Loughborough University

Modern Aspects of Organic Chemistry

21CMC001

Semester 1 2021/2022 (1a) Exam paper

This is a (1a) online 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

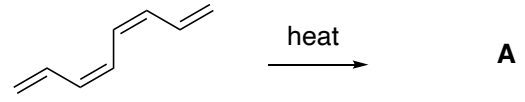
If you are experiencing difficulties in accessing or uploading files during the exam period you should contact the exam helpdesk. For urgent queries please call **01509 222900**.
For other queries email examhelp@lboro.ac.uk

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.

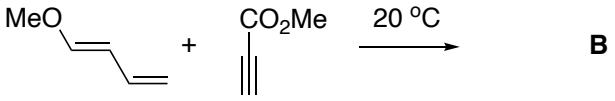
Answer **ALL** questions

1. Answer **ALL** parts

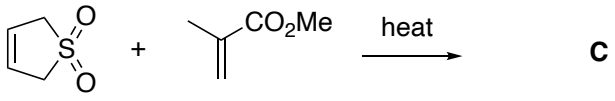
(a) Identify the products (**A-E**) formed in each of the following pericyclic reactions. Mechanisms are not required.



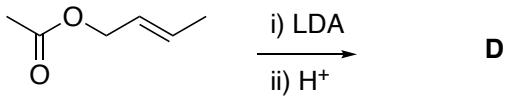
A [2]



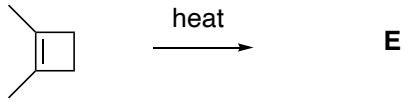
B [2]



C [2]

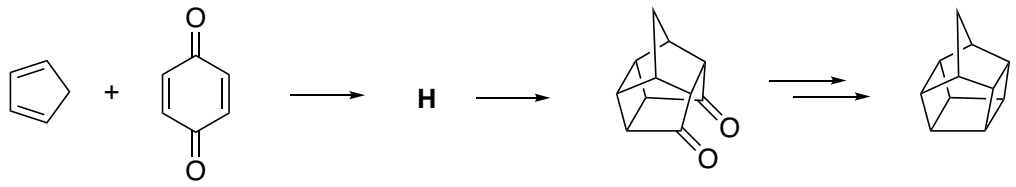


D [2]



E [2]

(b) The diketone **F** has been investigated as a precursor to the cage hydrocarbon homo-5-prismane **G**. The synthesis of **F** involves two pericyclic reactions as outlined below.



I **J** **F** **G**

i) Identify compound **H** formed on treating cyclopentadiene **I** with benzoquinone **J**. What type of pericyclic reaction is involved? [3]

ii) Draw a transition state for the reaction of **I** and **J** using Frontier Molecular Orbital (FMO) theory to account for the product formed. [4]

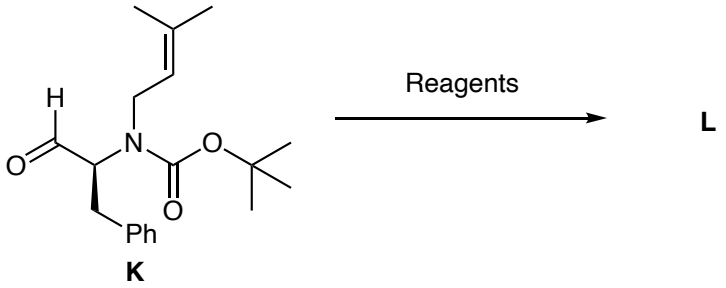
iii) Comment on the stereochemical outcome of this reaction, and account for the formation of the particular stereoisomer of the product you show. [2]

iv) Suggest reaction conditions to convert **H** into the diketone **F**. What type of pericyclic reaction is required and why? [3]

v) Use FMO theory to explain mechanistically how this product is formed. [3]

2. Answer **ALL** parts

When the substrate **K** is treated with reagents that induce a radical reaction **L** is afforded as the major product.



K

(a) What is the structure of **L** and what reagents are required for the radical reaction to proceed? [2]

(b) What is the mechanism for the formation of **L**? [5]

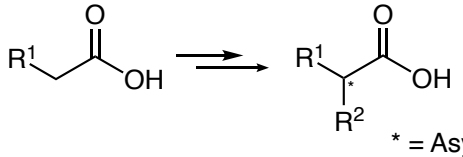
(c) According to Baldwin's guidelines what type of cyclisation reaction is this? [1]

(d) Predict the stereochemistry of major product **L** and explain your reasoning. [12]

(e) How could you alter the structure of **K** to confirm that the reaction is proceeding through a radical reactive intermediate? [5]

3. Answer **ALL** parts

(a) Using an oxazolidinone (Evans') auxiliary, describe how you could achieve the following stereoselective transformation. Your answer should include your choice of R groups and all details related to how the chiral auxiliary operates. [10]

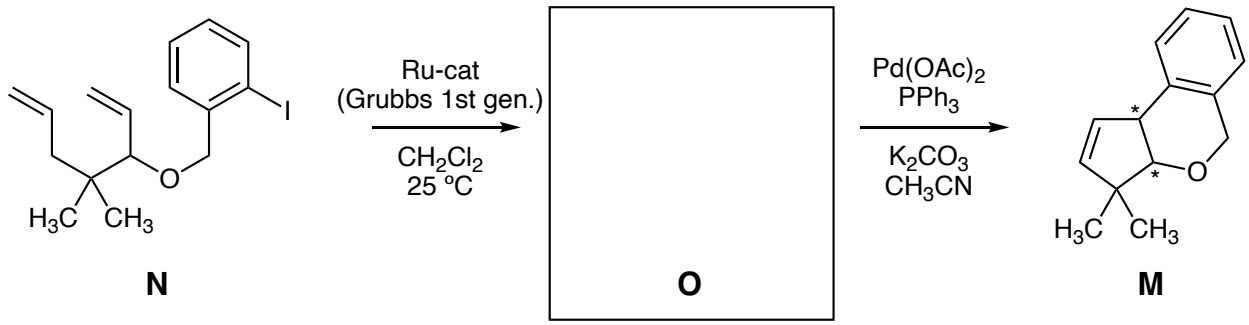


(b) Explain how epoxidation of alkenes can be controlled in both a diastereoselective manner, and in an enantioselective manner. You should include examples of both, with full mechanistic rationale to explain your answer. [10]

(c) Describe two different methods through which enantiomeric excess can be determined. Give at least one example of each of your chosen methods to illustrate your answer. [5]

4. Answer **ALL** parts

Product **M** can be synthesised from **N**, via **O**, using two organometallic transformations. (The relative stereochemistry of the product **M** has been left undefined).



N **O** **M**

(a) Predict the structure of **O**. [2]

(b) Provide a detailed mechanism for the formation of **O**. [9]

(c) Predict the relative stereochemistry of **M** and justify your choice. [11]

(d) How would you synthesise enantiopure **M**? [3]

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