



CEM 3B20: ADVANCED ORGANIC CHEMISTRY, 2018
SUPPLEMENTARY EXAM

ASSESSOR: PROF H KINFE AND PROF C MUAMELA

EXTERNAL MODERATOR: Dr L Pilcher

DURATION: 3 HOURS

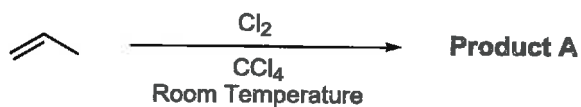
TOTAL MARKS: 98

PART I [45]

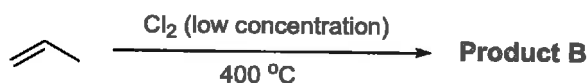
QUESTION 1 [4]

a. Provide the major product(s) for the following reactions (1 and 2)

(i) Reaction 1 (1)



(ii) Reaction 2 (1)



(a) Provide a detailed mechanism for Reaction 2 shown above [in a (ii)] (2)

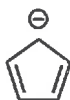
QUESTION 2 [2]

Draw all possible resonance forms for each of the species below.

a. (1)

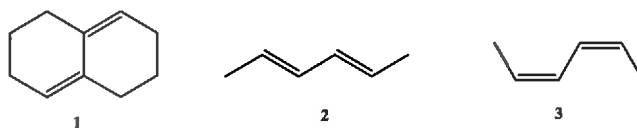


b. (1)

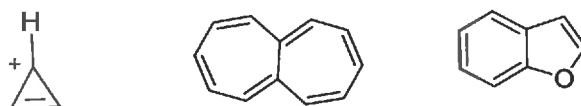


QUESTION 3**[6]**

Rank the following dienes in order of decreasing reactivity with a dienophile in a Diels-Alder reaction. Give a short explanation for your answer.

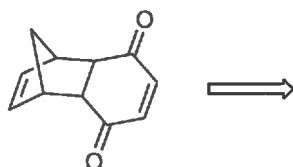
**QUESTION 4****[6]**

Classify the following molecules as aromatic or non-aromatic (anti-aromatic). Provide a short explanation for your answer. Assume all molecules are planar.

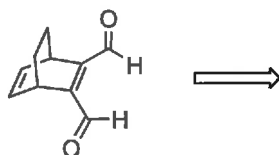
**QUESTION 5****[5]**

Show a combination of diene and dienophile starting materials required to produce each of the following Diels Alder adducts.

a. **(2)**

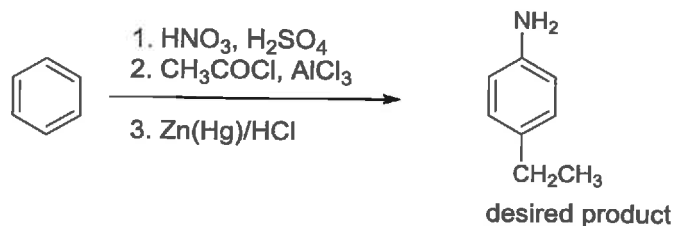


b. **(3)**



QUESTION 6**[8]**

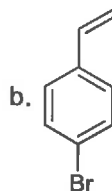
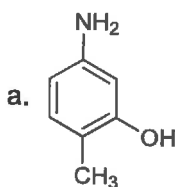
The following reaction will fail to provide the desired product if carried out under the reaction conditions.



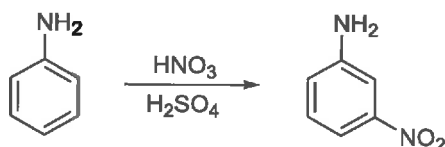
- a. Explain what is wrong with the reaction? (3)
- b. Outline a likely synthetic pathway for the synthesis of the desired product. (5)

QUESTION 7**[10]**

Propose a synthesis of each of the following compounds, starting with benzene or toluene. Assume that the *ortho*- and *para*-isomers can be separated.

**QUESTION 9****[4]**

The $-\text{NH}_2$ and $-\text{OCH}_3$ groups are known to be strongest *ortho/para*-directing activators in electrophilic aromatic substitutions reactions. However, when aniline is subjected to standard nitration conditions, the major product is *m*-nitroaniline, with very little *o*- and *p*-aniline formed, if at all.



Explain using both chemical structures and words why this is the case and why in the case of anisole (methoxybenzene), both the *ortho*- and *para*-nitro products are formed, and no *meta*-product at all.

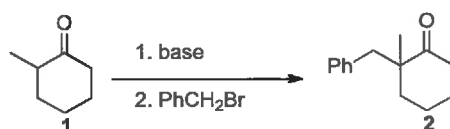
PART II

[53]

QUESTION 1

[5]

Thabo is a synthetic organic chemist at Zanele Pharmaceutical Company. He intends to carry out the following synthesis in order to prepare 2-benzyl-2-methylcyclohexanone **2** from starting material 2-methylcyclohexanone **1**. He has all kinds of bases that are usually employed in enolization reactions (the kind of bases discussed in my lectures) at his disposal.



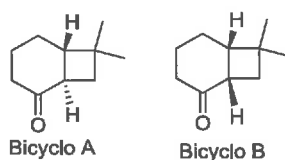
He adds LDA to 2-methylcyclohexanone **1** (in THF solution) to make the enolate ion; then he adds benzyl bromide to alkylate the enolate ion, and heats the solution for an hour to drive the reaction to completion.

- Predict the major product of the reaction he conducted.
- If you think the product he obtained is different from the desired 2-benzyl-2-methylcyclohexanone **2**, explain what went wrong and suggest how Thabo might synthesize the correct product.

QUESTION 2

[3]

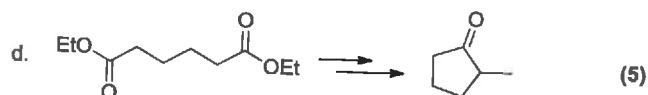
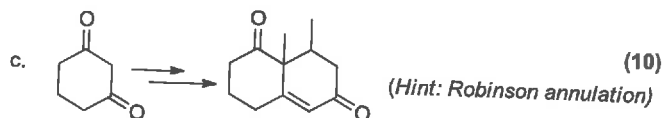
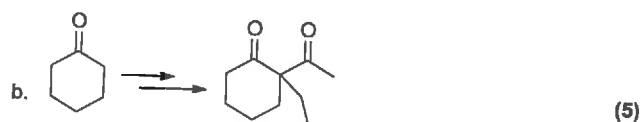
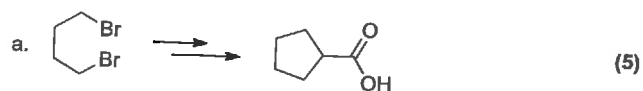
Optically active bicyclo A is converted to a mixture of bicycle A and B on standing in a solution of NaOEt in ethanol. Suggest reasonable explanation with the aid of reaction mechanism for the observation.



QUESTION 3

[25]

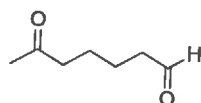
Outline a milder and economically viable reaction sequence for synthesis of each of the following compounds from the indicated starting material and any other organic and inorganic reagents needed. Multiple reaction steps will be required.



QUESTION 4

[10]

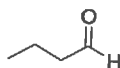
The following keto aldehyde can provide three possible cyclic-products if treated with a base (eg. NaOEt). Which would you expect to be the major product and why? (You can show the mechanism of the reactions to elaborate your answer).



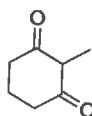
QUESTION 5

[10]

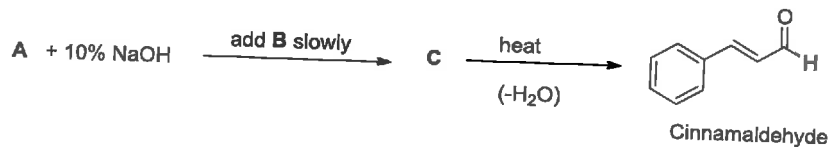
a. What condensation product would you expect to obtain by treating the following compound with NaOEt in ethanol? (5)



b. Show how you might synthesize the following compound using, as your starting material, esters, ketones, acyl halide, and so on as required. No need to show detailed mechanism. (2)



c. Out lined below is a practical crossed aldol reaction that can be used for the synthesis of cinnamaldehyde. Provide the missing ingredients for this recipe. (3)



[6]

The End.....

