

M. Sc. CHEMISTRY EXAMINATION, 2017

(3rd Semester)

ORGANIC CHEMISTRY SPECIAL**PAPER - XI-O**

Time : Two hours

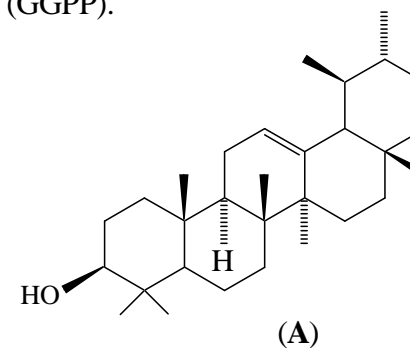
Full Marks : 50

(25 marks for each unit)

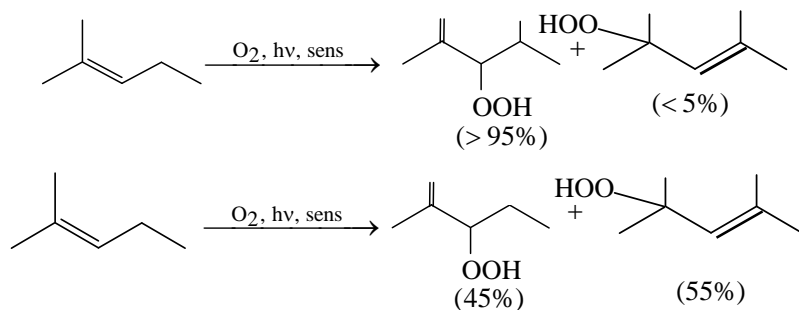
Use a separate answerscript for each unit.

UNIT - O - 3111

1. Delineate the biosynthetic routes for formation of *any three* of the following compounds : 3×3
- α -Amyrin (**A**) from squalene
 - Isopentenyl pyrophosphate (IPP) from 1-deoxy-D-xylulose 5-phosphate (DXP).
 - i) Lanosterol (**B**) from squalene
ii) Secologanin (**C**) from loganin (**D**)
 - Catharanthine (**E**) from tryptamine and secologanin (**C**)
 - Gibberellin – A₃ (**F**) from geranylgeranyl pyrophosphate (GGPP).

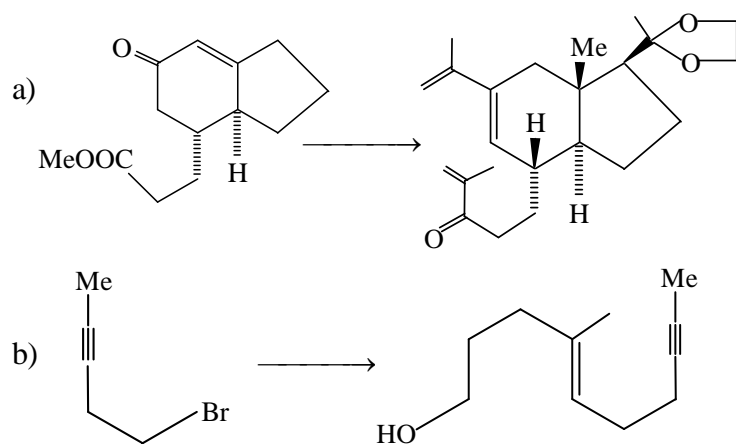


- c) How do you account for the following photochemical reactions ? 3

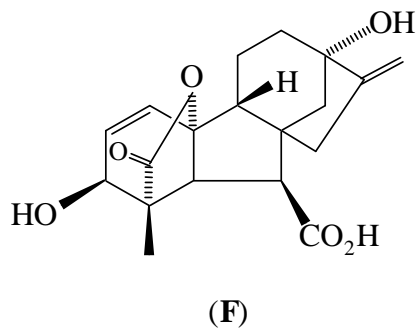
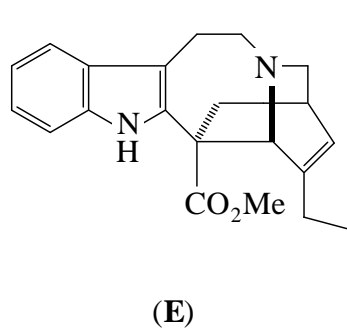
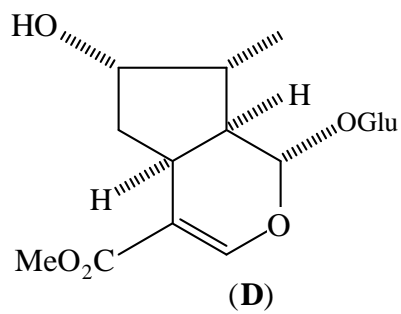
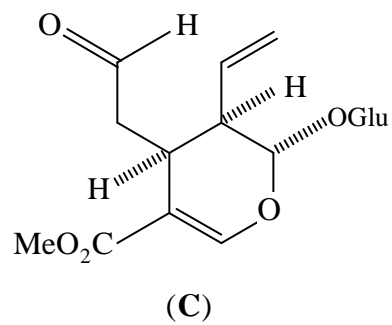
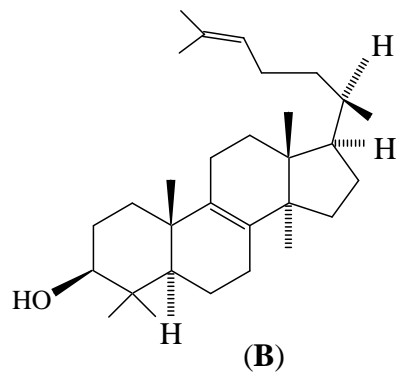


Explain the above apparently anomalous results.

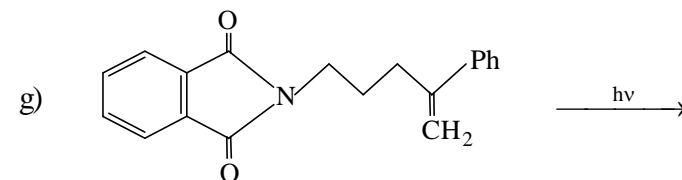
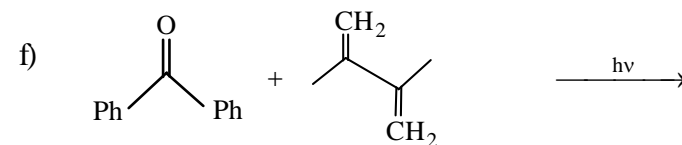
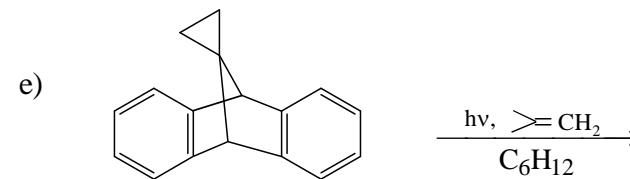
- d) 1, 3, 5-Trimethyl benzene on irradiation with UV-light gives 1, 2, 4-trimethylbenzene. This transformation is due to the 1, 2-alkyl group shift or 1, 3-alkyl group shift. Give mechanism for this transformation. 3
5. Discuss the synthetic steps for the following conversion and explain with mechanism. 4+3



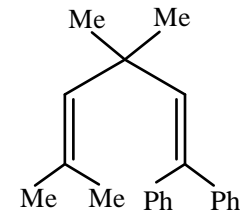
[2]



[7]



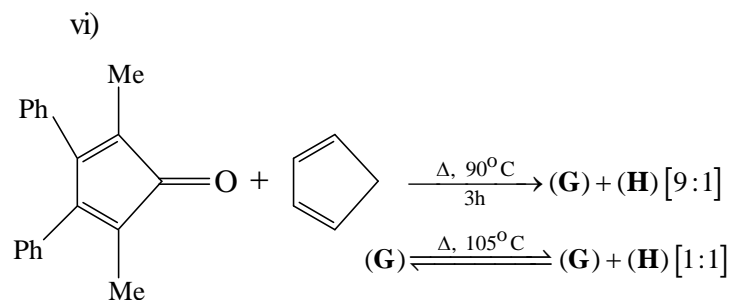
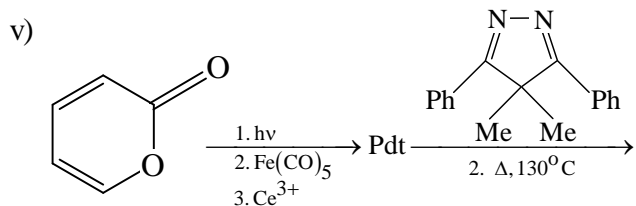
4. a) Explain why the following compound upon di-*f*-methane rearrangement gives just only one product out of two possibilities. 2



- b) Norbornene gives only norbornene dimer in the presence of acetone but in the presence of benzophenone gives different product. Explain. 2

[Turn over

[4]

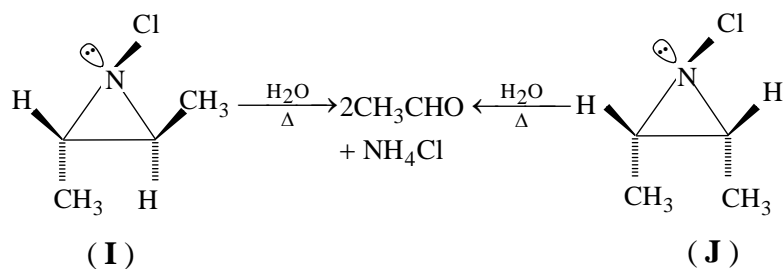


b) Attempt *any two* of the following questions : 4×2

i) A) Develop a state correlation diagram for the thermal electrocyclic reaction of butadiene.

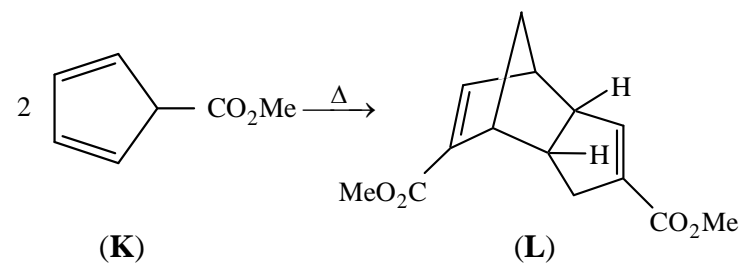
B) How would you synthesize basketene starting from cyclooctatetraene ? 2+2

ii) A) Comment on the relative rates of hydrolysis of **(I)** and **(J)**.

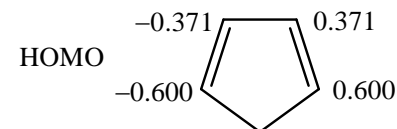
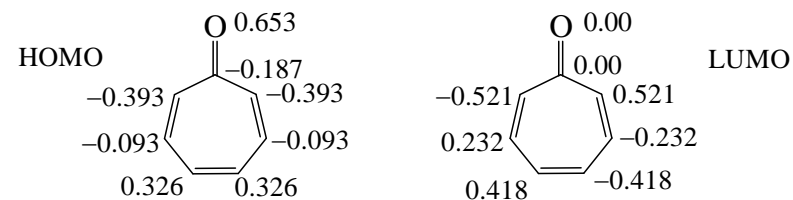


[5]

B) Explain why thermal dimerisation of the ester **(K)** gives Thiele's ester **(L)** as the major product.

 $1\frac{1}{2} + 2\frac{1}{2}$


iii) The frontier orbital coefficients of HOMO and LUMO of tropone and HOMO of cyclopentadiene are shown below :



Comment on the (i) regioselectivity of the [4+2] cycloaddition reaction of tropone with each of styrene and acrylonitrile and (ii) periselectivity of the cycloaddition reaction of tropone and cyclopentadiene.

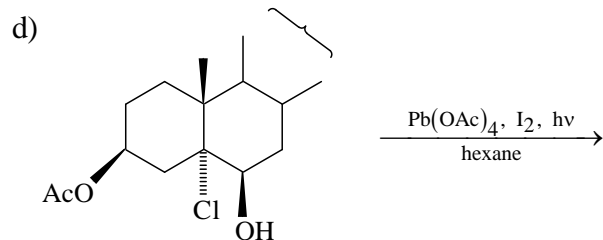
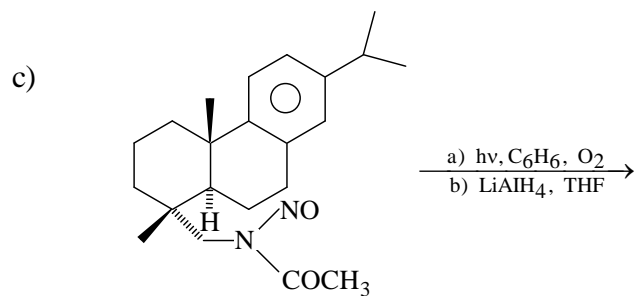
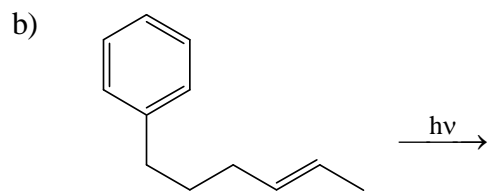
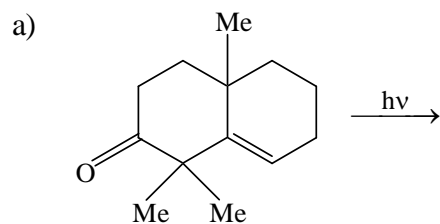
 $2\frac{1}{2} + 1\frac{1}{2}$

[Turn over

[6]

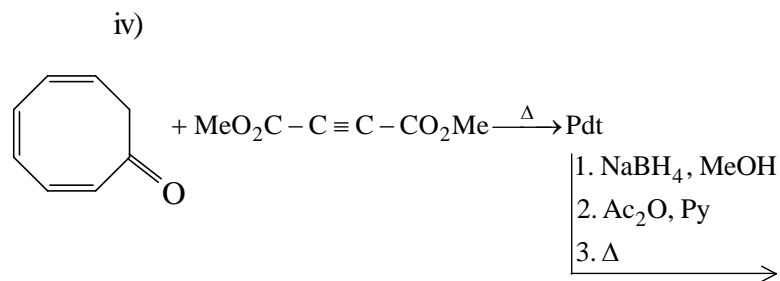
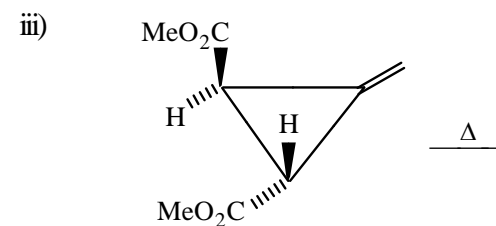
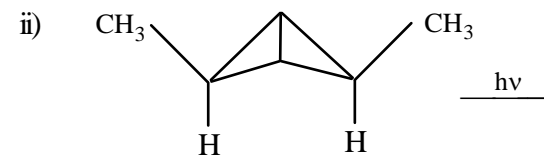
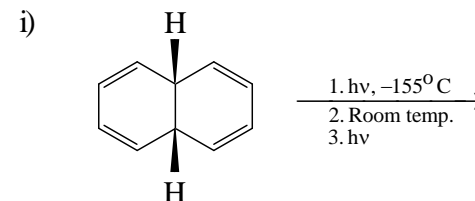
UNIT - O - 3112

3. Write the product(s) of the following photo chemical reactions and explain with appropriate mechanism in each case (*any four*): 2×4



[3]

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



[Turn over