Second Midterm – CHM1321-B

Professor Sandro Gambarotta

Date: 28th March 2019      Length: 80 min

Last Name: ____________________________
First Name: ____________________________
Student # ____________________________

- Instructions:
  - Molecular Model Kit strongly encouraged
  - Closed book exam
  - Periodic table allowed
  - NO REMARKING FOR EXAMS WRITTEN IN PENCIL

Read carefully:

By signing below, you acknowledge that you have read and ensured that you are complying with the following statement.

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: you will be asked to leave immediately the exam, academic fraud allegations will be filed which may result in you obtaining a 0 (zero) for the exam.

complying with the following statement.

Signature: ____________________________________

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1. (2 points)
Identify the most acidic proton in compound 1, draw the corresponding conjugate base, 2, and justify your choice.

Answ.

If we take the structure of 1, as drawn, and rotate it 180 degrees, the same image is obtained. As such, there are only four different locations (rather than eight) where deprotonation can occur.

The most acidic proton is the one whose removal generates a resonance-stabilized conjugate base.

2. (4 points)
Suggest an efficient synthesis for the following transformation:
Answ.
Treatment of the alkyl halide with a strong base gives an alkene which can then be converted into the desired product via ozonolysis:

3. (2 Points)
Which of the following represents an efficient method for preparing the alcohol shown? check your choice(s).

1. (a)
2. (b)
3. (c)
4. (d)
Answ:
Answer (a) is not correct, because the OH group would be installed at the more substituted position, as shown here:

Answer (b) is not correct, because the OH group would be installed at the less substituted position, as shown here:

Answer (c) is not correct, because a rearrangement is possible, giving a mixture of products:

Only one of these products is the desired product, so this method is not efficient.

Answer (d) is the correct answer, because hydroboration-oxidation involves installation of an OH group at the less substituted position:

4. (3 points)

Compound X has the molecular formula C₅H₁₀. In the presence of a metal catalyst, compound X reacts with one equivalent of molecular hydrogen to yield 2-methylbutane.

(a) Suggest three possible structures for compound X.

(b) Hydroboration-oxidation of compound X yields a product with no chiral centers. Identify the structure of compound X.

Answ.

(a) Compound X reacts with H₂ in the presence of a catalyst, so compound X is an alkene. The product of hydrogenation is 2-methylbutane, so compound X must have the same carbon skeleton as 2-methylbutane:
We just have to decide where to place the double bond in compound $X$. Keep in mind that the following two positions are identical:

So, there are only three possible locations where we can place the double bond:

this will generate an achiral product upon hydrob./ox

5. (4 points)
Compound $\text{A}$ is an alkyne with the molecular formula $\text{C}_5\text{H}_8$. When treated with aqueous sulfuric acid and mercuric sulfate, two different products with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$ are obtained in equal amounts. Draw the structure of compound $\text{A}$, and draw the two products obtained.

Answ.

If two products are obtained, then the alkyne must be internal and unsymmetrical. There is only one such alkyne with the molecular formula $\text{C}_5\text{H}_8$:
6. **(6 Points)**

Identify reagents that you could use to achieve this transformation:

![Conversion of alkene to methyl ketone](image)

Aansw.
The product is a methyl ketone, and the starting material is an alkene. We have not seen a method for directly converting an alkene into a ketone. However, we have seen a way of converting a terminal alkyne into a methyl ketone.

Completing the synthesis requires that we first prepare the alkyne above from the starting alkene, shown in the problem statement. This can be accomplished via a two-step procedure. The alkene is treated with molecular bromine (Br₂) to give a vicinal dibromide, which is then treated with excess NaNH₂ (followed by water work-up) to give an alkyne. And as mentioned earlier, the alkyne can be converted into the desired methyl ketone via acid-catalyzed hydration in the presence of mercuric sulfate:

![Conversion steps](image)

7. **(5 points)**

Identify the starting materials needed to make each of the following acetals:
1. The desired product is a cyclic acetal, which will require a diol and the appropriate ketone or aldehyde. To determine the identity of the starting ketone or aldehyde, we find the carbon atom that is connected to two oxygen atoms (highlighted):

This carbon atom bears the acetal group, so this carbon atom must have been the carbonyl group in the starting materials, as shown. The starting materials are 1,3-propanediol and acetone.

2. (b) This compound is a cyclic acetal, which can be made from the corresponding hydroxy-ketone and ethanol, as shown:

8. (4 points)

Identify the structures of compounds A to D below and then identify reagents that can be used to convert cyclohexene into compound D in just one
Cyclohexene is converted to cyclohexanol upon treatment with aqueous acid (acid-catalyzed hydration). Cyclohexanol is oxidized to cyclohexanone upon treatment with a strong oxidizing agent. Upon treatment with hydrazine in acid-catalyzed conditions, cyclohexanone is converted into the corresponding hydrazone. A Wolff-Kishner reduction then gives cyclohexane.

The conversion of cyclohexene to cyclohexane can be achieved more directly, in one step, via hydrogenation: