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UNIVERSITY OF RUHUNA – FACULTY OF MEDICINE

ALLIED HEALTH SCIENCES DEGREE PROGRAMME

FIRST BPHARM PART II EXAMINATION – MAY 2015

PII 1213: PHARMACEUTICAL CHEMISTRY II (SEO)

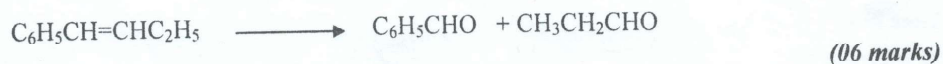
TIME: 3 HOURS

INSTRUCTIONS

- Answer **all** questions.
- Do not use any correction fluid.
- Answer questions in the given answer book.
- Marks will be penalized for illegible hand writing.

01. Answer **all** parts

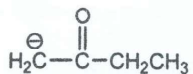
- 1.1. Fats and oils are two types of lipids which are made of triglycerides. Name two components which are combined to result a triglyceride. **(10 marks)**
- 1.2. Name one monounsaturated fatty acid which is derived from 18 carbon atoms. **(05 marks)**
- 1.3. Giving two examples, explain what is meant by “essential fatty acids”. **(15 marks)**
- 1.4. Define the term “saponification number”. **(05 marks)**
- 1.5. Explain briefly the three phases in the lipid oxidation. **(12 marks)**
- 1.6. Define the term “antioxidant.” **(05 marks)**
- 1.7. Draw the chemical structure for the antioxidant of BHA. **(05 marks)**
- 1.8. Define the term “polymer”. **(05 marks)**
- 1.9. Name three types of factors affects on biodegradation of polymers. **(09 marks)**
- 1.10. Name three primary mechanisms by which active agents can be released from a delivery system. **(12 marks)**
- 1.11. Define the term “hydrogel”. **(06 marks)**
- 1.12. Give the structure of an ester that yields a mixture containing equimolar amounts of 1-propanol and 2-propanol on reduction with lithiumaluminiumhydride (LiAlH₄). **(05 marks)**
- 1.13. Give the necessary reagents and reaction conditions for the following conversion.



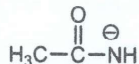
02. Answer all parts

2.1

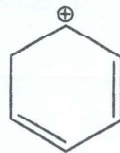
2.1.1 Draw the resonance structures for each of the following molecules/ions.



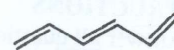
2.1.1.1



2.1.1.2



2.1.1.3



2.1.1.4

2.1.2 Of the resonance structures drawn above, show the one that would contribute most to the hybrid of each structure. Explain your answer.

(28 marks)

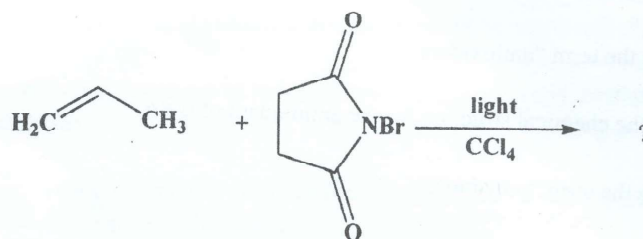
2.2

2.2.1 The bond length between C2-C3 of 1,3-butadiene is 1.47 Å whereas the bond length of C-C in ethane is 1.54 Å". Using theory of resonance explain why C2-C3 bond length of 1,3-butadiene is less than that of single C-C bond.

2.2.2 Explain the stability of 1,3-butadiene using molecular orbital/energy level diagram.

(22 marks)

2.3 Consider the following reaction:



2.3.1 Draw the structure of the product(s) formed in this reaction.

2.3.2 Giving the mechanism, explain why the above product is formed exclusively.

(20 marks)

2.4

2.4.1 State the Hukel rule pertaining to aromaticity.

2.4.2 Using the above rule, explain why cyclopentadienyl cation is not aromatic.

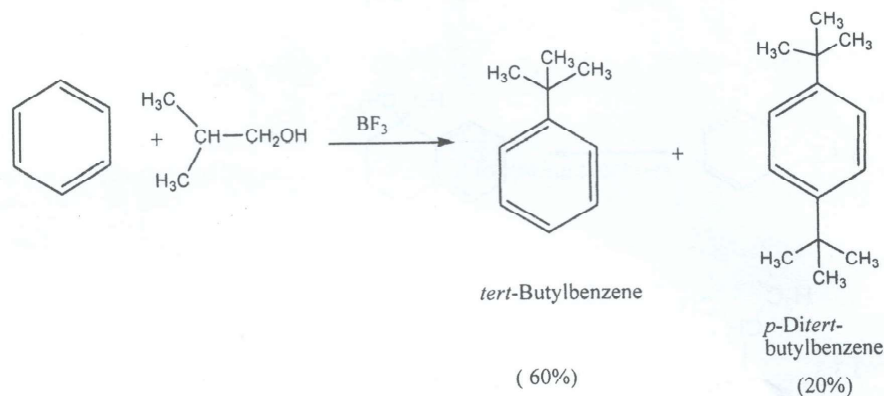
2.4.3 Explain the stability of cyclopentadienyl anion using its electrons filling to π -molecular orbitals.

2.4.4 Show how negative charge of cyclopentadienyl anion is delocalized.

(30 marks)

3.0 Answer all parts

3.1 Benzene was reacted with 2-methylpropanol in the presence of trifluoroborane in order to synthesize 2-methylpropyl benzene. The product formed in this reaction was not 2-methylpropylbenzene but a mixture of *tert*-butylbenzene (major) and *p*-diterbutylbenzene (minor) as shown below.



3.1.1 Giving reactions, explain the role of BF_3 in the above reaction.

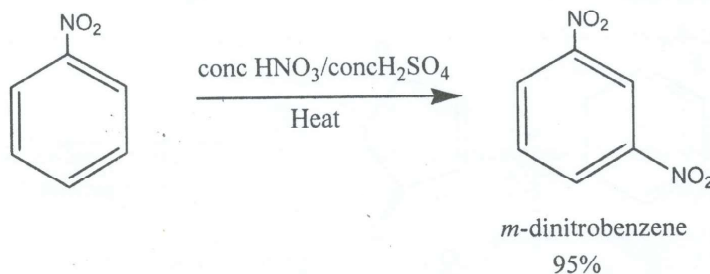
3.1.2 Giving necessary structures, explain why the above reaction would not produce the desired product, 2-methylpropyl benzene.

3.1.3 Describe the formation of disubstituted product (*p*-diterbutylbenzene) in the above reaction.

3.1.4 Propose a synthetic scheme to be used in preparation of desired product, 2-methylpropyl benzene.

(42 marks)

3.2 Nitration of nitrobenzene shown below needs heating with the mixture of conc. HNO_3 /conc. H_2SO_4 and the product formed is *m*-dinitrobenzene (95%). This reaction is 10,000 times slower than that of benzene.

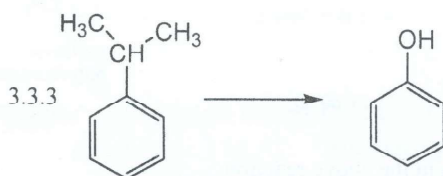
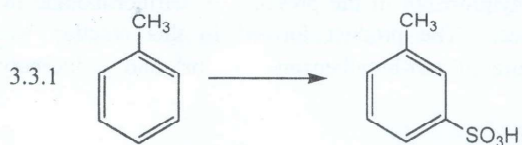


3.2.1 Using electronic effects explain why nitration of nitrobenzene is slower than that of benzene.

3.2.2 Considering the stability of intermediates formed, explain why nitration occurs mainly at the meta position.

(30 marks)

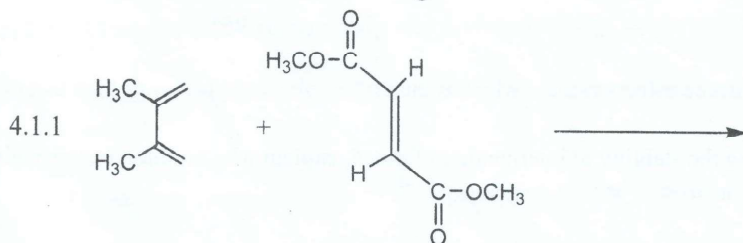
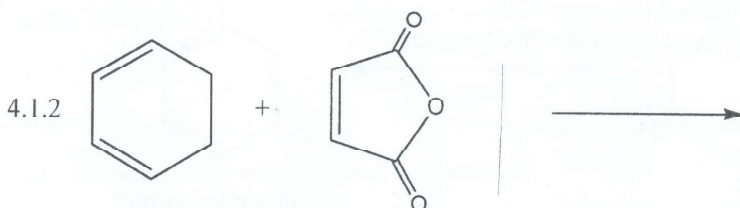
3.3 Giving necessary reagents, reaction conditions and intermediates formed, show how you would carry out following conversions of aromatic compounds.



(28 marks)

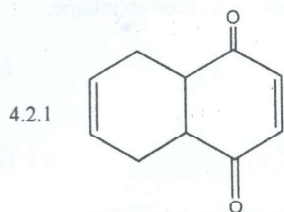
04. Answer all parts

4.1 Whenever necessary, giving emphasize to stereochemistry show the product(s) formed in the following reactions.

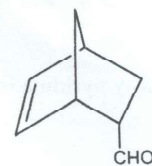


(16 marks)

4.2. Which dienes and dienophiles would you employ to synthesize following compounds?

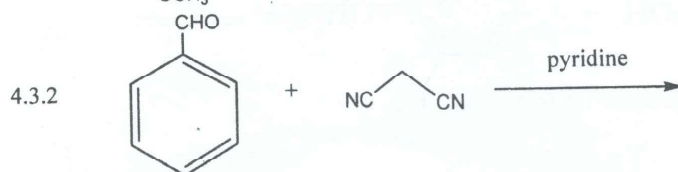
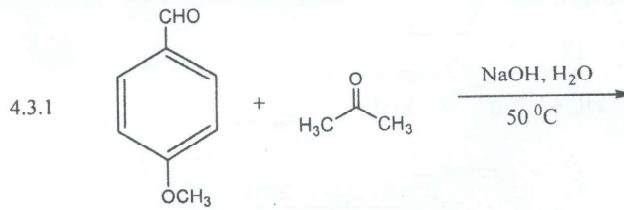


4.2.2



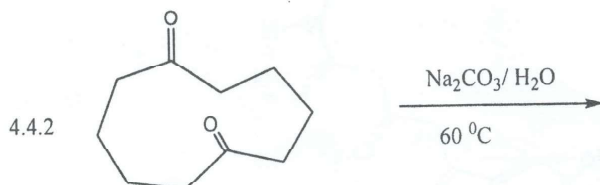
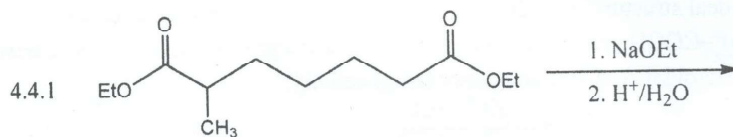
(20 marks)

4.3. Give the structure of the product(s) formed in following reactions.



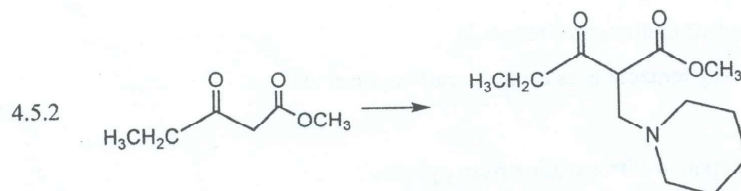
(16 marks)

4.4. Giving plausible mechanisms predict the product(s) of the following reactions.



(32 marks)

4.5. Giving necessary reagents, reaction conditions and intermediates formed show how you would carry out following conversions.



(16 marks)

05. Answer **all** parts

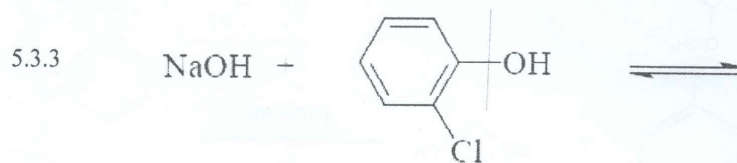
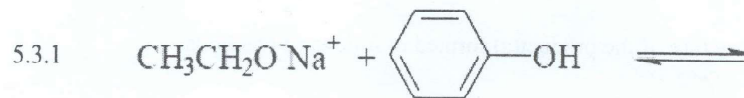
5.1 Explain why the H's in ethyne are considerably more acidic than those in ethane. Illustrate your answer with chemical equations.

(10 marks)

5.2 Explain why pyridine is more basic than pyrrole.

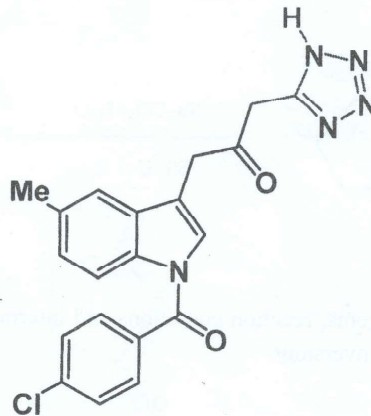
(10 marks)

5.3 Complete each of the following reactions and indicate whether the equilibrium is favored to the right or left.



(10 marks)

5.4 Shown below is tetrazole substitute for the anti-arthritis drug indomethacin. Tetrazole which exists as a single isomer has two tautomers. It ($\text{pK}_a \sim 5$) is as acidic as carboxylic acids making it an ideal structural replacement for $-\text{COOH}$ group in medicinal drugs. The isosteric replacement of $-\text{COOH}$ group for a tetrazole reduced the gastric irritation while retaining the *NSAID* (Non Steroidal Anti-inflammatory Drug) activity.



5.4.1 Draw the two tautomers of tetrazole.

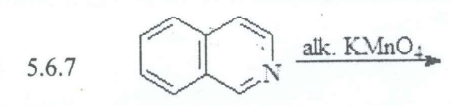
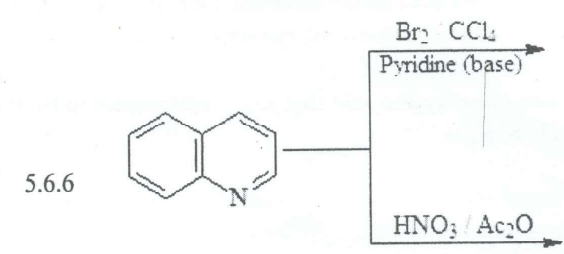
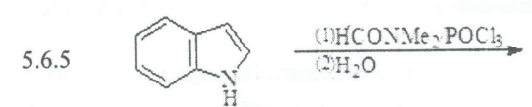
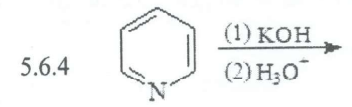
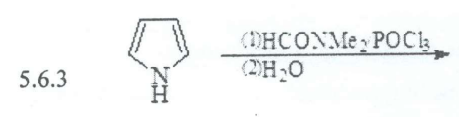
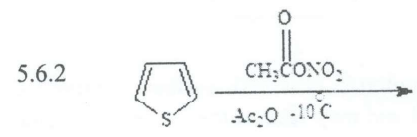
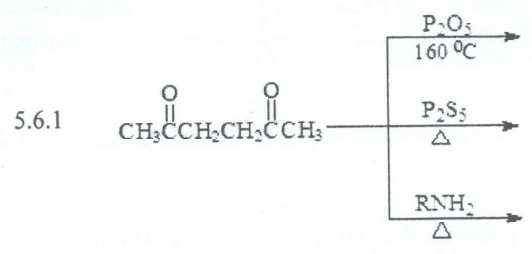
5.4.2 Explain why tetrazole is as acidic as carboxylic acid.

(10 marks)

5.5 How do you prepare 4-nitropyridine from pyridine?

(10 marks)

5.6 Predict the products of each of the following reactions.



(50 marks)

06. Answer **all** parts

6.3.1 Categorize carbohydrate into three groups based on the number of sugar molecules present and give main feature(s) of each category. Also provide an example for each category.

(09 marks)

6.3.2 Give the mechanism for the conversion of (D)-glucose into α -D-(+)-glucopyranose form.

(09 marks)

6.3.3 With the structures, explain why sucrose does not give positive results for reducing sugar identification tests.

(07 marks)

6.4 In higher organisms where aerobic respiration is observed, various reactive oxygen species (such as O_2^- , H_2O_2 , OH^\cdot) may be formed and may lead to the oxidation of guanine residues (G) of DNA to 8-oxoguanine (oxoG).

6.4.1 Draw the structures of both guanine and 8-oxoguanine residues.

6.4.2 Draw the syn and anti conformations of guanosine.

6.4.3 In the guanine base, using arrows mark each of the hydrogen bond donors (pointing out) and hydrogen bond acceptors (pointing out).

(25 marks)

6.5

6.5.1 What are the reasons to be an amino acid being essential for the human body?

(03 marks)

6.5.2 Of the common amino acids which amino acids would be negatively charged above pH 7.

(02 marks)

6.5.3 Draw the chemical structures of **two** such amino acids and label them with their names and one-letter codes.

(08 marks)

6.5.4 Name and draw the structure of **an amino acid** that you would expect to be able to detect on the UV-visible spectrophotometer.

(04 marks)

6.6

6.6.1 Define the term isoelectric point of amino acids.

(05 marks)

6.6.2 How does the charge of the amino acids will be affected with the pH of the medium and isoelectric point of amino acids?

(08 marks)

6.7 Giving reasons derive the product(s) obtained from the following treatments of the peptide. GQLEDKLWELMESRLYHLEN.

6.7.1 with CNBr

(06 marks)

6.7.2 with trypsin

(08 marks)

6.7.3 with chymotrypsin

(06 marks)
