

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2002

FINAL EXAMINATION FOR THE DEGREE OF B.Sc. HONOURS

CHEMISTRY (CH401)

CHEMISTRY AND APPLIED CHEMISTRY (DENOMINATED) (CH401)

THIRD PAPER: ORGANIC CHEMISTRY

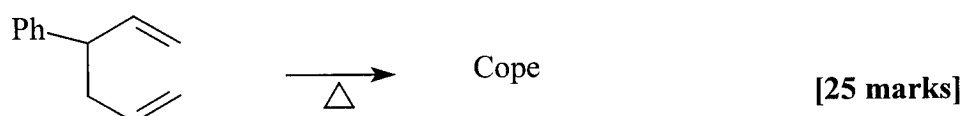
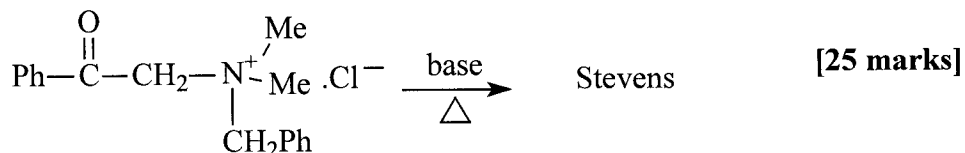
**Professor I. Fleming, FRS
Professor R.N. Butler
and Internal Examiners**

**Time Allowed: Three Hours
Answer five questions**

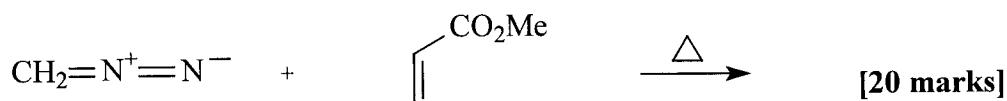
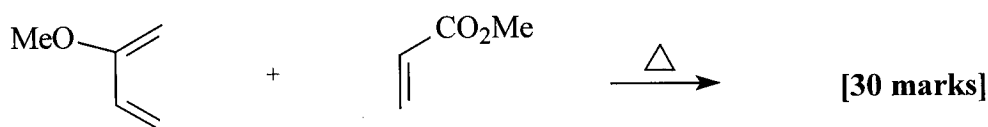
All questions carry 100 marks distributed as shown where appropriate. Leave the first page of the answer book blank and list on it clearly the number of the questions attempted.

1. **Answer (i) and (ii):**

- (i) Compare and contrast the mechanisms of the following reactions and comment on the evidence for them.

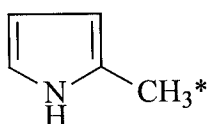


- (ii) Complete the following Diels-Alder and 1,3-dipolar cycloaddition reactions and explain their mechanisms and regiochemistry:



2. **Answer each of the following:**

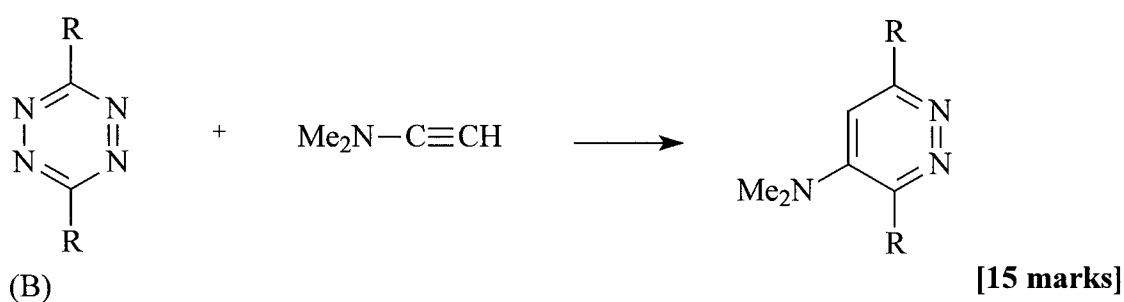
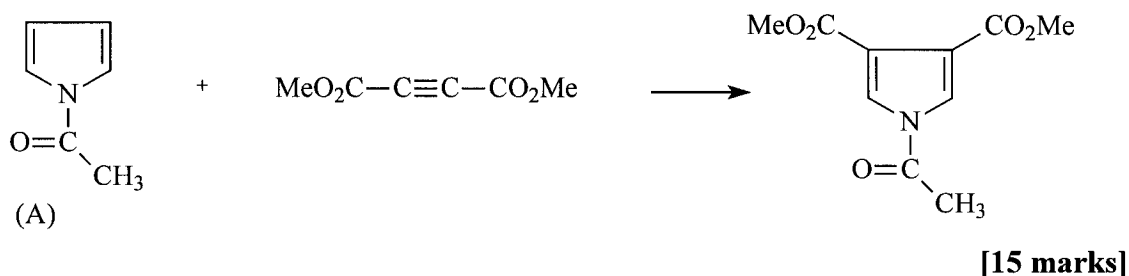
- (i) Compare and contrast the E1 and E1cb mechanisms in the 1,2-elimination reactions of alkyl halides and briefly summarise the experimental evidence on which they are based. [20 marks]
- (ii) Suggest and explain a degradation process for the following molecule which would allow the isolation of the labeled carbon atom.



[20 marks]

(iii) Briefly discuss the relative aromaticities of the molecules pyrrole, furan and thiophene. **[30 marks]**

(iv) Suggest mechanisms for the following reactions of the molecules (A) and (B)



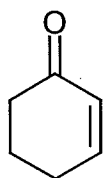
3. Answer each of the following:

(i) Dimethylcopper lithium (Me_2CuLi) is probably the most widely used organocopper reagent in organic synthesis.

(a) Show how this reagent may be prepared from iodomethane and any inorganic reagents necessary **[10 marks]**

(b) What experimental precautions would need to be observed for the production of dimethylcopper lithium? **[8.33 marks]**

(c) Draw and account for the product formed if 2-cyclohexen-1-one (see below) were treated initially with dimethylcopper lithium, followed by addition of benzyl bromide and standard aqueous work-up? **[15 marks]**



2-cyclohexen-1-one

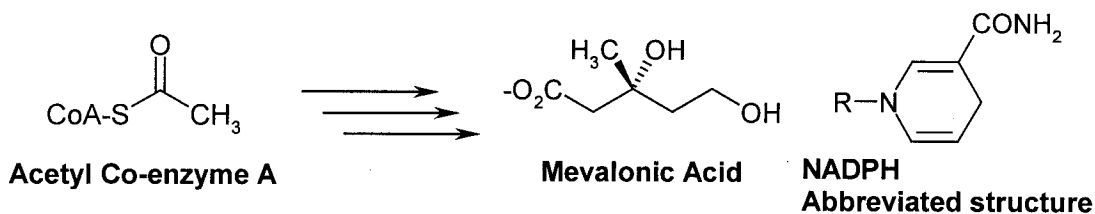
(ii) Mevalonic acid is bio-synthesised from three building blocks of acetyl co-enzyme A (see below). Show the details of this biosynthesis with reference to the following transformations.

(a) Coupling of two molecules of acetyl co-enzyme [9 marks]

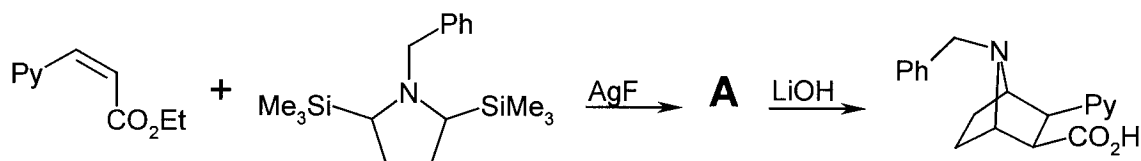
(b) Addition of the third molecule of acetyl co-enzyme A [9 marks]

(c) Selective hydrolysis [6.33 marks]

(d) Reduction by NADPH [9 marks]



(iii) Pandey *et al* constructed the 7-azabicyclo[2.2.1]heptane core of the potent analgesic epibatidine according to the outline scheme below.

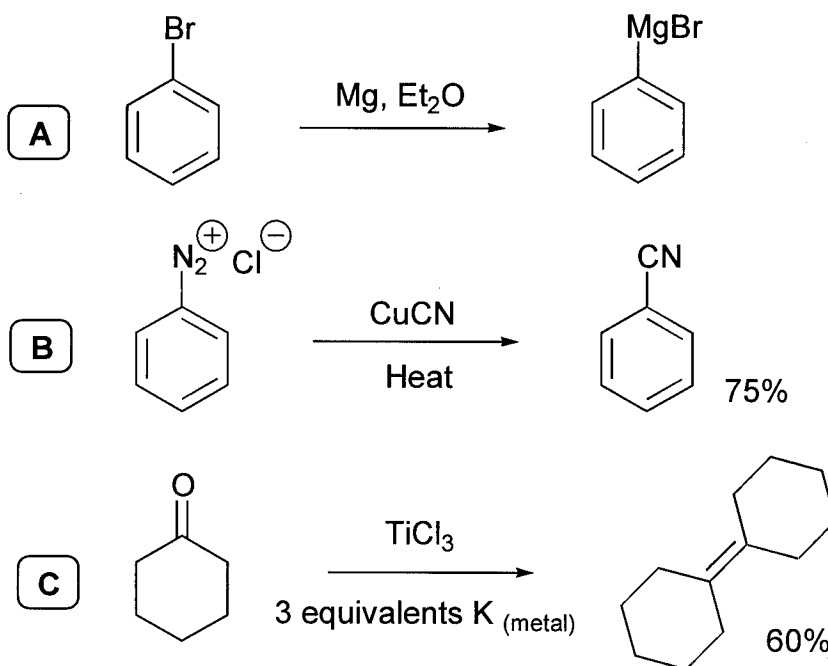


(a) Deduce the structure of **A** [10 Marks]

(b) Describe in full mechanistic detail formation of the reactive intermediate produced during reaction giving **A** [18.33 Marks]

(c) How might the racemic epibatidine formed via this route be resolved? [5 Marks]

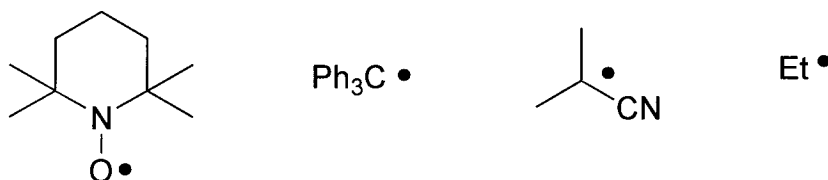
4. Answer each of the following:



(i) Draw radical mechanisms to rationalise **reactions A-C**.

[50 Marks]

(ii) Predict the half-lives and reactivity of the following radicals. Explain your answers in terms of kinetic and thermodynamic stability. Draw resonance structures where possible. Why is the ethyl radical the most reactive towards acrylonitrile ($\text{CH}_2=\text{CHCN}$)?



[50 Marks]

5. Answer each of the following:

- (i) The use of phase transfer (PT) methods has resulted in many improvements in organic reactions in relation to:
- yields obtained
 - shorter reaction times
 - product control and
 - trapping of transient intermediates.
- Cite and illustrate two or three examples in each case of such improvements.

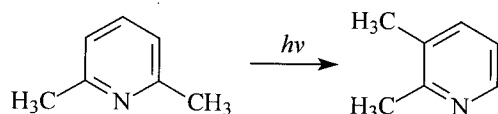
[60 marks]

- (ii) Show how in industry PT procedures have proved to be of considerable importance.

[40 marks]

6. Discuss the photochemistry of simple aromatic systems under the following headings:
- (a) cycloaddition reactions [35 marks]
 - (b) rearrangement reactions [35 marks]

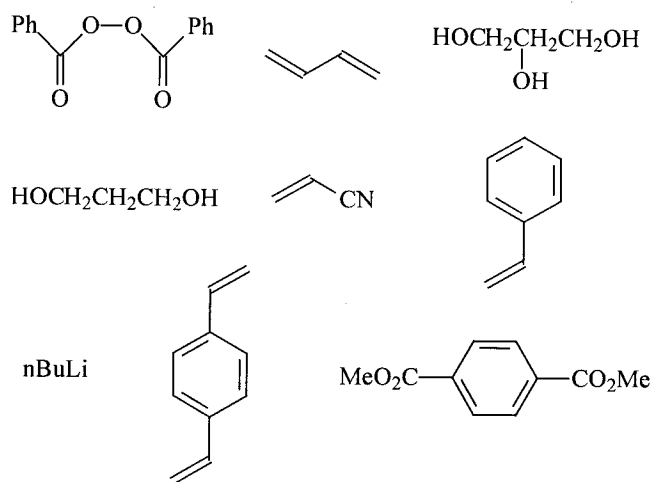
Provide a simple mechanism for the following transformation which involves a prismane type intermediate:



[30 marks]

7. **Answer each of the following:**

- (i) Write notes on the chemistry of each of the following:
 - (a) polyurethanes [35 marks]
 - (b) biodegradable polymers [35 marks]
- (ii) Show how the following polymers could be prepared using an appropriate combination of some of the molecules whose structures are provided below:
 - (a) a non-crosslinked polymer formed by chain-growth (addition) anionic polymerization. [10 marks]
 - (b) a polyester with a small amount of cross-linking [10 marks]
 - (c) a chain-growth (addition) co-polymer, with a small amount of crosslinking, formed by radical polymerization [10 marks]



8. **Answer each of the following:**

- (a) Draw the structure of β -D-Glcp. [10 marks]
- (b) Draw the structure of lactose. [20 marks]
- (c) Compare and contrast the structures of cellulose and starch. [50 marks]
- (d) Discuss briefly the synthesis and properties of *any two* industrially important derivatives of cellulose [20 marks]