7. Discuss the synthetic route for cholesterol from the compound **C**. Explain with mechanism. 5

→ Cholesterol

C
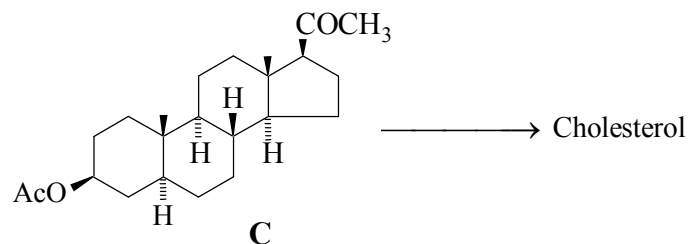
8. Carry out the following conversions : $2\frac{1}{2}\times 2$

a)

(Progesterone)

b)
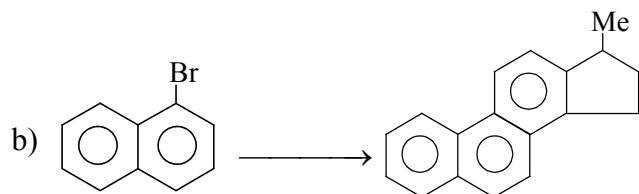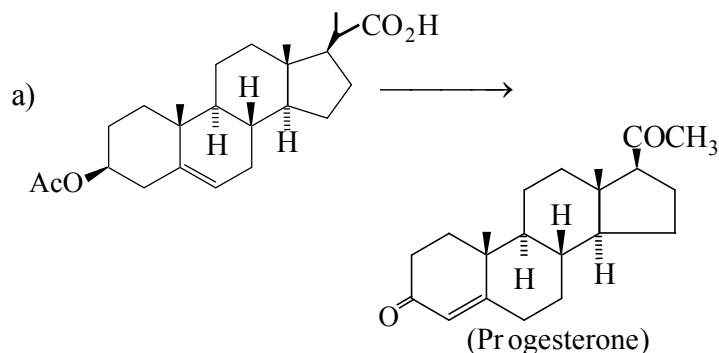
M. Sc. Chemistry Examination, 2019

(3rd Semester)

Organic Chemistry Special

Paper XI - O

Time : Two hours   Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - O-3111

1. a) Draw the π-MO's, deduce the energy for HOMO and LUMO and also calculate the HOMO lobe coefficient of butadiene molecule using HMO theory.   2+2+2

   b) Develop a state correlation diagram for the conrotatory butadiene-cyclobutene interconversion and discuss their implications.   3+1

2. Answer *any five* of the following questions :   2×5

   a) Write down the major product of the following reaction with explanation.
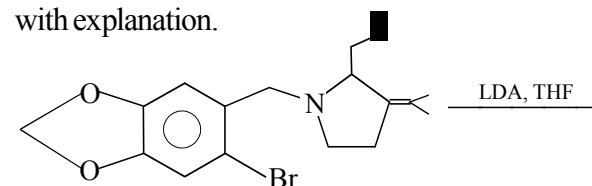
   b) Explain the rate of endo product formation in the following reaction in different solvents.
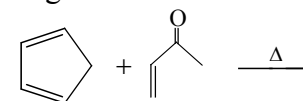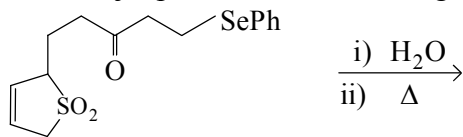

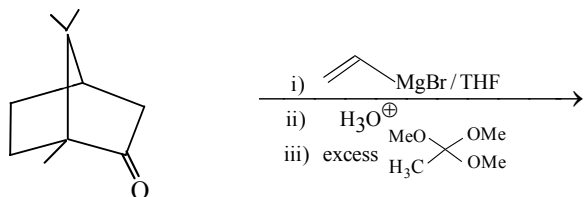[Turn over

Solvent	$k \times 10^5$ (M^{-1} s^{-1})
Isooctane	5.94
CH_3OH	75.50
H_2O	4410
$H_2O/LiCl$	10800
H_2O / guanidinium	4300
H_2O/β -CD	10900

c) Predict the major product in the following reaction.

$$\begin{array}{l} i)\ H_2O \\ ii)\ \Delta \end{array}$$

d) Identify the product formed in the following reaction.

i) allyl-MgBr / THF
ii) $H_3O^\oplus$
iii) excess $MeO \! \! - \! \! C(CH_3) \! \! - \! \! OMe$ (with OMe groups)

e) Show the mechanism of the following transformations.

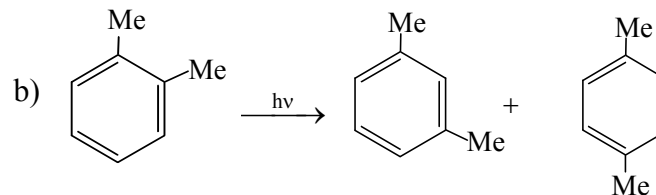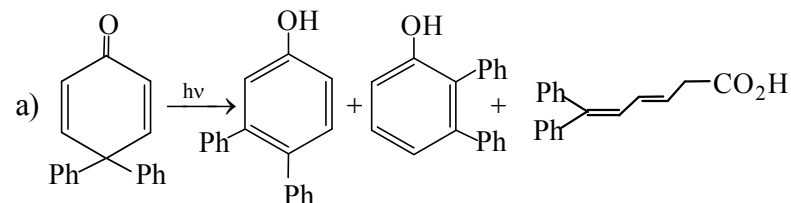CH_3CHO, CSA
EtOH, $78°C$

R=Me

R=CHPh₂
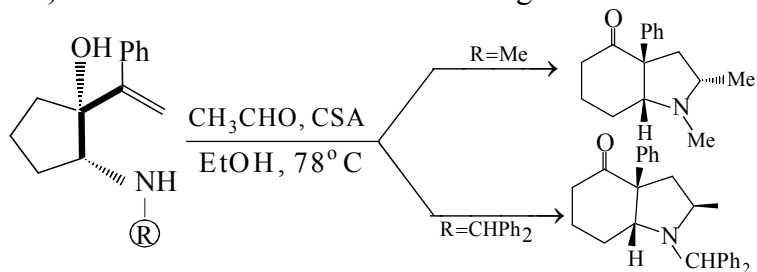
5. Give mechanistic explanation for the following conversion. (Answer *any one*) 3×1

a)

b)

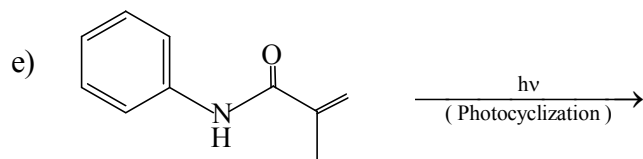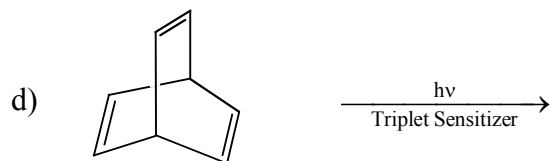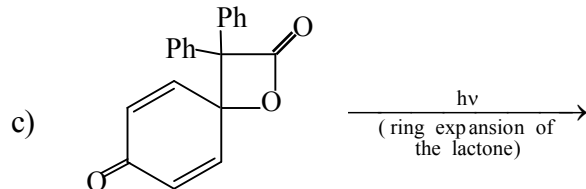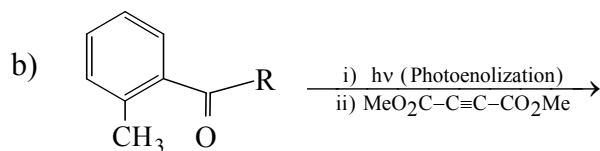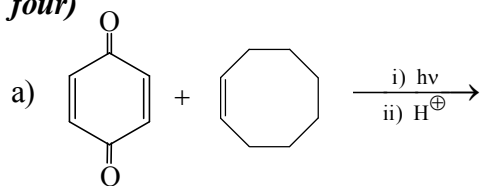6. Prove the following statements with the help of suitable examples (Answer *any two*) : 2×2

a) Paterno- Büchi reaction takes place through diradical intermediate.

b) Barton reaction proceeds *via* a six-membered cyclic transition state.

c) In an enamide compound, [1, 3]-acyl shift occurs through radical mechanism.

UNIT - O-3112

4. Write down the product(s) with mechanism. (*Answer any four*) 2×4

a) + $\xrightarrow[\text{ii) H}^{\oplus}]{\text{i) h}\nu}$

b) $\xrightarrow[\text{ii) MeO}_2\text{C–C}\equiv\text{C–CO}_2\text{Me}]{\text{i) h}\nu \text{ (Photoenolization)}}$

c) $\xrightarrow[\substack{(\text{ring expansion of}\\ \text{the lactone})}]{\text{h}\nu}$

d) $\xrightarrow[\text{Triplet Sensitizer}]{\text{h}\nu}$

e) $\xrightarrow[(\text{Photocyclization})]{\text{h}\nu}$

f) Predict the major product formed in the following reaction
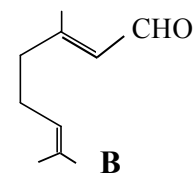
 $+$ $\xrightarrow{\Delta}$

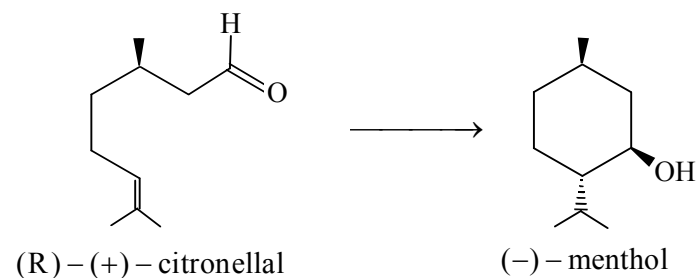3. Answer *any two* of the following questions : $2\frac{1}{2}$×2

a) Synthesize the drug molecule Zwiebelane from the following molecule **A** present in onion.

A Zwiebelane
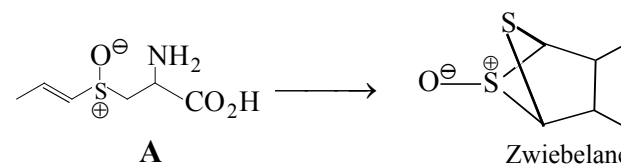
b) Synthesize the compound **B** from suitable starting materials using pericyclic chemistry.

B

c) Synthesize (–) – menthol from (R)-(+)-citronellal using ene reaction.

(R) – (+) – citronellal (–) – menthol

[Turn over