c) Suggest a plausible mechanism for the following reaction.

3

$$\begin{array}{c} & \begin{array}{c} R^2 \\ & N - R^1 \end{array} \end{array} \begin{array}{c} O \\ & \\ PhCHO \end{array} \xrightarrow{Base(Cat.)} \end{array} \begin{array}{c} O \\ & \\ OH \end{array} \begin{array}{c} O \\ & \\ OH \end{array}$$

d) Discuss how you can synthesize the given compound C starting from an appropriate amino acid derivative with temporary construction of an azole moiety as the intermediate (only suggest the steps with reagents, no mechanism is needed).

$$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{HO} \\ \text{Me} \\ \text{C} \end{array}$$

e) Suggest a scheme for the synthesis of the following compound **D** (only mention the steps with reagent, no mechanism is necessary).

M.Sc. Chemistry Examination, 2019

(2nd Semester)

ORGANIC CHEMISTRY

PAPER - VI

Time: Two hours

Full Marks: 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - 2061

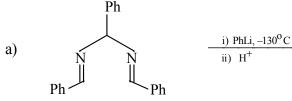
1. $[\pi^4 s + \pi^2 s]$ Cycloaddition reaction is allowed under thermal condition – explain with the help of correlation diagram.

4

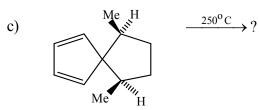
2. Write down the product(s) with proper justification.

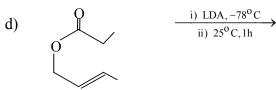
(Attempt any three)

 $1\frac{1}{2} \times 3$



b)
$$H \xrightarrow{\text{Me}} Me$$
 $H \xrightarrow{180^{\circ} \text{C}} f$





3. Answer *any two* of the following questions: 2×2

a) The value of reaction constant (ρ) for substituted benzoic acid dissociation changes with change of the solvent system as below:

Solvent	ρ -value
H ₂ O, 25°C	1.00
50% aq. EtOH, 25°C	1.60
EtOH, 25°C	1.96

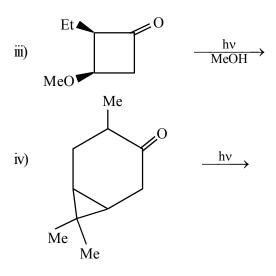
Give reason for this type of variation of the ρ -values.

b) The substituent constants (σ_p) for the substituents COCH₃, COCH₂CH₃, COCH(CH₃)₂ and COC(CH₃)₃ at the *para*-position of the aromatic ring are 0.5, 0.48, 0.47, and 0.32, respectively. How will you justify the sharp decrease of the σ_p value in the case of COC(CH₃)₃?

- c) Give experimental evidence with proper justification in favour of the fact that the piperidine ring in ψ -tropine can exist in boat conformation. $1\frac{1}{2}$
- d) Justify whether the following statement is correct or not.
 "3, 5-Dinitrobenzoyl chloride reacts with (+) neomenthol at a higher rate compared to (+) neoisomenthol."
- 7. a) How can you obtain the following compound **A** from an appropriate amino acid without using any reagent containing transition metal?

b) Design a scheme for the synthesis of the given compound
 B starting from appropriately protected amino acids (only mention the steps with reagent, no mechanism is needed).

[Turn over



5. a) Predict the product(s) of the following reactions and explain their form ations with plausible mechanism. (any two)

ii)
$$\frac{a) \text{ i-Bu}_2\text{AlH, hexane, -78}^{\circ}\text{C}}{b) \text{ H}_3\text{O}^+}$$

AcO
$$\xrightarrow{p-\text{Ts NH NH}_2, \text{AcOH}} \text{then NaCN BH}_3, 70^{\circ}\text{C}$$

$$iv)$$

$$\xrightarrow{Ag_2CO_3 \text{ on Celite}} C_6H_6, \text{reflux}$$

b) Schematically show how you can prepare Dess-Martin periodinane (DMP) reagent from *o*-iodobenzoic acid. 1

UNIT - 2062

6. a) Carry out the following transformations clearly indicating the steps involved (mechanism is not required)

[Turn over

iii) $O \longrightarrow COOH$ $O \longrightarrow COOH$ $O \longrightarrow COOH$

iv)
$$\sim$$
 CHO \sim CN $1\frac{1}{2}$

$$V)$$
 OH \longrightarrow

b) Predict the product of the following reaction (no mechanism is needed).

$$\begin{array}{c|c} Me \\ H & \begin{array}{c} & & \\ \hline \\ H & \end{array} \\ OH & \begin{array}{c} & & \\ \hline \\ ii) \ MeI \ (excess) \\ \hline iii) \ AgOH \\ \hline \\ iii) \end{array}$$

c) Establish the following relation with proper logic.

$$\sigma_{\rm R} = \sigma_{\rm p} - \sigma_{\rm m}$$

4. a) What happens when benzophenone is irradiated in 2-propanol? Comment on the quantum yield of this photolytic conversion. Write down the product of the following reaction mentioning the structure of the intermediates. $1+\frac{1}{2}+1\frac{1}{2}$

$$\begin{array}{c|c} Me \\ \hline \\ O \end{array} \qquad \begin{array}{c} \text{i) hv} \\ \hline \\ \text{ii) MeOOC-C=C-COOMe} \\ \text{iii) H}_3O^{\oplus} \end{array}$$

b) Predict the product(s) and formulate reasonable mechanisms for the following reactions (any three)

 $1\frac{1}{2}\times3$

i)
$$Ar$$
 Me Me Me hv hv hv hv

[Turn over