UNIVERSITY OF NAIROBI

THIRD YEAR FIRST SEMESTER EXAMINATIONS 2013-2014

FOR THE DEGREE OF

BACHELOR OF SCIENCE (CHEMISTRY, ANALYTICAL AND INDUSTRIAL CHEMISTRY)

(DAY PROGRAMME)

SCH 302: STEREOCHEMISTRY AND SYNTHESIS OF ORGANIC COMPOUNDS

DATE: **TIME: 2 HOURS**

Answer ALL Questions

Q1.

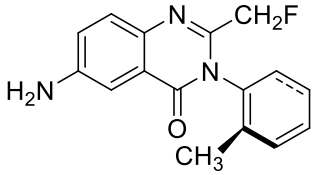
(a) Differentiate between the following stereochemical terms: (2 Marks each)

(i) Conformer and enantiomer

(ii) Optical rotation and specific rotation

(Total Marks: 4 Marks)

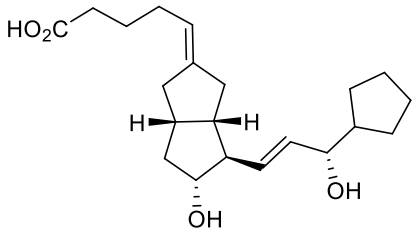
(b) (i) Determine the configuration of the muscle relaxant afloqualone based on both the R_a/S_a and P/M systems of designating configurations (2 Marks each)



Afloqualone

(Total Marks: 4 Marks)

(ii) Assign configuration to each stereochemical unit in ataplast, the inhibitor of platelet aggregation. (7 Marks)



Ataplast

(Total Marks: 7 Marks)

Q2.

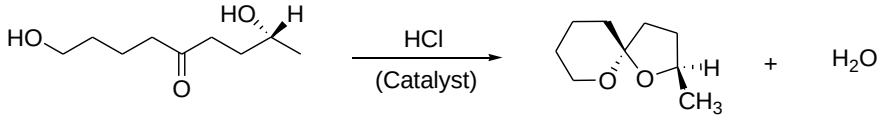
(a) Protecting groups are a common feature in multi-step organic synthesis. Explain the following observations:

(i) Carbamates and not amides are commonly used as protecting groups for the amino group. (3 Marks)

(ii) Acetals are a commonly used as protecting for alcohols, but alkyl ethers are rarely used. (3 Marks)

(Total Marks: 6 Marks)

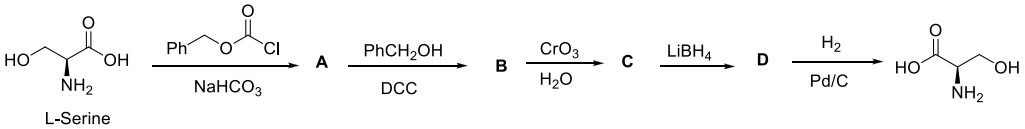
(b) Propose a reasonable reaction mechanism for the acid-catalyzed synthesis of the pheromone of the common wasp (*Vespula vulgaris*) based on the reaction shown below:



(Total Marks: 10 Marks)

Q3.

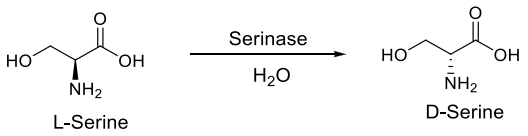
(a) The natural amino acid L-serine can be converted to its unnatural D-enantiomer according to the pathway highlighted below.



Deduce the structures of the missing intermediate compounds (**A**-**D**) in this synthesis. (2 Marks each)

(Total Marks: 8 Marks)

(b) A biotechnologist attempted to bioengineer parasites to produce enzyme systems to convert L-amino acids to D-amino acids in an effort to produce these unnatural amino acids cheaply. The pilot study examined two new enzyme systems (serinase A and serinase B) on their ability to convert enantiopure L-serine to D-serine.



L-Serine D-Serine

At the beginning of the experiment, the researcher observed that 0.25 g of the test sample of enantiopure L-serine dissolved in 5 mL of water, measured in a cell of path length 10 cm, gave an optical rotation of -0.7 degrees.

At the conclusion of the experiment and purification and isolation of the serine obtained, the biotechnologist observed that 0.1 g of the product sample from serinase A reaction dissolved in 1 mL of water, measured in a cell of path length 10 cm, gave an optical rotation of +1.2 degrees, while a similar weight of sample from the serinase B reaction in the same cell gave an optical rotation of +1.4 degrees.

Assuming that only serine is present in the test and reaction samples, determine:

(i) the specific rotation of L-serine and D-serine? (2 Marks)

(ii) the enantiomeric excess of the serinase A and serinase B reactions (4 Marks)

(iii) Which of the two systems would be preferred for the production of D-serine? (2 Marks)

(iv) Explain the rationale for the answer in 3b (iii) above (2 Marks)

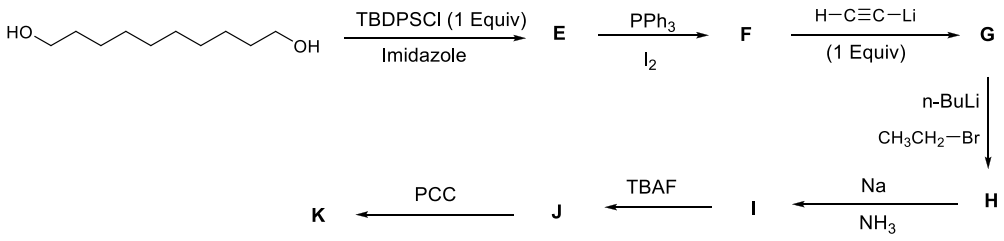
(Total Marks: 10 Marks)

Q4.

(a) Differentiate between the terms: biosynthesis and biomimetic synthesis

(Total Marks: 3 Marks)

(b) The pheromone of the spruce budworm can be synthesized based on the pathway highlighted below.



(i) Deduce the structures of the missing intermediate compounds (**E-J**) in this synthesis and of the pheromone **K**. (2 Marks each).

(ii) Propose a retrosynthetic pathway for pheromone that is consistent with synthetic scheme above. (4 Marks)

(Total Marks: 18 Marks)