OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE; NIGERIA

B.Sc (CHEMISTRY) DEGREE EXAMINATIONS

CHM 432— TOPICS IN ADVANCED HETEROCYCLIC NITROGEN COMPOUNDS

RAIN SEMESTER EXAMINATION **2011/2012 SESSION**

JANUARY 2013 **TIME ALLOWED: 2 HOURS**

INSTRUCTION: **ANSWER ALL QUESTIONS**

QUESTION 1

(a) Define the term "alkaloids".

(b) Describe a general procedure for the isolation of alkaloids from alkaloid-containing plant leaves.

(c) What are the major constituents of tea leaves ?

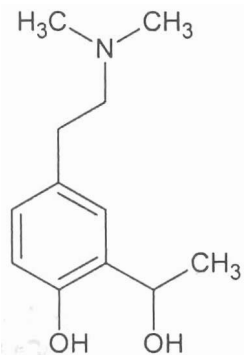
QUESTION 2

(a) Write the structure of each of the following nitrogen-containing compounds:

(i) Imidazole (ii) Oxazole (iii) 2-Pyrrolesulfonic acid (iv) 2-Bromopyrazine

(v) 4-Chloropyrimidine (vi) Quinoxaline (vii) 2-Hydroxybenzimidazole

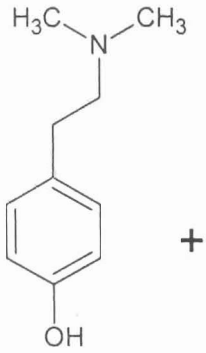
(b) Hordenine is an alkaloid which occurs naturally in germinating barley. One of its derivatives has structure A:



A

(i) What chemical tests would you carry out to show that Hordenine (A) contains the appropriate hydroxyl groups and that it is a tertiary base?.

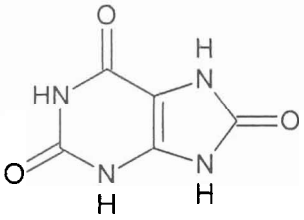
(ii) Complete the following reactions of Hordenine:



$$\xrightarrow{\text{aq } OH^-} P_1$$

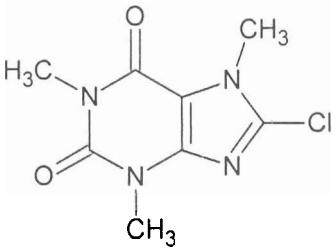
$$P_1 + KMnO_4 \xrightarrow{\text{aq } OH^-} P_2$$

© A synthetic route to caffeine is as follows:



$$+ \; xCH_3I \,/\, \text{aq NaOH} \longrightarrow (B)$$

$$(B) + PCl_5 \,/\, POCl_3 \longrightarrow$$

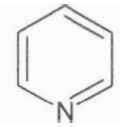


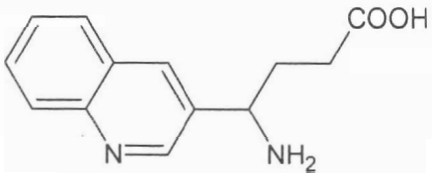
$$\xrightarrow[\text{heat}]{HI} \text{Caffeine}$$

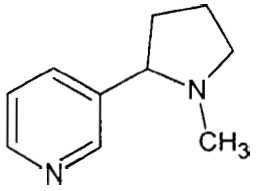
Write the structures for compounds **B** and caffeine.

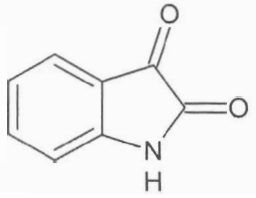
QUESTION 3

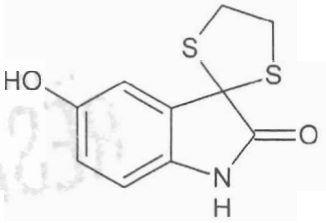
Identify the lettered products in the following reactions:

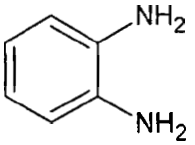
(i)  + CrO_3 + c.HCl ⟶ P_1

(ii)  pyrolysis, heat ⟶ P_2

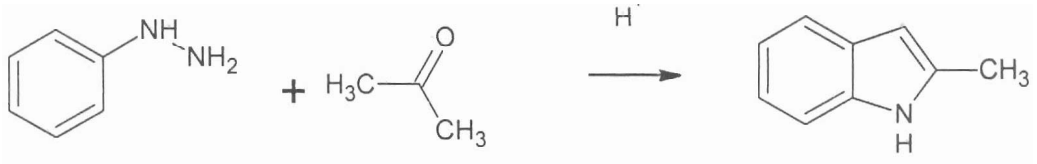
(iii)  + aq. $KMnO_4$, reflux ⟶ P_3

(iv)  + Br_2 in EtOH ⟶ P_4

(v)  + Br_2 in EtOH ⟶ P_5

(vi)  + HOOCCOOH, aq H^+, reflux ⟶ P_6

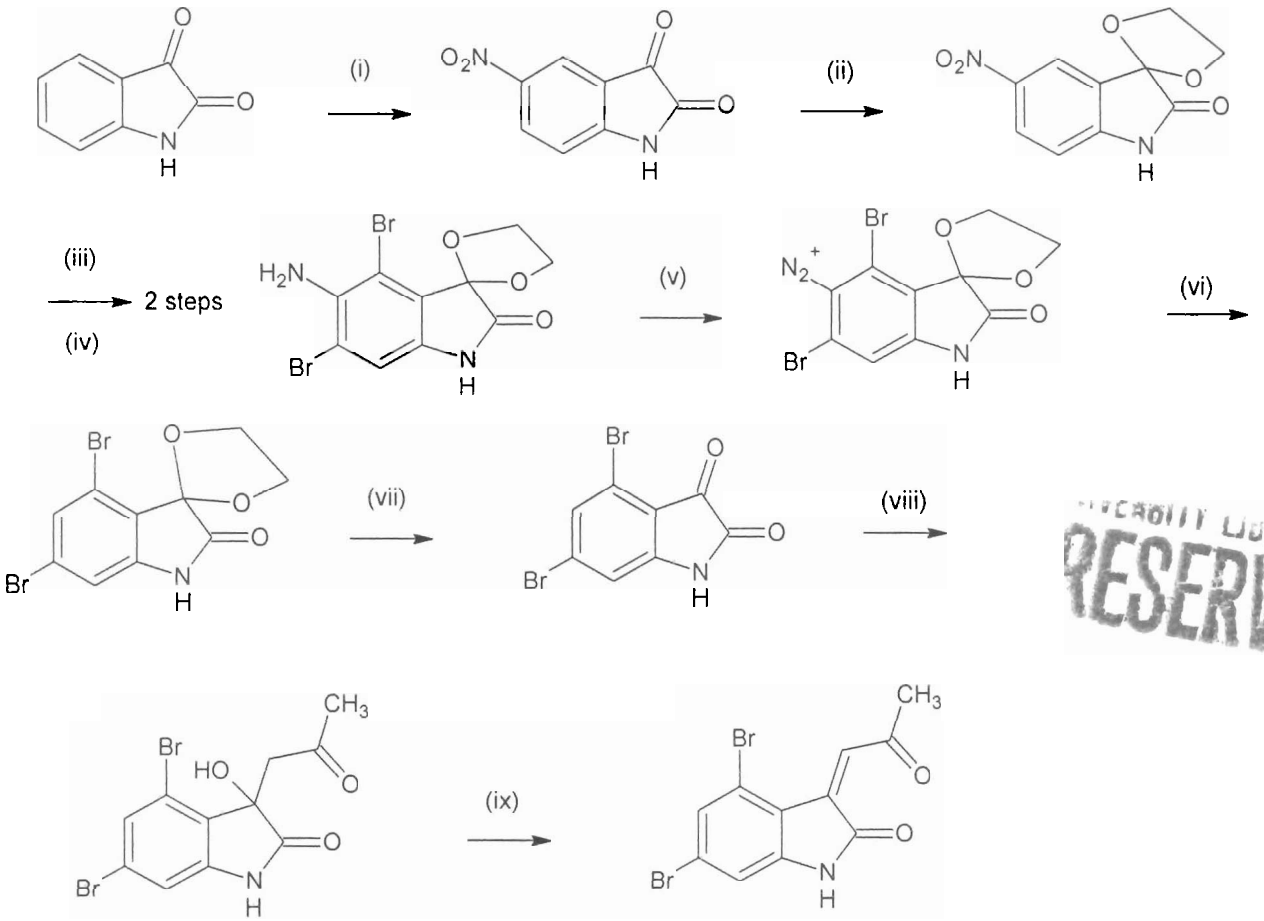
(b) 2-Methylindole has been prepared by the acid-catalyzed condensation of phenylhydrazine with propanone:



Suggest a mechanism for this reaction.

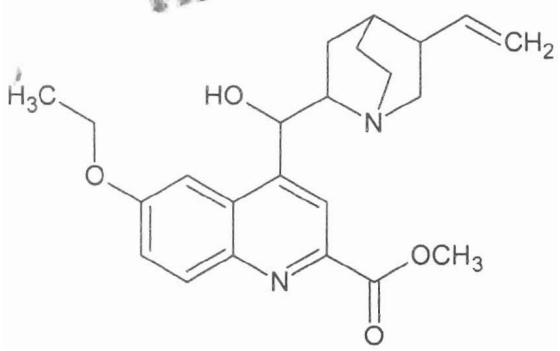
QUESTION 4.

(a) **Suggest** suitable reagents and reaction conditions for the following organic transformations:



(b) Quinine is an active constituent of Cinchona bark which has been used as an antimalarial agent for several hundred years.

(c) Examine carefully the following structure of a quinine derivative:



Write the full structure(s) of the product(s) which you would expect from the reaction of the compound with each of the following reagents:

(i) $NaBH_4$ in ethanol (reflux)
(ii) $LiAlH_4$ in ether (reflux)
(iii) H_2 /Ni catalyst at room temperature
(iv) Hot aqueous NaOH (prolonged refluxing)
(v) Hot aqueous HCl (prolonged refluxing)
(vi) Pyridinium chlorochromate (PCC)
(vii) Acetic anhydride
(viii) Bromine in CCl_4