Modern Aspects of Organic Chemistry

22CMC001

Semester 1 2022/23 Online Long-window Exam paper

This is an online long-window examination, meaning you have **23 hours** in which to complete and submit this paper. How you manage your time within the 23-hour window is up to you, but we expect you should only need to spend approximately **3 hours** working on it. If you have extra time or rest breaks as part of a Reasonable Adjustment, you will need to add this to the amount of time you are expected to spend on the paper.

It is your responsibility to submit your work by the deadline for this examination. You must make sure you leave yourself enough time to do so.

It is also your responsibility to check that you have submitted the correct file.

Exam Help

If you are experiencing difficulties in accessing or uploading files during the exam period, you should contact the Exam Helpline. For urgent queries please call **01509 222900**.

For other queries email examhelp@lboro.ac.uk

Where a question involves drawing molecular reaction schemes or mechanisms, you must include a detailed commentary explaining each step of the transformation. If a diagram is required, this must be hand drawn rather than copied and pasted from another source.

Answer **ALL** questions

1. Answer **ALL** parts

(a) Identify the major product expected, or intermediate formed (**A-E**), in each of the following pericyclic transformations. Give an 'arrow pushing' mechanism for each reaction involved (analysis of the molecular orbitals is NOT required).

[3]

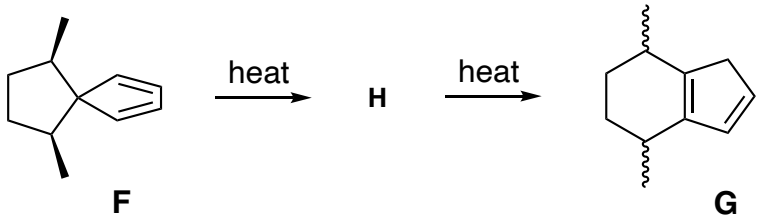
[3]

[3]

[3]

[3]

(b) The spirocyclic pentadiene derivative **F** shown below is converted stereospecifically into compound **G** on heating. The transformation involves *two* consecutive pericyclic reactions of the same type, and proceeds via compound **H** which is not isolated.



i) Identify the type of pericyclic reaction occurring, and determine the structure of compound **H**. [2]

ii) Draw 'arrow pushing' mechanisms to show how **H** is formed from **F** and then further converted into the diene product **G**. [2]

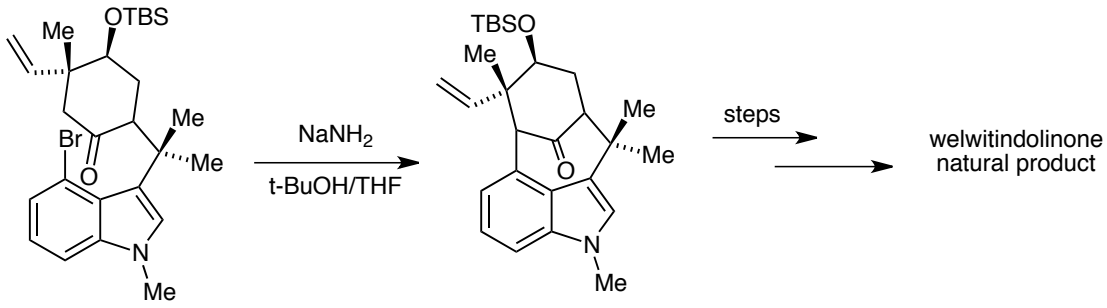
iii) Using the Frontier Molecular Orbital (FMO) approach sketch the orbitals involved in the conversion of **F** to **H** to show it is a thermally allowed process. [4]

iv) Assign the relative stereochemistry of the methyl substituents in diene **G** based on your FMO analysis. [1]

v) Comment on the thermodynamic factor driving the conversion of intermediate **H** to compound **G**. [1]

2. Answer **ALL** parts

a) The key step in the synthesis of a welwitindoline natural product used an aryne reactive intermediate to form compound **I**.

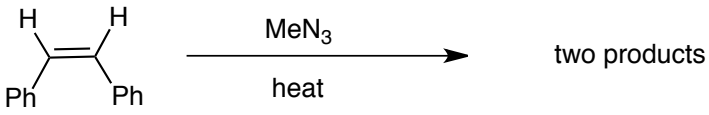


I

i) Provide a suitable mechanism for this key transformation [5]

ii) How could you prove that an aryne intermediate is formed under these reaction conditions. [5]

b) Nitrenes are also a class of reactive intermediates. In the reaction below the (*Z*)-alkene **J** is treated with methylazide and under heating affords two products.



J

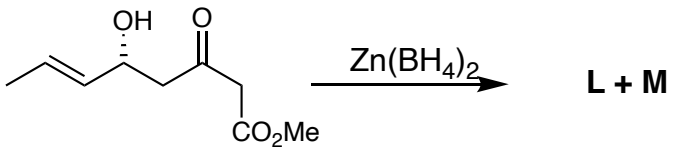
i) Identify each product and provide a mechanism for their formation [9]

ii) What type of nitrene must be in operation for these two products to occur? [2]

iii) Write out the structure of singlet and triplet nitrenes derived from MeN_3 [4]

3. Answer **ALL** parts

a) Compound **K** was treated with $Zn(BH_4)_3$ to afford two products **L** & **M**.



K

i) Draw the two isomers **L** and **M** produced in the reaction above. [2]

ii) One isomer is formed in preference to the other explain why? Use a full mechanism to illustrate your answer. [8]

iii) Define the term diastereomeric excess (de) and explain how you could determine the de of the reaction above. [3]

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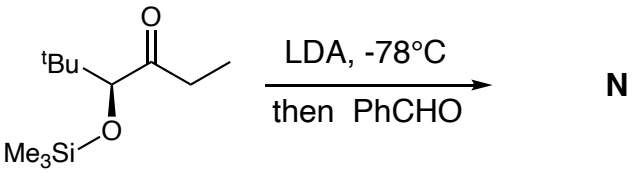
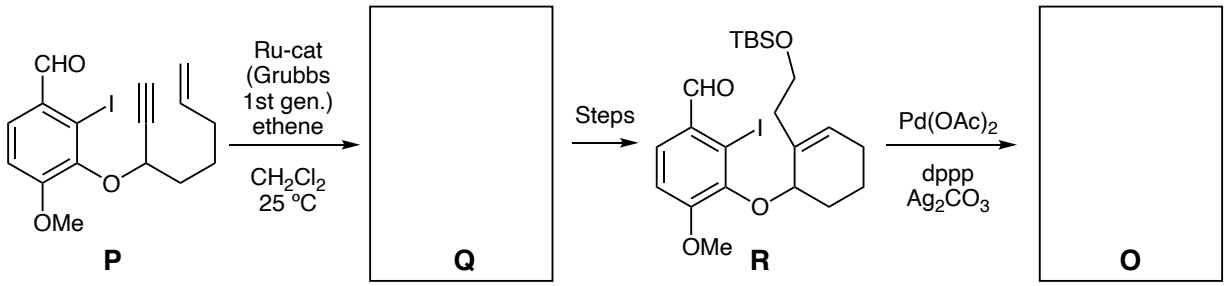
b) Explain the diastereoselective outcome of the reaction below, give a full mechanism, predict the major diastereoisomer of the reaction and explain why it is the major product **N** formed.



[12]

4. Answer **ALL** parts

The following scheme describes the synthesis of **O** from an acyclic precursor **P**. This is accomplished using two well-known organometallic transformations.



a) Predict the structure of product **Q**. [2]

b) Provide a detailed mechanism for the formation of **Q** [9]

c) For the conversion of **R** to **O**, predict the structure of product **O** including a justification of the relative stereochemistry. [10]

d) How would you synthesise enantiopure **O**? [4]