

M. Sc. CHEMISTRY EXAMINATION, 2018

(3rd Semester)

ORGANIC CHEMISTRY SPECIAL**PAPER XI - O**

Time : Two hours

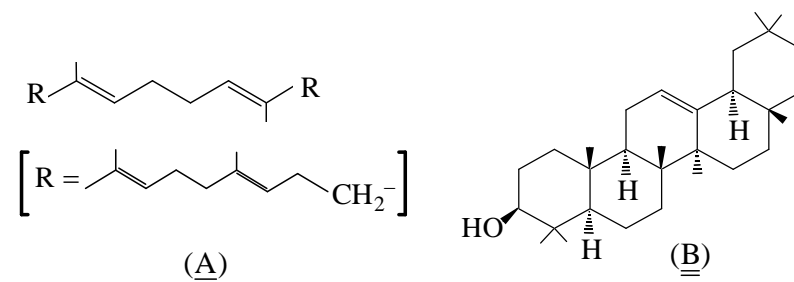
Full Marks : 50

(25 marks for each unit)

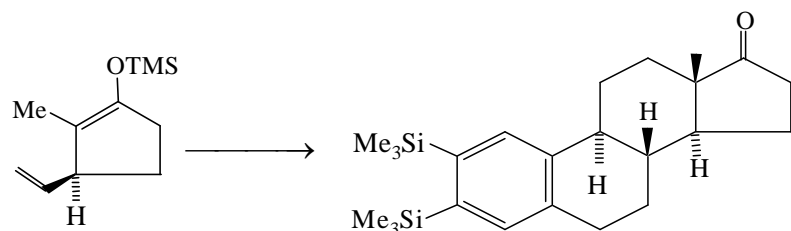
Use a separate answerscript for each unit.

UNIT - O-3111

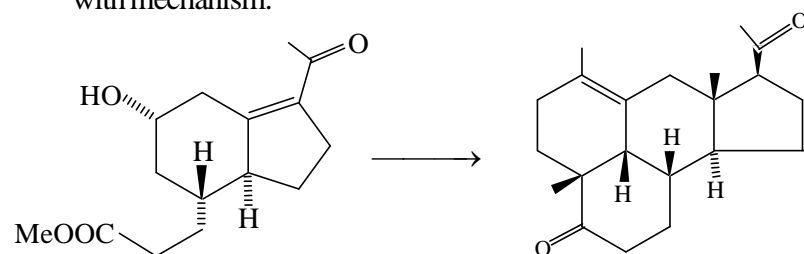
1. Delineate the biosynthetic routes for formation of *any three* of the following compounds : 3×3

a) Squalene (A) from IPP and DMAPP.b) β -Amyrin (B) from squalene.c) Loganin (C) from R-mevalonic acid.d) Azmalicine (D) from tryptamine and secologanin (E).e) Cholesterol (F) from lanosterol (G)CH₂⁻

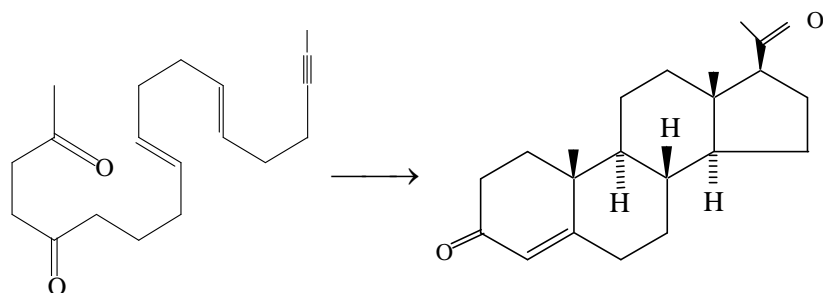
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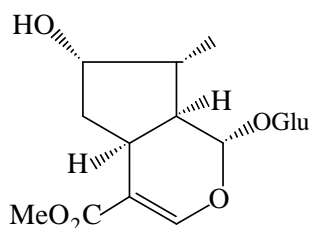
- b) Delineate synthetic route for the following conversion. Explain with mechanism.



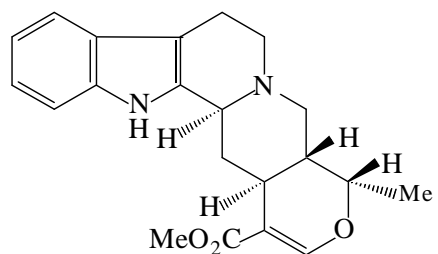
- c) How do you carry out the following conversion in the total synthesis of (\pm) Progesterone. Explain with mechanism.



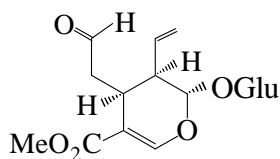
[2]



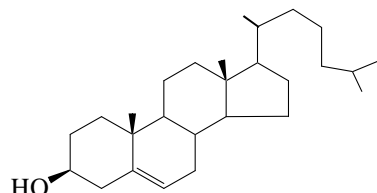
(C)



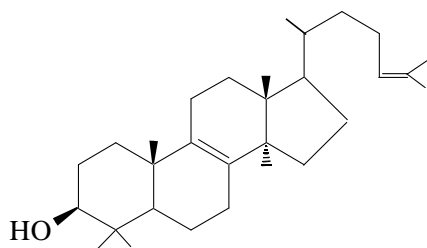
(D)



(E)



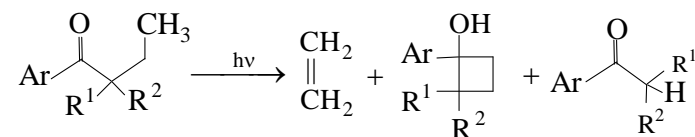
(F)



(G)

[7]

4. a) Explain the variation of the percentage of cyclised product with the nature of the substituents generated in the following reaction. 2 $\frac{1}{2}$

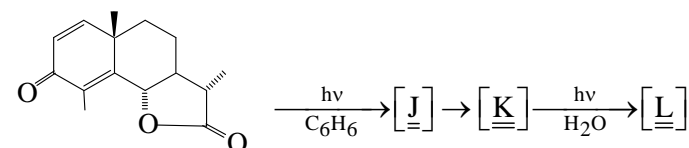


$$R^1 = R^2 = H \text{ } 10\%$$

$$R^1 = H, R^2 = Me \text{ } 29\%$$

$$R^1 = R^2 = Me \text{ } 89\%$$

- b) Identify the structures of [J], [K] and [L] in the following photochemical reactions. Explain with mechanism. 3



- c) 1 $\frac{1}{2}$

Predict the product and explain with mechanism.

5. Answer **any two** of the following questions : 4x2
- a) Discuss the synthetic steps to accomplish the following conversion in the total synthesis of (\pm) oestrone.

[4]

b) Attempt **any four** of the following questions : 2×4

- Develop a state correlation diagram for the photochemical electrocyclic reaction of butadiene.
- Outline a synthesis of basketene (C₁₀H₁₀) from two common starting materials and by proper use of pericyclic reactions.
- Comment on the site selectivity of the thermal dimerisation of E-hexatriene. The HOMO and LUMO coefficients for this compound are as follows :

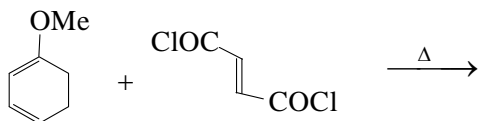
HOMO coefficients :

C-1 (0.521), C-2 (0.232), C-3(-0.418),
C-4(-0.418), C-5(0.232), C-6 (0.521)

LUMO coefficients :

C-1 (0.521), C-2 (-0.232), C-3(-0.418),
C-4 (0.418), C-5(0.232), C-6(-0.521)

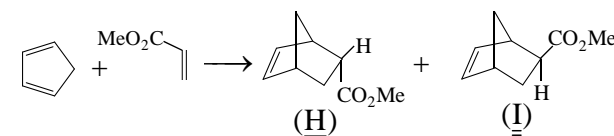
- Write down the structures of the possible products of the following reaction. Identify the major product and give proper explanation for its formation.



- Write down the structure of the dimer of cycloheptatriene formed under thermal condition. Give appropriate mechanism for the transformation.

[5]

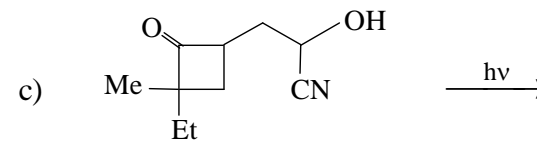
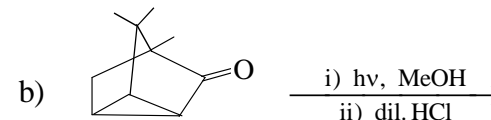
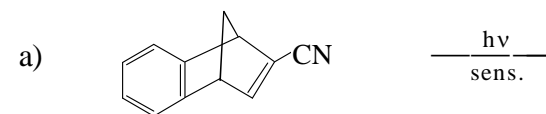
- Give proper explanation for the outcome of the following cycloaddition reaction performed under the specified reaction conditions.



			(H)	(I)
without	AlCl ₃ at 0°C	88	:	12
with	AlCl ₃ at 0°C	96	:	4
with	AlCl ₃ at -80°C	99	:	1

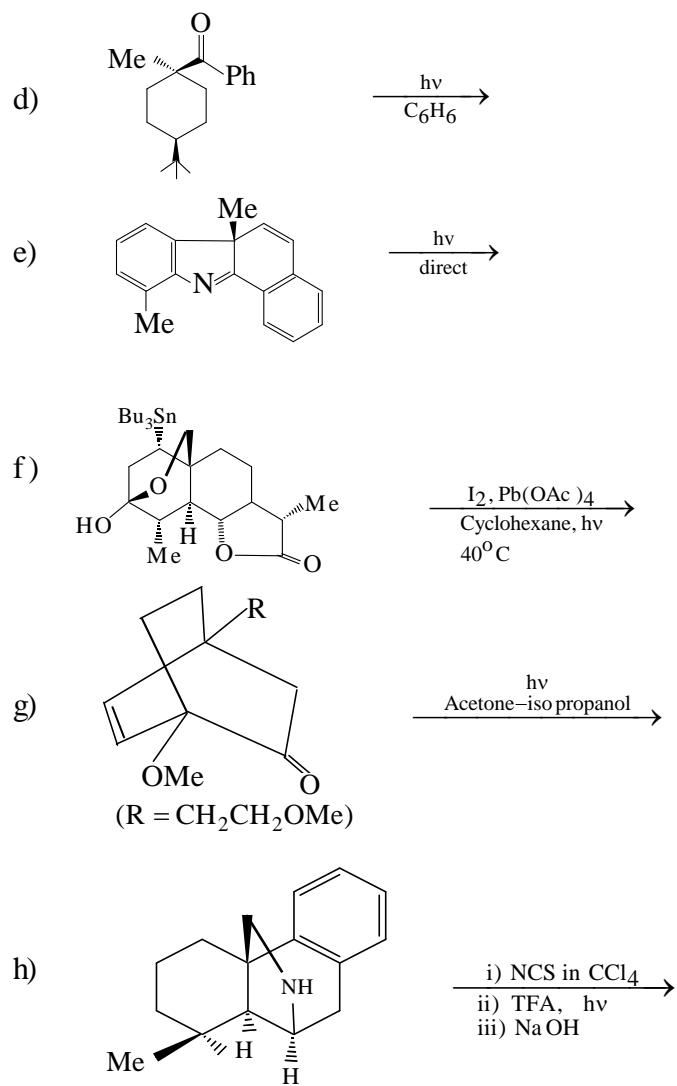
UNIT - O-3112

- Predict the product(s) of the following photochemical **(any five)** 2×5



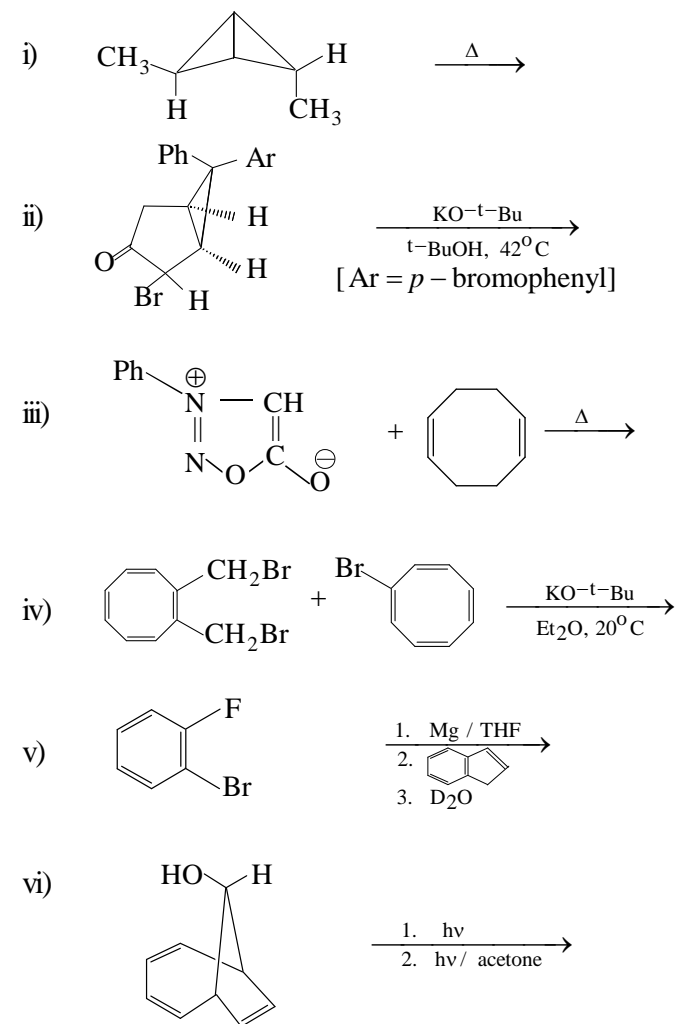
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[6]



[3]

2. a) Predict the products of the following reactions and explain their formation through occurrence of pericyclic processes. (*Attempt any four*) 2×4



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