

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY

END OF SECOND SEMESTER EXAMINATIONS - MAY 2011

ORGANIC CHEMISTRY II – SCH 1202

FOR SCH AND TTE CANDIDATES:

TIME – THREE HOURS.

INSTRUCTIONS TO CANDIDATES:

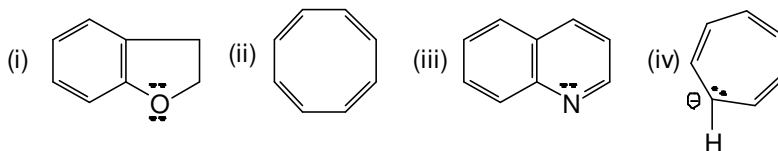
1. ANSWER ALL QUESTIONS FROM SECTION A AND ANY THREE FROM SECTION B. SECTION A CARRIES 40 MARKS AND EACH QUESTION IN SECTION B CARRIES 20 MARKS. MARKS ARE ALLOCATED AS INDICATED IN BRACKET.
2. START EACH QUESTION ON A NEW PAGE. (NOT EACH PART OF A QUESTION).
3. SHOW MECHANISM, CHEMICAL STEPS OR SYNTHESIS BY MEANS OF CURVED ARROWS.

TOTAL MARKS = 100

THIS QUESTION PAPER CONSISTS OF FIVE PRINTED PAGES (ON ONE SIDE ONLY) INCLUDING THE TOP PAGE WITH THE INSTRUCTIONS.

SECTION A:

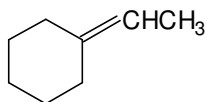
1. (a) Suggest four criteria which indicate that benzene is a very stable compound. (4 Marks)
- (b) Draw isomeric structures for the molecular formula C_7H_7Cl (4 Marks)
- (c) Explain Huckel's rule in your own words. (4 Marks)
- (d) State whether the following compounds are aromatic or non-aromatic and also indicate the number of pi electrons present in the compounds. (Marks will be deducted if one of the answers is not correct).



- (4 Marks)
- (e) *trans*-(*e,e*)-1,4-dimethyl cyclohexane is more stable than its *cis*-(*e,a*)-isomer. Explain this observation with an appropriate chair confirmation. (4 Marks)
- (f) Explain with the aid of chemical equations, why phenol is more acidic than ethanol. (6 Marks)
- (g) With an appropriate example, define a tautomer. (4 Marks)
- (h) Draw the structure for the following compounds: (2 Marks)
- 2,4-dichlorophenoxy acetic acid..
 - butylated hydroxyl toluene
- (i) Predict the product/s of mononitration of the following compounds. Which one of the two reacts faster and which one reacts slower than benzene? Give your reason. (4 Marks)
- chlorobenzene
 - nitrobenzene
- (j) Pyridine and pyrrole are both heterocyclic aromatic compounds with one nitrogen atom in the ring. Explain why pyridine is more basic than pyrrole. (4 Marks)

SECTION B:

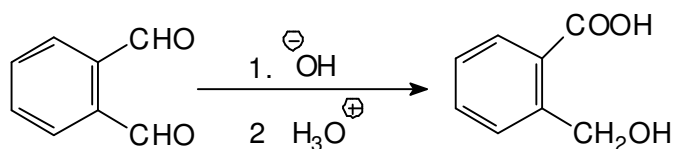
2. (a) What carbonyl compound and what phosphorus ylide might you use to prepare the following compound?



Outline the possible synthesis of ylide starting from triphenyl phosphine and halide of your choice. What is the name of this reaction? Why is this reaction important?

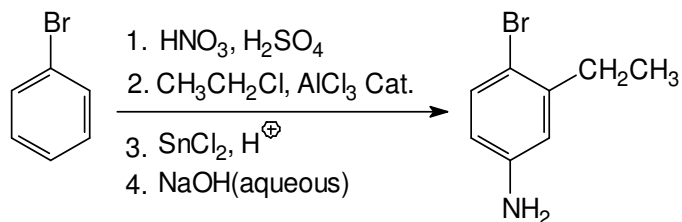
(10 Marks)

- (b) When *O*-phthalaldehyde is treated with base, *O*-(hydroxyl methyl) benzoic acid is formed. Propose a mechanism for this reaction.



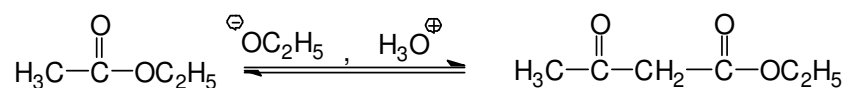
(6 Marks)

- (c) In the following reaction, the synthetic routes are not correct. How would you correct the route(s) to obtain the given product?



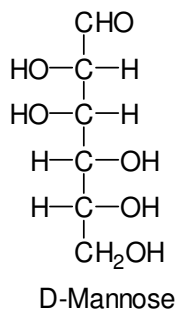
(4 Marks)

3. (a) Suggest the mechanism for the following Claisen condensation reaction.



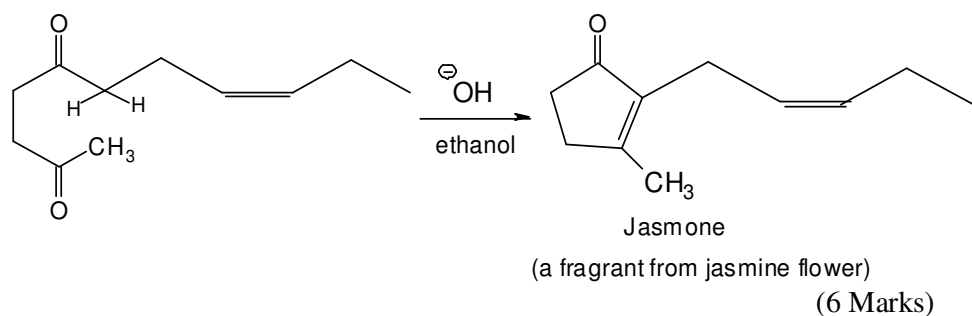
(5 Marks)

(b) You are given the following monosachharide:



- (i) Write reaction mechanism for the Haworth projection and also indicate the type of reaction involved. (4 Marks)
- (ii) Write Kiliani-Fischer synthesis (chain lengthening) for D-mannose. For this reaction you may need HCN, acidic solution and reducing agent. (No mechanism required). (3 Marks)
- (iii) What will be the products when D-mannose reacts with (I) reducing agent such as sodium borohydride and (II) oxidizing agent such as nitric acid. (2 Marks)

(c) Jasmone, a fragrant from jasmine flower, is a cyclic enone and is prepared through internal aldol reaction from the following compound. Write reaction mechanism for the reaction. The mechanism should not take more than five steps.



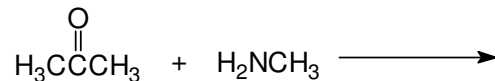
4. (a) Pyrrol and pyridine are both aromatic compounds. Explain why pyrrol undergoes electrophilic substitution at position two while pyridine undergoes electrophilic substitution at carbon three. (8 Marks)

(b) Why is $-\text{NHCOCH}_3$ group substituted to benzene ring found to be

moderately *o*- and *p*- directing while -NH_2 group substituted to benzene ring is highly reactive and forms 2,4,6- substituted product.

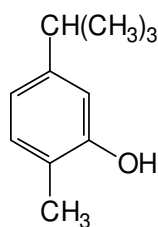
(4 Marks)

- (c) Write reaction mechanism for the reaction between propanone and methylamine. What is the general name of the final product?



(8 Marks)

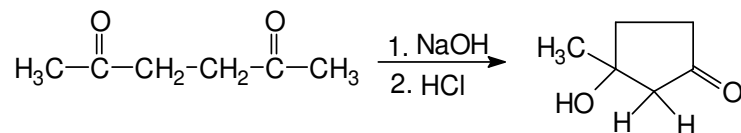
5. (a) Carvacrol is a natural product isolated from herbs such as oregano, thyme and marjoram. Synthesise carvacrol from benzene. Do not use more than five steps. You are provided with the following reagents; AlCl_3 , $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$, CH_3Cl , $\text{SO}_3/\text{H}_2\text{SO}_4$, NaOH solution, acidic solution and any other reagents you may need. (No mechanism required).



carvacrol

(5 marks)

- (b) Write reaction mechanism for the following reaction.



(5 Marks)

- (c) With the aid of chemical reactions explain the major difference(s) between (i) Friedel-Crafts alkylation and (ii) Friedel-Crafts acylation reactions. (No mechanism required).

(10 Marks)
