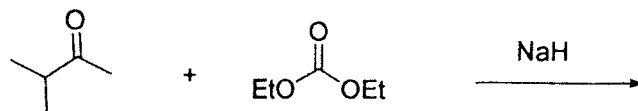
(b) Write the mechanism involved when vinyl chloride is polymerised in the presence of benzoyl peroxide ?

4

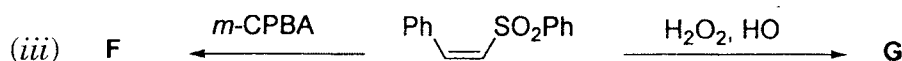
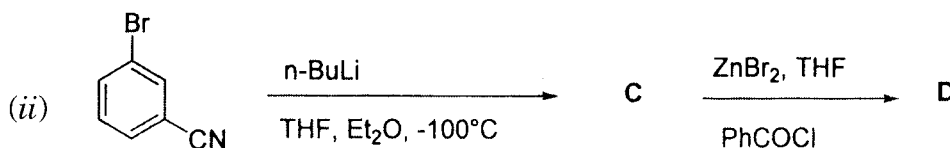
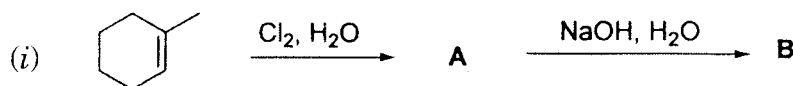
(c) Methoxy-polyethylene glycol shows a strong signal at 3.7 ppm (Integral = 155 protons) originating from the CH₂ groups, while the signal at 3.4 ppm (Integral = 3H) originates from the methoxy end group in ¹H-NMR spectrum. Calculate the degree of polymerisation and molecular weight of the polymer.

5

- (d) Complete the following reaction and write the mechanism and name of the reaction : 5



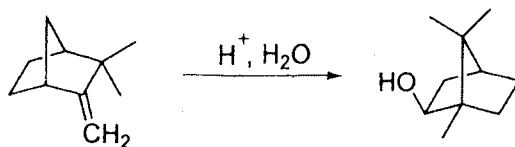
4. (a) Complete the following reactions with correct stereochemistry of product wherever applicable : 6



- (b) Explain an atom economy, a principle of the green chemistry. 5
- (c) Why hydrolysis of 2-bromo-3-methylbutane yields only 2-methyl-2-butanol ? 3
- (d) Why the reaction of iodide (I^-) with *meso*-2,3-dibromobutane gives *trans*-2-butene while (*S,S*)-2,3-dibromobutane gives *cis*-2-butene ? 4
- (e) Give *two* examples of the biodegradable polymers. 2

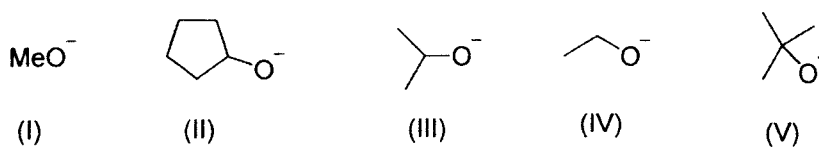
5. (a) Write the suitable mechanism for the following reaction :

5



(b) Arrange the following alkoxides nucleophile in decreasing order of S_N2 reactivity with appropriate reason ?

4

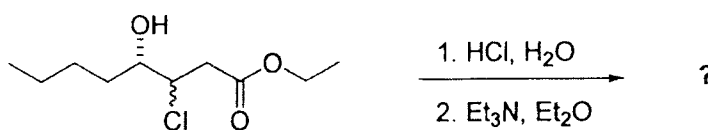


(c) An unknown organic compound with molecular formula C_4H_5NO displays strong intensity band at 2250 cm^{-1} and 1720 cm^{-1} . The compound shows only two singlets in the ratio of 3 : 2 in 1H NMR spectrum. Identify the compound.

3

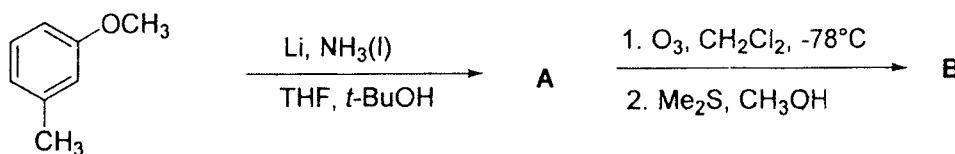
(d) Write the product and mechanism for the following reaction :

4



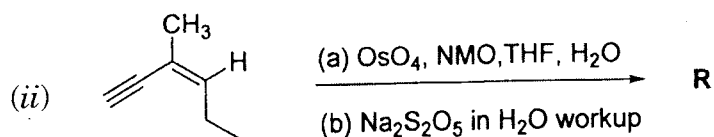
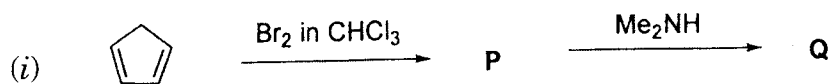
(e) Write the products A and B of the following reaction :

4



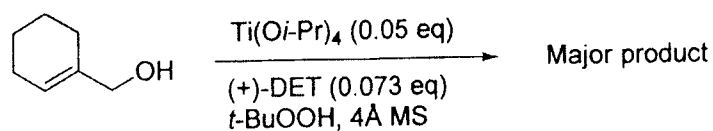
6. (a) Write the product(s) of the following reactions :

6



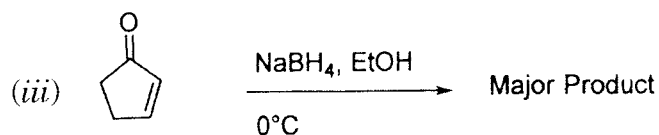
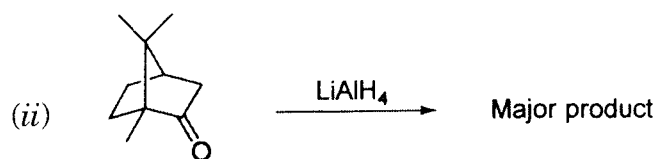
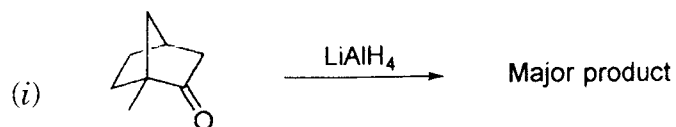
(b) Write the major product formed in the following reaction and also provide the absolute configuration of the product :

4



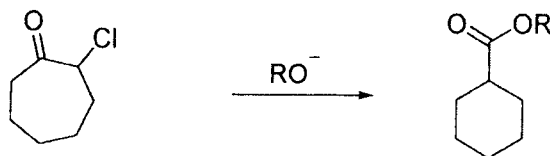
(c) Write the major product of the following reactions :

6



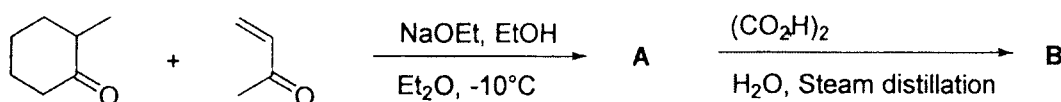
(d) Write the mechanism for the following reaction :

4



7. (a) Write the product A and B in the following reaction :

4



(b) ¹H NMR of two compounds C₅H₈O (A) and C₅H₁₀O (B) are given below :

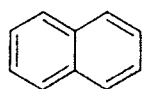
Compound A : ¹H NMR (δ, CDCl₃, 200 MHz) : 1.2 (s, 6H), 2.6 (s, 1H),
3.2 (s, 1H)

Compound B : ¹H NMR (δ, CDCl₃, 200 MHz) : 1.25 (s, 6H), 3.3 (s, 1H),
4.8-5.1(m, 2H), 5.7-6.0 (m, 1H)

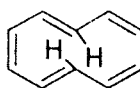
Resonance at δ 3.2 and 3.3 disappears on shaking with D₂O. Elucidate the structure of compounds A and B and assign the peaks. 6

(c) Comment on aromaticity of the following compounds :

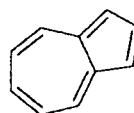
3



(i)

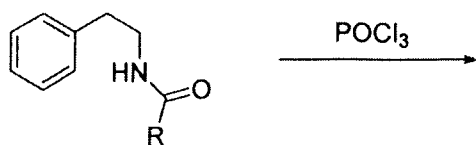


(ii)

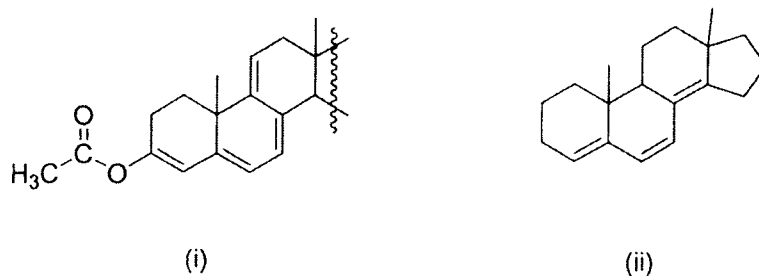


(iii)

- (d) A doubly charged compound shows a peak at m/z 59, what would be the molecular weight of the compound. 2
- (e) Briefly explain Hammett equation and linear free energy relationship with suitable example. 5
8. (a) How will you differentiate 2-methyl-butanal and 3-methyl-butanal by mass spectrometry? 3
- (b) Write the product and mechanism of the following reaction: 5



- (c) Calculate the λ_{\max} of the following compounds by using Woodward-Fieser rule. 4



Given λ_{\max} : Cisoid = 253 nm; Transoid = 214 nm; Ring residue = 5 nm;
 Alkyl substituent = 5 nm; Exocyclic double bond = 5 nm; Double bond
 extended conjugation = 30 nm; and $\text{OCOCH}_3 = 0$ nm.

(d) Arrange the following compounds in increasing order of C=C stretching frequencies (cm^{-1}) in IR spectroscopy (Give appropriate reason) : 4



(i)



(ii)



(iii)



(iv)

(e) Explain briefly Jablonski diagram.

4