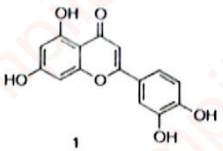
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
DEPARTMENT OF CHEMISTRY
RAIN SEMESTER EXAM
EXPERIMENTAL ORGANIC CHEMISTRY II (CHM 312)
2018/2019 SESSION (DECEMBER 2019)

Time: 90 minutes

1a. Predict the products of the following ketones with Semicarbazide hydrochloride



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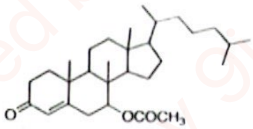

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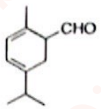

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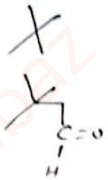
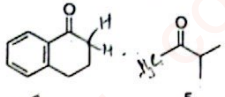


1b. Write the mechanism (using arrow formalism) for the formation of the Semicarbazide hydrazone of cyclohexanone assuming the reaction is acid catalyzed

1c. Describe how the acid brings about the catalysis (speeds up the reaction) and the effect of adding too much acid on the rate of the reaction.

2a. Draw the structure of the expected products of the following compounds with one molar equivalent of benzaldehyde, assuming that reaction is catalyzed by base (alcoholic KOH)



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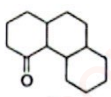

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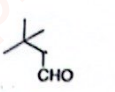

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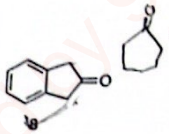

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2b. Which of the compounds in question 2a would react with 2-molar equivalents of benzaldehyde to give a product? Draw the structure of the expected product of the selected compound with 2-molar equivalents of benzaldehyde.

2c. Write a generally acceptable mechanism for the formation of the product from the reaction of compound 4 with benzaldehyde.

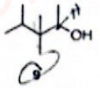
3a. Draw the structures of all the possible isomers of the compound with molecular formula C_7H_9N

3b. Group the compounds into different classes based on structural features and describe how a simple chemical test can be used to distinguish the classes of compounds that you have drawn

3c. In the electrophilic aromatic substitution reaction of aniline with Bromine (Br_2/acetic acid), draw the structure of the expected product and give reasons for the observed product.

3d. Describe using a scheme of reactions (with appropriate reaction conditions) how to prepare a monobrominated aniline starting from aniline. You can use any reagent that you wish to achieve the synthetic transformations that you propose.

4a. Which of the following alcohols is oxidizable?



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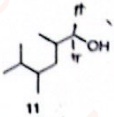

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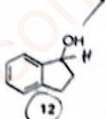

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4b. Draw the structure of the expected oxidation product assuming the alcohols were oxidized with Jones reagent ($Na_2Cr_2O_7$/concH_2SO_4)

4c. Which of the alcohols in question 4a will give an oxidation product that can react with DNP

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

DEPARTMENT OF CHEMISTRY

B.Sc., Degree (Chemistry) Examination

Part III Rain Semester 2021/2022

CHM 312: EXPERIMENTAL ORGANIC CHEMISTRY

Attempt ALL Questions **Time allowed: 1¼ Hrs**

QUESTION 1

In identifying an unknown ketone, the ketone was reacted with 2,4-dinitrophenylhydrazine and semi-carbazide separately under moderate acidic condition to give crystalline derivatives.

(i) Why is moderate acidic condition important for the reaction?

(ii) Why is it necessary to re-crystallise the product obtained before determination of melting point?

(iii) Mention two properties of a good solvent for recrystallization

(iv) Propose a suitable mechanism for the reaction

QUESTION 2

The reaction between 2-hydroxybenzoic acid and ethanoic anhydride gives predominantly 2-acetylbenzoic acid in the presence concentrated sulphuric acid

(i) Why is the phenolic -OH group preferred to the carboxylic -OH for acetylation reaction?

(ii) How can you confirm by chemical tests that the reaction product is indeed 2- acetylbenzoic acid?

(iii) Mention two ways to hasten formation of crystals during recrystallization process.

QUESTION 3

(i) Write the structures, if any, of the expected products of the reaction of benzaldehyde with half its molar equivalent of each of the following compounds in the presence of base

a) Cyclohexanone
b) 2,6-dimethylphenol
c) 2-methylcyclopentanone
d) Cyclohexanol

(ii) In Claisen –Schmidt condensation reaction, 2.5 cm^3 of benzaldehdye reacted with its half molar equivalent of propanone in the presence of a base. If the weight of dibenzalpropanone obtained was 2.0 g. Calculate

(a) the volume of propanone used for the reaction

(b) the percentage yield of dibenzalpropanone

(Specific gravity: benzaldehyde, 1.05 and propanone, 0.80. Molecular mass: benzaldehyde, 106.12 g/mol, propanone, 58.08 g/mol and dibenzaladehyde, 234 g/mol)

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QUESTION 4

(i) What is a Jones reagent?

(ii) In identifying a secondary alcohol, a student oxidized the alcohol using Jones reagent and thereafter prepared its 2,4-dinitrophenylhydrazone derivative. Upon the determination of the melting point, the derivative was identified as cyclohexanone-2,4-dinitrophenylhydrazone.

(a) Identify the alcohol

(b) When you performed the above experiment in the laboratory, the reaction mixture was diluted with cold water saturated with sodium chloride and thereafter extracted with chloroform using separating funnel. What is the use of sodium chloride in the experiment?

(i) Hasten precipitate formation.

Deter
Determination of the correct melting Point.

methanol

Department of Chemistry
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
Part III B.Sc. Chemistry Degree Examination
RAIN SEMESTER EXAMINATION, 2022/2023 SESSION

CHM 312 – Experimental Organic Chemistry **TIME ALLOWED: 1 Hr 15 mins**

INSTRUCTION: Answer all questions

1 (a.) Cyclohexanone reacts with 2,4-dinitrophenylhydrazine under moderate acidic condition to give a precipitate.

(i) Write the structure of the solid product
(ii) Why is moderate acidic condition necessary for the reaction?
(iii) *Mention a simple laboratory procedure* that can be used to purify the product

(b.) (i) What is Jone's reagent?
(ii) If 0.05 mole of cyclohexanol is completely oxidised by 17 mL of Jone's reagent, what volume of the reagent would be required for complete oxidation of 15 cm^3 the alcohol?
(Molar mass and specific gravity of cyclohexanone are 100 and 0.947 respectively)

2. The reaction between 2-hydroxybenzoic acid and ethanoic anhydride gives predominantly 2-acetylbenzoic acid in the presence of concentrated sulphuric acid

(i) Write the structures of all the possible acetylated products
(ii) Which of the products mentioned in (i) above is most likely to be formed and why?
(iii) Mention a simple laboratory test for the presence of the following functional groups (a) phenolic (b) carboxylic
(iv) Mention two properties to consider in choosing a solvent for recrystallization of the product

3. In Claisen –Schmidt condensation reaction, benzaldehdye reacts with its half molar equivalent of acetone in the presence of a base.

(i) Write the structure of the product
(ii) Deduce the structure of product, if any, when acetone is replaced in the reaction above with the following compounds
(a) cyclobutene (b) cyclobutanone and (c) cyclobutanol
(iii) Write the structure of the product formed if equal moles of benzaldehyde and acetone were used in the reaction

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY

B.Sc. DEGREE EXAMINATION
RAIN SEMESTER, 2023/2024 SESSION

CHM 312: EXPERIMENTAL ORGANIC CHEMISTRY

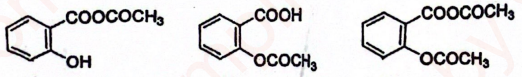
TIME ALLOWED: 1 hour 45 minutes **DATE: Saturday, 12th July 2025**

INSTRUCTIONS: Answer All Questions

1 An unknown ketone could be identified by preparing its 2,4-dinitrophenylhydrazone derivative and recrystallized in a suitable solvent mixture. The melting point of the recrystallized product could be used to identify the ketone. Cyclohexanone was identified in such an experiment;

(i) Write the structure of the product formed and give its name.
(ii) Propose a suitable mechanism for the reaction.
(iii) What physical measurement can be used to identify the unknown ketone if there are two or more 2,4-dinitrophenylhydrazone derivatives with melting points that could march the melting point of the cyclohexanone derivative?

2. In the treatment of *o*-hydroxybenzoic acid with ethanoic acid anhydride in the presence of concentrated sulphuric acid, a product whose structure could in principle be **I**, **II** or **III** below is formed;



I **II** **III**

(i) Which of the above structures is the correct structure for the product?
(ii) What are the chemical tests you will carry out to support your choice of structure? (tabulate to show the chemical tests, observations and inferences).
(iii) Which of the hydroxyl groups from the phenolic and carboxylic acid is more nucleophile and why?

3. (a) In a claisen-Schmidt condensation reaction between benzaldehyde and half its molar equivalent of propanone in the presence of a base. Outline the mechanism of the reaction and hence deduce the structure of the product formed.

(b) Write structures, if any, you will expect if you react benzaldehyde with half its molar equivalent of each of the following compounds in the presence of a base;

(i) Cyclohexanol
(ii) 2,6-dimethylphenol
(iv) 2-methylcyclohexanone
(v) Cyclohexanone

4. A primary aromatic amine, **X**, C_7H_9N was acetylated using acetic acid anhydride to give an amide, **Y**. **Y** was brominated using solution of bromine in acetic acid to give predominantly **Z**, which is one of the two possible monobromo derivatives. **Z** was hydrolysed to give the monobromoamine **P**. The melting point of recrystallized **P** was used to identify it as 4-bromo-2-methylaniline.

(i) Write the structures of X, Y and Z.
(ii) Write the structures of other 4 isomeric amines with same molecular formular.
(iii) Explain what might have happened if you had brominated the free amine, X instead of its acetyl derivative Y.

5. In the oxidation of secondary alcohol using Jones reagent, a student followed the procedure given in their practical manual. The manual went forward to ask the student to prepare the 2,4-dintrophenylhydrazone derivative of the product of the oxidation. The melting point of the DNP derivative was determined and this was used to identify the DNP derivative as cyclohexanone-2,4-dinitrophenylhydrazone.

(i) Identify the alcohol and draw its structure
(ii) Write a general and a balanced chemical equation for the oxidation of secondary alcohol (RR'CHOH) to ketone (RR'CO) with Jones reagent.
(iii) What is the chemical composition of a Jones reagent?