

SECOND PUBLIC EXAMINATION
Honour School of Chemistry

ORGANIC CHEMISTRY IB – SAMPLE PAPER 1 (2012)

Candidates should answer *FOUR* questions.

Time Allowed: 2.5h

Please begin your answer to each question in a new booklet.

The numbers in square brackets on the right of the pages indicate the approximate marks the examiners intend to assign to each part of the question.

The following abbreviations are used:

Me = CH₃

s-Bu = CH₃CH₂CH(CH₃)

Ph = C₆H₅

Ac = CH₃C(O)

MCPBA = *m*-ClC₆H₄CO₃H

Et = CH₃CH₂

t-Bu = (CH₃)₃C

Bn = CH₂C₆H₅

Ts = CH₃C₆H₄SO₂

py = C₅H₅N

Pr = CH₃CH₂CH₂

Hex = C₆H₁₃

DMF = Me₂NCHO

Tf = CF₃SO₂

Acidic, basic or aqueous work-up conditions are assumed, with concomitant protonation or deprotonation of charged intermediates. Assume reactions are carried out at room temperature, unless otherwise indicated. Structural formulae depicting chiral molecules refer to racemic mixtures unless a single enantiomer is explicitly specified.

Guide to Questions

1. Aromatic and Heterocyclic Chemistry

2. Heteroatom Chemistry

3. Synthesis

4. Biological chemistry

5. Conformation and Stereoselectivity

6. Spectroscopy

Do not turn over the page until told you may do so.

This is a mock exam paper, designed to illustrate the possible *style* of questions for Part 1B 2012, but not necessarily the exact content. The titles in the Guide to Questions will not necessarily be conserved from one year to the next.

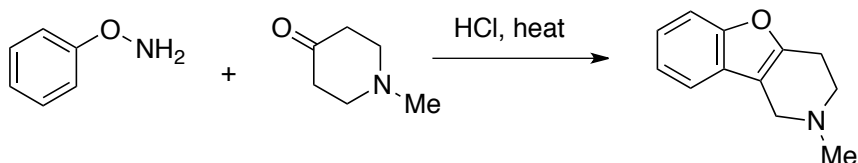
1. Answer **both** Parts A and B.

Part A

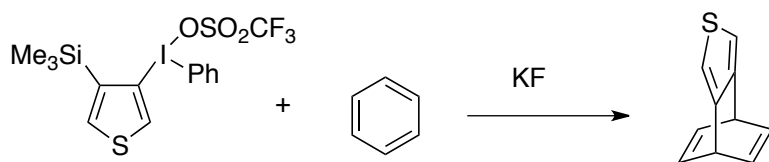
Provide mechanisms for **four** of the following reactions.

[4 × 4]

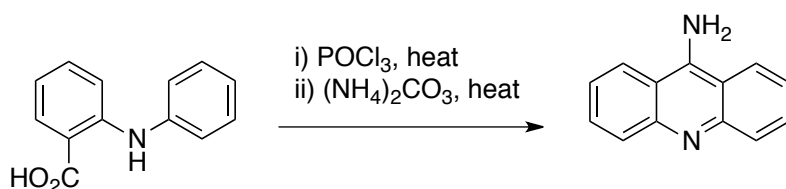
a)



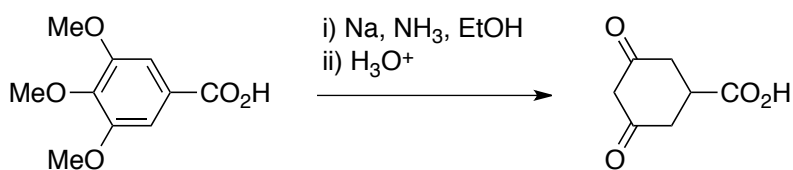
b)



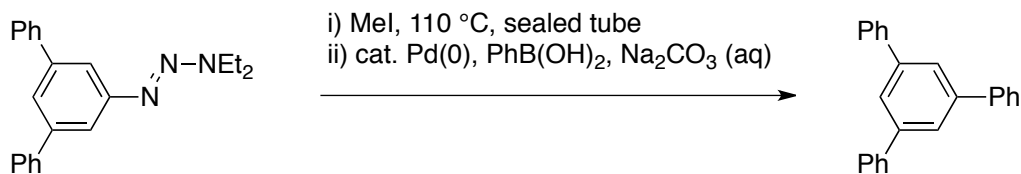
c)



d)



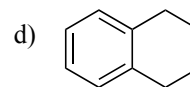
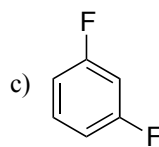
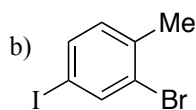
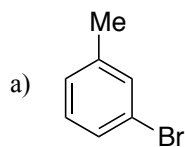
e)



Part B

Suggest a synthesis for **three** of the following, starting from either benzene or toluene (mechanisms are not required).

[3 × 3]

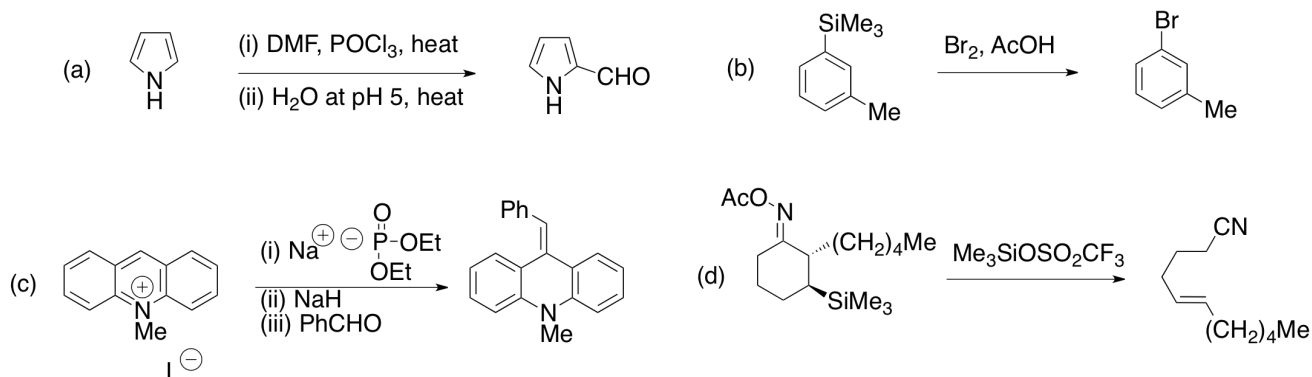


2. Answer Parts A, B and C.

Part A.

Provide a mechanism which accounts for the product formation for *three* of the following.

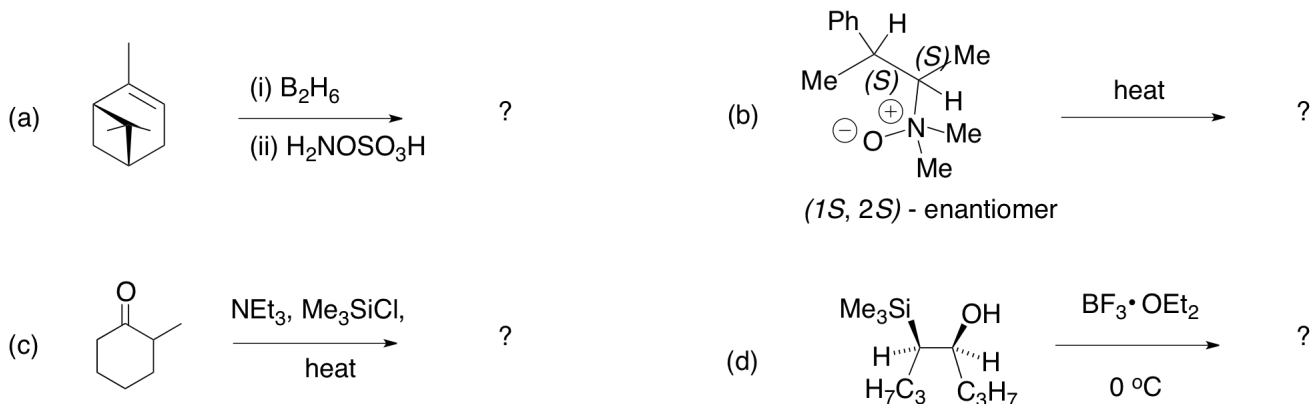
[3 × 3]



Part B.

Identify the product, and provide a mechanism which accounts for its formation, for *three* of the following.

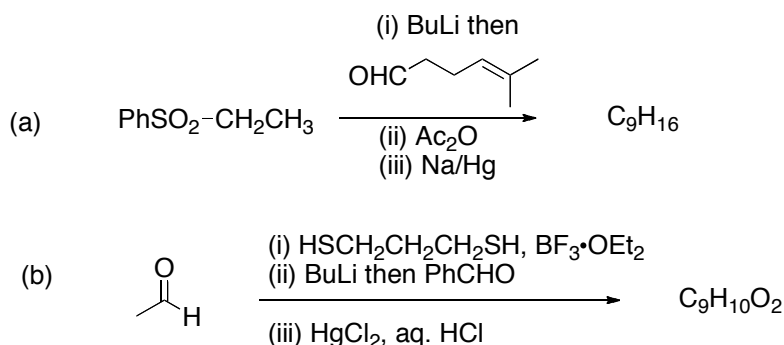
[3 × 4]



Part C.

Provide an explanation for *one* of the following, making specific reference to the roles played by participating heteroatoms.

[4]



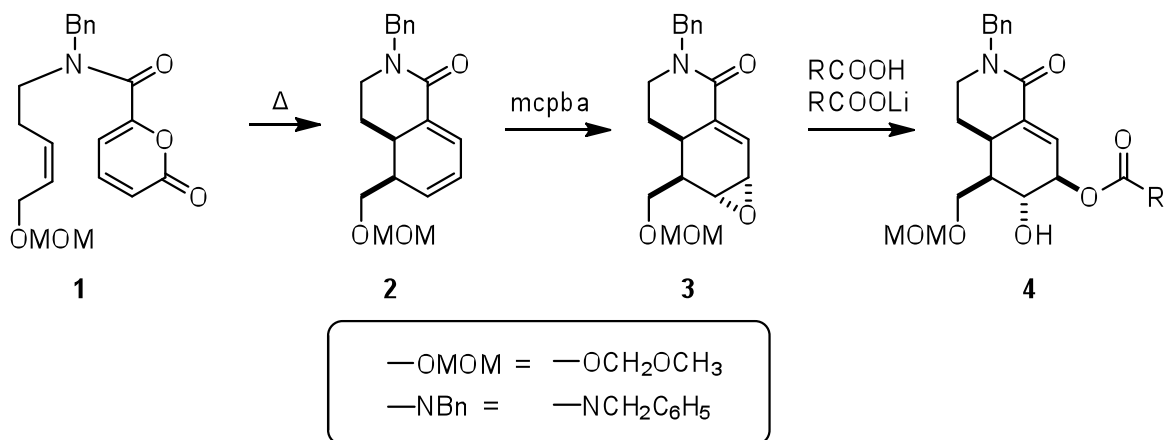
TURN OVER

3. Answer both Parts A and B.

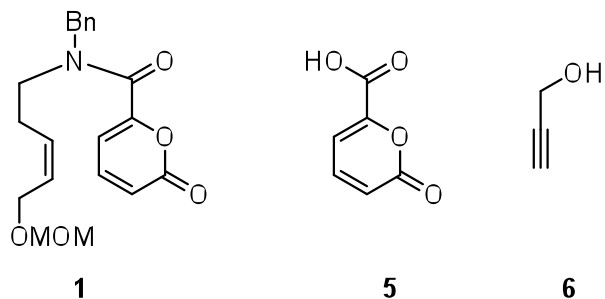
Part A

[13 marks]

The following sequence is taken from a recent synthesis of reserpine: answer the following questions.



- (i) Describe a mechanism that explains the transformation of **1**→**2**.
- (ii) Explain the regio- and stereoselectivity displayed in the conversion of **2** into **3**.
- (iii) Draw a mechanism for the conversion of **3** into **4**.
- (iv) How would you deprotect the OMOM group and (separately) the N-Bn group from **4**? What problems might you encounter with standard reagents?
- (v) Devise a synthesis of compound **1**. You may use **5** and **6** as starting materials if you wish.

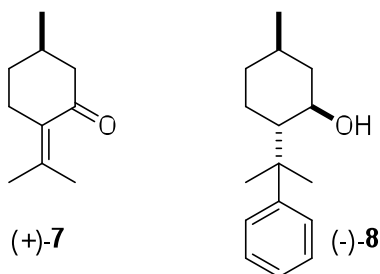


QUESTION CONTINUES

Part B.

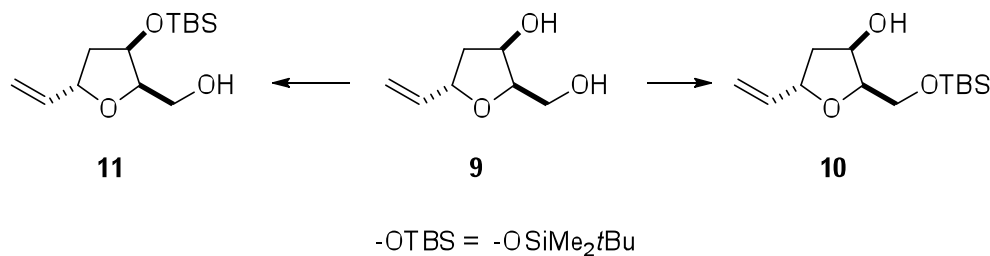
[12 marks]

(i) (-)-8-Phenylmenthol (**8**) is a valuable organic compound that is made from (+)-pulegone (**7**). How might you accomplish this transformation (more than one step is required). Discuss your tactics for controlling the stereochemistry in the product.



(ii) Assign each stereogenic centre in (+)-**7** and (-)-**8** according to the Cahn-Ingold-Prelog rules.

(iii) Describe how you would convert **9** into **10** and also into **11**. More than one step may be required.



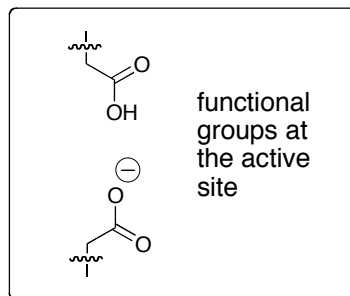
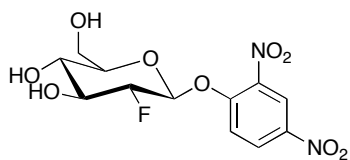
END OF QUESTION

TURN OVER

Part B

Suggest a mechanism of action for the compound shown below, which is an irreversible inhibitor of retaining glycosidases and briefly indicate how it might be used to probe for unidentified glycosidases in cell extracts.

[5]



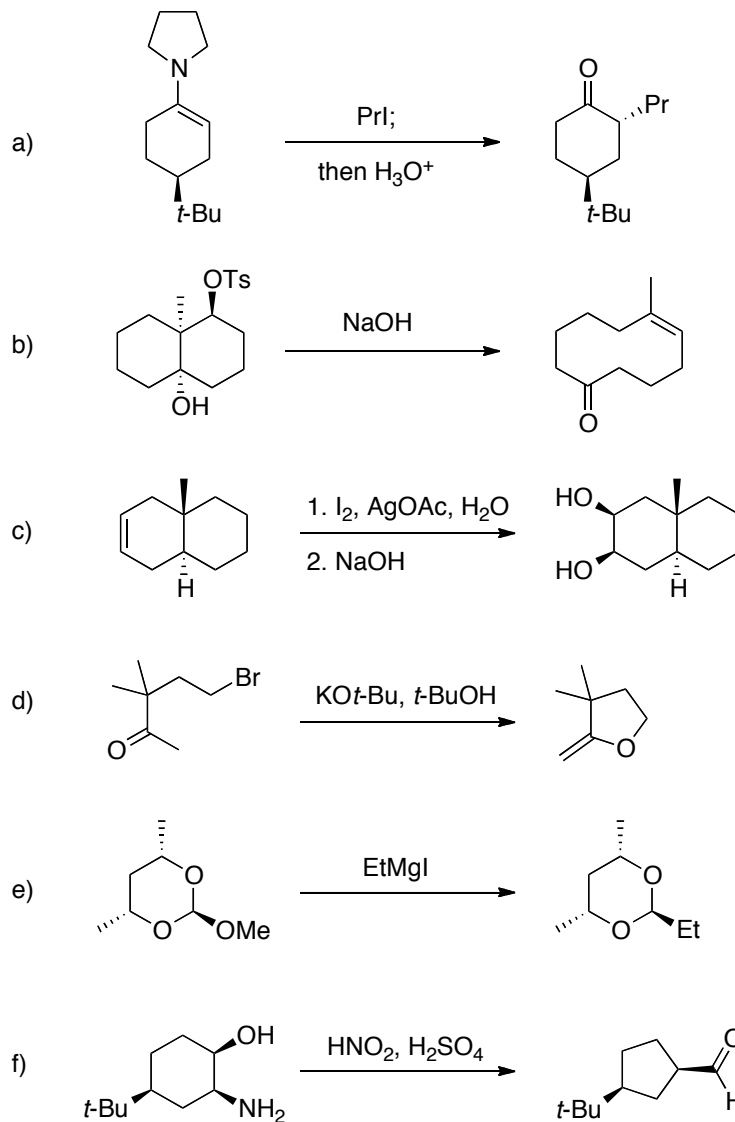
END OF QUESTION

TURN OVER

5. Answer *both* Part A and B.

Part A: Provide mechanisms for the **four** of the following reactions, and explain any stereoelectronic effects which influence the reaction selectivity.

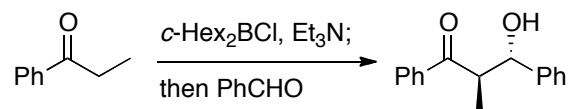
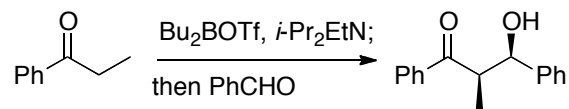
[4 x 5]



QUESTION CONTINUES

Part B: Propose models to explain, and discuss, the stereochemical outcome of **both** of the following reactions:

[5]



END OF QUESTION

TURN OVER

6. Answer Parts A, B and C.

Part A

Identify the isomers **A**, **B**, and **C**, molecular formula C_4H_8O , on the basis of the provided spectroscopic data. [3 × 2]

A 1H NMR δ_H 1.05 (3 H, t, J 7.5 Hz), 2.15 (3 H, s), 2.45 (2 H, q, J 7.5 Hz)
 IR ν_{max} 1715 cm^{-1}

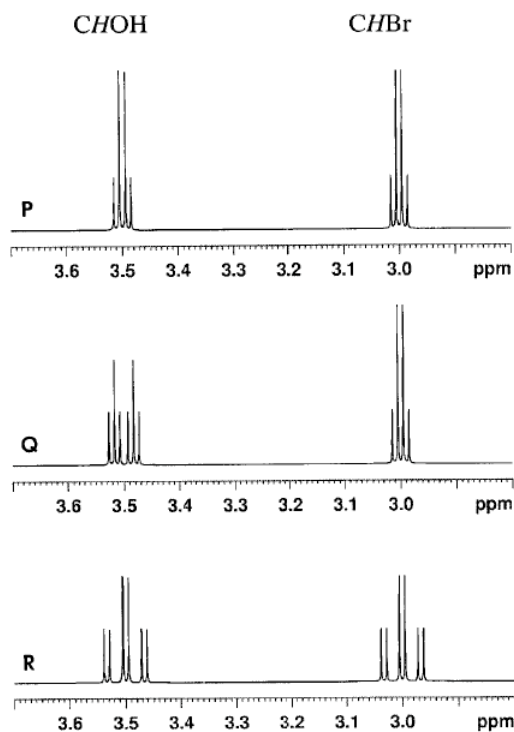
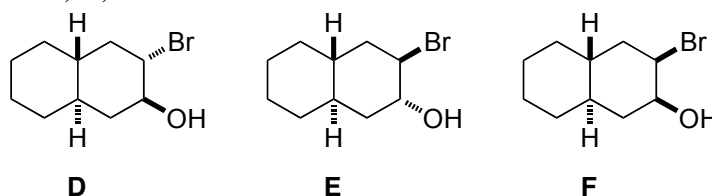
B 1H NMR δ_H 1.10 (6 H, d, J 7.5 Hz), 2.45 (1 H, m), 9.65 (1 H, d, J 2.0 Hz)
 IR ν_{max} 1720 cm^{-1}

C 1H NMR δ_H 1.85 (4 H, m), 3.75 (4 H, m)
 IR ν_{max} no strong absorption in the range 1600–1900 cm^{-1}

Part B

(a) Sketch the relationship between the dihedral angle θ and the $^3J_{HH}$ coupling constant J . [2]

(b) Assign, with reasoning, the partial NMR spectra **P**, **Q**, and **R**, below, to the following bromohydrin isomers **D**, **E**, and **F**. [3 × 3]

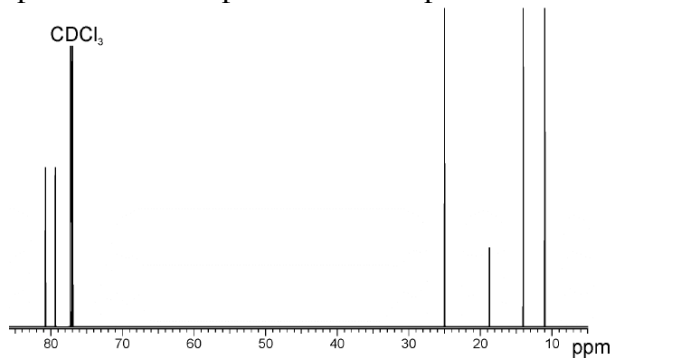
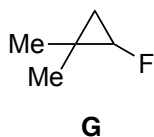


QUESTION CONTINUES

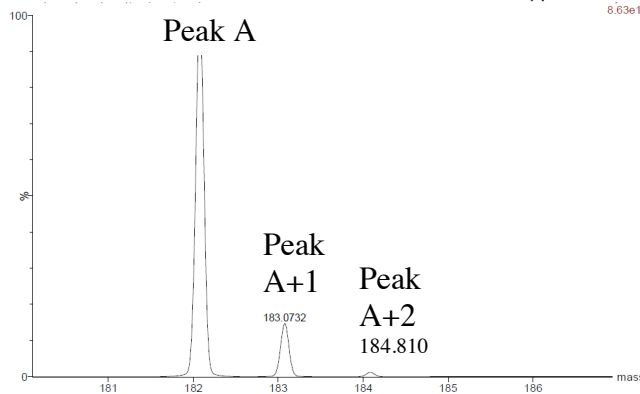
Part C Answer *two* of the following.

[2 × 4]

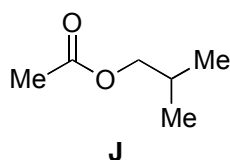
(a) Account for the observed proton decoupled ^{13}C NMR spectrum of compound **G**.



(b) Accurate mass analysis predicted the molecular formula $\text{C}_n\text{H}_{n-3}\text{O}$ for the compound represented by Peak A. Suggest the isotopic composition of Peaks A+1 and A+2.

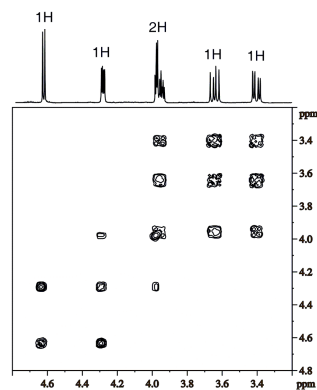
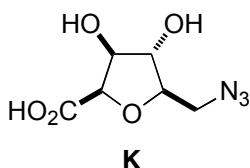


(c) Provide fragmentation pathways that account for the significant peaks in the electron impact (EI) mass spectrum of isobutyl acetate (**J**) listed below.



m/z	relative intensity
73	20%
56	40%
43	100%

(d) Explain the terms *diagonal peak* and *cross-peak* and show how they can be used to assign the 2D ^1H - ^1H correlation spectrum (COSY) of **K** in CD_3OD shown below; integral values are given for the ^1H NMR spectrum as indicated below.



END OF PAPER