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Laboratory Report

Experiment 5.

Reactions of Carbonyls Under Basic Conditions

Introduction

In this experiment, an aldol condensation was performed between benzaldehyde and acetophenone to form benzalacetophenone in part A, and in part B a haloform reaction was performed between acetophenone and sodium hypochloride (NaOCl) to form a carboxylate product.

Aldehydes and ketones are able to dimerize under basic conditions, forming a new C-C bond, and the product is called an aldol. However, this product is an intermediate and can further react with the base to form an aldol condensation product, in this case an α,β-unsaturated ketone, by eliminating the hydroxyl group on the molecule. The reaction requires at least two α-proton, one for the aldol reaction and another one so that the elimination of the hydroxyl group can occur. The first α-proton is removed by the base, producing an enolate (contains a negatively charged carbon), which then attacks the carbonyl of the second molecule, which acts as an electrophile. A second α-proton is removed by the base, which is in excess, leading to the elimination of the hydroxyl group and the formation of the α,β-unsaturated product[1], as shown below in figure 1.

Cross-condensation can occur when two different carbonyl compounds are reacted with each other. Here, one forms an enolate which acts as a nucleophile and the other forms an electrophile, and both self- and cross-condensed products can be expected. Usually only one compound is chosen so that it is able of forming an enolate and will not self-condense too quickly. In this experiment, the reactant capable of self-condensing is acetophenone and the process occurs very slowly. Benzaldehyde cannot self-condense as it does not contain any α-protons.

For part B of this experiment, a haloform reaction was performed. A haloform reaction involves the reaction of a methyl ketone with a halogen, here acetophenone and sodium hypochloride (NaOCl), in the presence of NaOH and yields a carboxylate and a haloform. In this experiment NaOH was not required as a reagent since NaOCl was used, which is a source for electrophilic halogens and can also act as a base. Since NaOCl can act as a base, NaOH is no longer needed as a base in this case.

An enolate is formed as a product of the first reaction of acetophenone with the NaOCl, and the α-carbon of the enolate further reacts with the hypochloride (Cl-OH) to form an α-haloketone. Due to the formation of the α-haloketone and the resulting inductive effect, the α-protons become more acidic and are more easily deprotonated by the NaOCl. The deprotonation of the α-haloketone is repeated until an α,α,α-trihaloketone is formed.

NaOH is produced during the reaction of enolate with the NaOCl. The hydroxide of NaOH attacks the electrophilic α-carbon of the trihaloketone, causing the elimination of the $^{-}CCl_3$ anion and transforming the trihaloketone into a carboxylic acid. The $^{-}CCl_3$ anion then deprotonates the carboxylic acid, producing the final products, the carboxylate and the haloform[2]. This reaction is shown below in figure 2.

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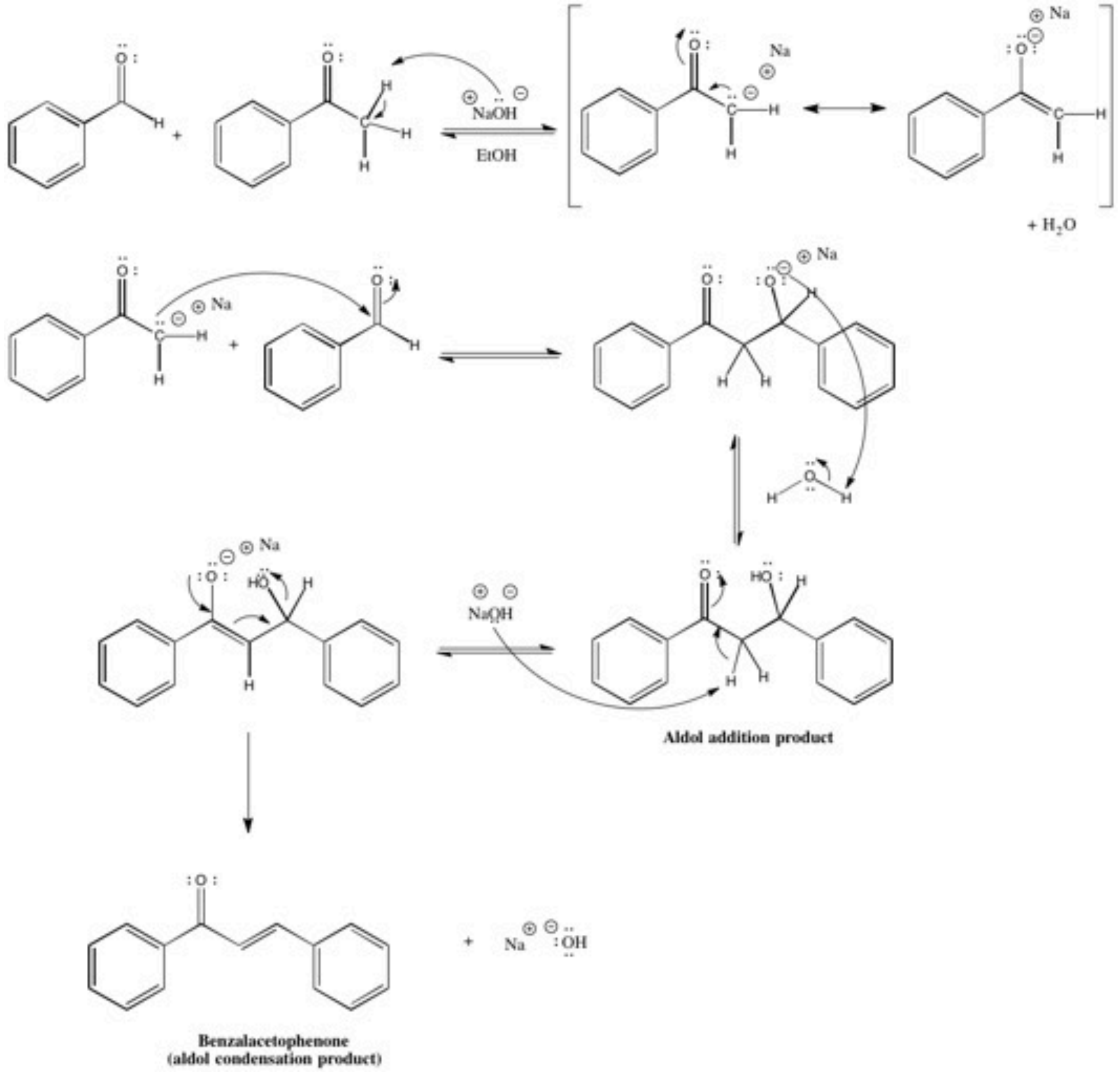
[1] "Laboratory of Organic Chemistry II", Fall 2017Laboratory Manual by Katherine McGilvray, page 61.

[2] "Laboratory of Organic Chemistry II", Fall 2017Laboratory Manual by Katherine McGilvray, page 64.

Mechanism

Part A

Figure 1: Reaction mechanism showing the base-catalyzed aldol condensation of benzaldehyde and acetophenone to form benzalacetophenone.



Part B

Figure 2: Reaction mechanism showing the haloform reaction between acetophenone and sodium hypochlorite (NaOCl) to form the carboxylate product.

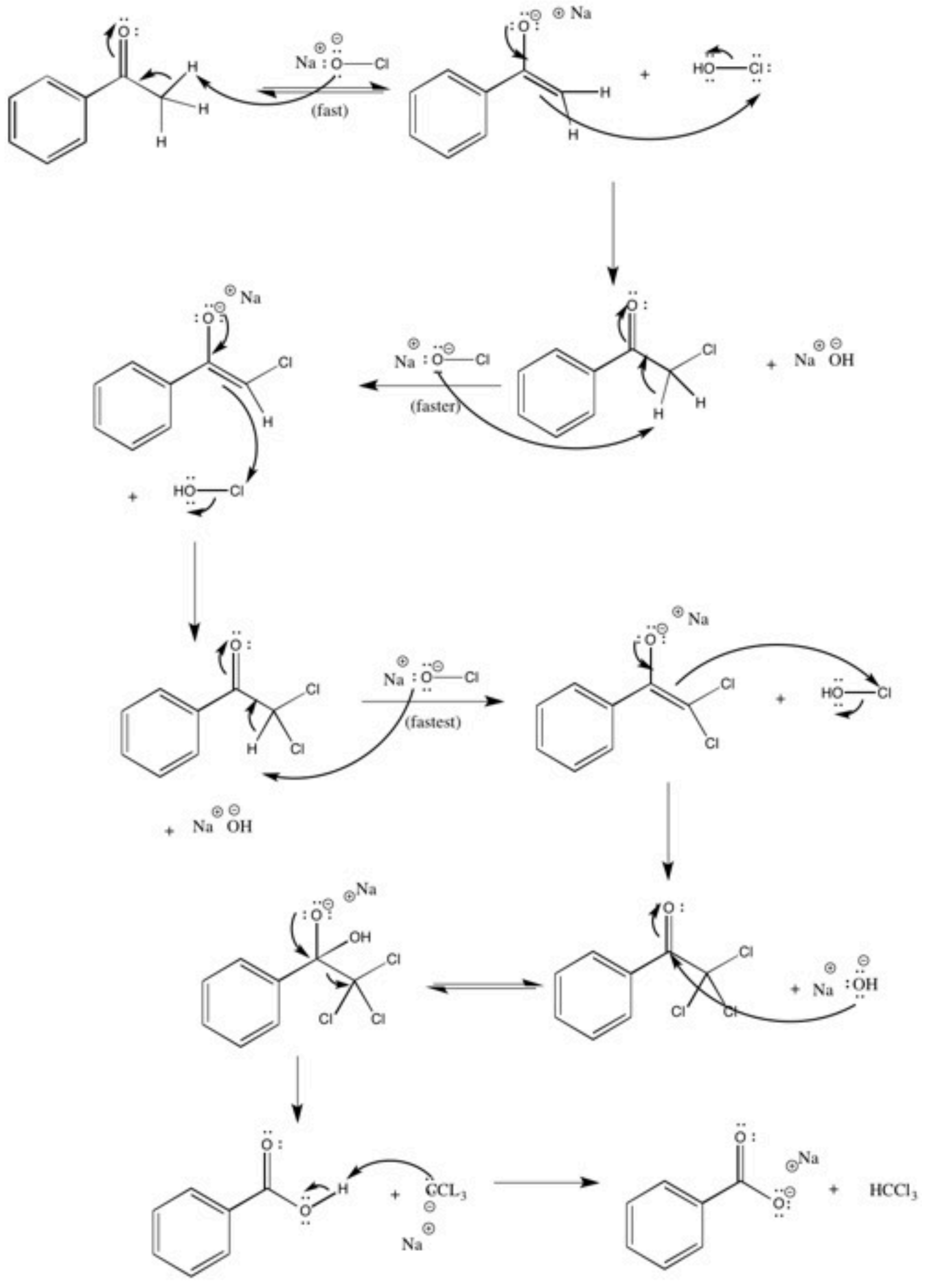


Table of Reagents

Part A

Reagent	Literature Boiling Point (°C)	Molecular Mass (g/mol)	Quantity	Density (g/mL)	Mmol	Equivalents
Acetophenone	202.0	120.16	1.0 mL	1.03	8.6	1
Benzaldehyde	178.0	106.13	1.0 mL	1.044	9.8	1.14
EtOH	-	46.07	4.0 mL	0.789	86.82	10.1
10% NaOH	-	39.997	4.0 mL	0.11	100.01	11.63

Part B

Reagent	Literature Boiling Point (°C)	Molecular Mass (g/mol)	Quantity	Density (g/mL)	Mmol	Equivalents
Acetophenone	202.0	120.16	1.0 g	1.03	8.32	1
5% NaOCl in H_2O	-	74.44	40 mL	1.097	537.35	64.59
Acetone	-	58.08	0.5 mL	0.791	8.61	1.03

Experimental Procedure

“Laboratory of Organic Chemistry II”, Fall 2017 Laboratory Manual by Katherine McGilvray pages 60 to 67.

Modifications

No modifications were made for this lab.

Observations

Part A

Key Step	**Observation**
4.0 mL of 10% NaOH combined with 4 mL of EtOH in a 50 mL round bottom flask	10% NaOH and EtOH are clear, colorless, strong-smelling liquids.
1.0 mL of acetophenone dissolved in the above solution.	Acetophenone is a clear, colorless, sweet-smelling liquid.
1.0 mL of benzaldehyde added to mixture along with a magnetic stir bar.	Benzaldehyde is a clear, colorless, strong-smelling liquid. Mixture turned cloudy with a slight yellow color soon after the stir plate was turned on.
Mixture was left to react and was monitored for 45 minutes.	Mixture becomes more and more yellow as time goes by and the reaction goes on. After 45 minutes a yellow precipitate formed at the bottom of the flask. The product formed is yellow, causing the yellow color of the reaction mixture. The more product is formed, the yellower the reaction mixture becomes.
Reaction mixture was transferred into an Erlenmeyer flask using a filter funnel and was cooled an ice bath.	Some product might have been lost while transferring the reaction mixture because crystals already started forming while the mixture was being filtered through the filter paper. Thus, our crude product yield was very low and we only had 0.01 g of crude product. More crystals were formed in the Erlenmeyer flask while the mixture was being cooled in the ice bath.
The crude crystals were filtered by suction filtration and were washed with cold ethanol and cold water.	A white opaque mother liquor was formed when the crude product was washed with cold ethanol and cold water.
Crude product was dissolved in a minimum amount of boiling ethanol.	Crude product dissolved ethanol was a clear yellow liquid and did not form crystals while being air cooled or cooled in the ice bath. We did not achieve a purified product yield, thus data for the crude product and purified product and TLC for part A was borrowed from Krista Blais and Cameron Hines.

Part B

Key Step	**Observation**
1.0 g of acetophenone were added to 40 mL of bleach solution.	Reaction mixture was initially colorless, then turned a pale yellow, transparent liquid. Reaction mixture turned colorless again after boiling.
Solution was acidified drop-wise with HCl until the pH was near 1 and no more precipitate was formed.	White precipitate formed while HCl was being added step-wise to reaction mixture. pH paper turned from blue to pink when the pH of the reaction mixture turned acidic.

Results

Part A

Compound	**Molecular Mass (g/mol)**	**Quantity**	**Mmol**	**Yield (%)**	**Literature melting point (°C)**	**Experimental melting point (°C)**
Crude product	-	0.63 g	-	-	-	50.1 – 51.3
Benzalacetophenone (purified product)	208.26	0.81 g	3.89	45.23	58 - 59	55.4 – 56.0

Part B

Compound	**Molecular Mass (g/mol)**	**Quantity**	**Mmol**	**Yield (%)**	**Literature melting point (°C)**	**Experimental melting point (°C)**
Carboxylate product	121.12	1.93 g	15.93	191.47	-	109.5

Melting Points

Part A

The melting point for the crude product was measured to be in the range of 50.1 – 51.3°C and the melting point for the purified product, benzalacetophenone, was measured to be in the range of 55.4 – 56.0°C.

Part B

The melting point of the carboxylate product was measured to be 109.5°C.

Calculations

Sample mole calculation:

$$n(benzalacetophenone) = \frac{mass}{molecular\ mass} = \frac{0.81\ g}{208.26\ {}^{g}/_{mol}}\ x\ \frac{1000\ mmol}{1\ mol}$$

$$n(benzalacetophenone) = 3.89\ mmol$$

Sample calculation for the percentage yield for benzalacetophenone.

$$\%yield = \frac{mol\ product}{mol\ starting\ material}\ x\ 100\% = \frac{3.89\ mmol\ benzalacetophenone}{8.6\ mmol\ acetophenone}\ x\ 100\%$$

$$\%yield = 45.23\ \%$$

TLC

Part A

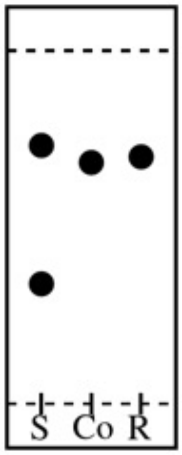


Figure 3: TLC plate for part A of the experiment.

Solvent system: 1:4 ethyl acetate:hexanes
Sample spot: acetophenone and benzaldehyde
Co-spot: crude product in acetone
Reference spot: purified product in ethanol

R_f values for the reference lane is: 0.34, 0.73
R_f value for the co-spot lane is: 0.68
R_f value for the sample lane is: 0.70

Part B

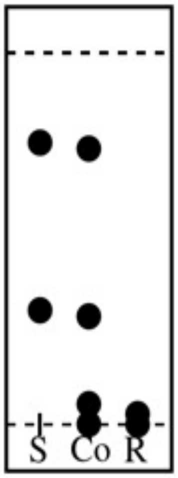


Figure 4: TLC plate for part B of the experiment.

Solvent system: 1:4 ethyl acetate:hexanes
Sample spot: acetophenone
Co-spot: acetophenone and reaction mixture
Reference spot: reaction mixture

R_f values for the reference lane is: 0.31, 0.76
R_f values for the co-spot lane is: 0.0, 0.05, 0.29, 0.74
R_f values for the sample lane is: 0.0, 0.02

Discussion

Part A

The purpose of part A pf this experiment was to an aldol reaction between acetophenone and benzaldehyde in order to form benzalacetophenone. The base catalyst sodium hydroxide (NaOH), the solvent ethanol (EtOH), and the reactants acetophenone and benzaldehyde were combined in a round-bottom flask and equipped with a magnetic stir bar. The flask as then clamped above a stir plate and was left to react for 45 minutes. The reaction mixture initially started off as an opaque, light yellow liquid, and became a stronger yellow color over time due to the formation of a solid yellow product being formed at the bottom of the flask over time.

The reaction was stopped after 45 minutes and the reaction mixture was filtered into an Erlenmeyer flask using a filter funnel. The flask was rinsed with ethanol to ensure the complete transfer of the reaction mixture in to the Erlenmeyer flask.

Some product already started forming crystals while the mixture was being poured through the filter paper, leading to the loss of some crude product. Thus, our crude product yield was very low, with only 0.01 g of crude product.

After the transfer was complete, the reaction mixture was cooled in an ice bath and was left to sit for 30 minutes so the product could crystallize. The resulting crystals were filtered by suction filtration using a Buchner funnel, were washed with cold water and cold ethanol, were dried by aspiration. The product was weighed, measuring 0.01 g. When attempting to determine the melting point of the crude product, the product got stuck at the open end of the sample tube and could not be brought to the bottom, meaning that the melting point could not be determined.

Next, a recrystallization was performed. The crude product was dissolved in a small amount of boiling ethanol and the solution was allowed to cool at room temperature for 10 minutes, allowing crystallization to occur, and was cooled further in an ice bath for another 5 minutes.

After 5 minutes in the ice bath, recrystallization should have been completed and the resulting purified product would then be filtered by suction filtration and dried by aspiration. After the mass of product formed would be determined, a small amount of pure product would be dissolved in ethanol and a TLC would be taken to verify the purity of the product. Finally, the melting point would have been determined.

However, our crude product dissolved in ethanol did not form crystals while being air cooled or cooled in the ice bath, and we did not achieve a purified product yield. Because of this, data for the crude and purified products for part A of this experiment were obtained from Krista Blais and Cameron Hines. The obtained data showed that the crude product obtained had a mass of 0.63 g, with a melting point range of 50.1°C – 51.3°C. The mass of benzalacetophenone, the purified product, obtained was 0.81 g and had a 45.23% yield. The measured melting point for benzalacetophenone was in the range of 55.4°C – 56.0°C. From the TLC plate, which was taken in order to verify the purity of the final product, it can be concluded that the purified product does not contain the impurities that the reaction mixture (sample lane) contained, meaning that it had been successfully purified. This can be seen because there are two spots in the lane containing the reaction mixture, one with an R_f value of 0.34 and the other with an R_f value of 0.73. In the lane containing benzalacetophenone only (reference lane), only one spot with an R_f value of 0.70 can be observed. Thus, we can say that the purified product does not contain any of the more polar compounds, which correspond to the dot with an R_f value of 0.34 in the sample lane, that the reaction mixture does.

Error committed in this part of the experiment were filtering the reaction mixture with filter paper instead of just pouring it directly into an Erlenmeyer flask using a filter funnel. This lead to the loss of some crude product because the crystals already started forming in the filter paper instead of the Erlenmeyer flask. Thus, our crude product yield was very low, with only 0.01 g of crude crystals. Another error that could have been committed was using too much ethanol as a solvent when attempting recrystallization. Using too much solvent would leave too much pure product in solution, resulting in a lower yield of pure product than expected. Using too little solvent would lead to a very fast crystal growth, resulting in the formation of impure crystals and the formation of very small pure crystals. The small size of the pure crystals can lead to the loss of product as the crystals might be able to fit through the filter paper used for suction filtration.

Part B

The purpose of part B of this experiment was to perform a haloform reaction between acetophenone and sodium hypochloride (NaOCl). NaOCl provides a great source of electrophilic halogens, since oxygen is more electronegative than both chlorine and bromine. It can also act as a base, meaning that of NaOH is not required as a reagent[3].

To start off, the reactants, acetophenone and bleach solution, which consisted of 5% NaOH in water, were combined in a round bottom flask equipped with a magnetic stir bar, which was clamped above a stir plate. The reaction was left to run until it subsided and the reaction mixture was boiled gently for 10 minutes using a heating mantle. A TLC was taken of the reaction mixture. From the TLC plate, we can conclude that the reaction mixture contains a more polar product

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[3] "Laboratory of Organic Chemistry II", Fall 2017Laboratory Manual by Katherine McGilvray, page 63.

than the less polar acetophenone starting material. This can be observed because the sample lane, containing acetophenone has two spots, one with an R_f value of 0.31 and the other with an R_f value of 0.76, indicating fairly non-polar compounds which, due to their polarity or lack thereof, had the ability to move further up the TLC plate. The reference lane containing the reaction mixture contains two spots which correspond to more polar compounds, as they did not move as far up the TLC plate. These spots have R_f values of 0.0 and 0.02. These TLC results show that the product formed the product formed is more polar than the starting material. This is true as the product contains a carboxylate functional group and the starting material, acetophenone only contains a carbonyl functional group. Since a carboxylate has more electronegative atoms than a carbonyl, the product containing the carboxylate is a more polar molecule and will not travels as far up the TLC plate as the acetophenone which only contains one electronegative atom.

Next, acetone was added to the reaction mixture to destroy any unreacted NaOCl. The acetone will destroy any unreacted NaOCl by reacting with it and forming chloroform, which can then be removed along with any unreacted acetone by boiling the reaction mixture for an additional 15 minutes.

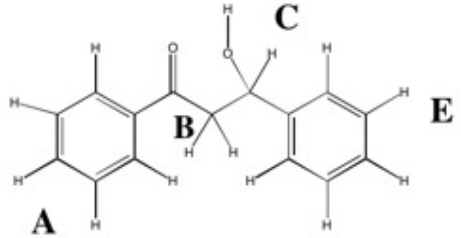
The mixture was poured into am Erlenmeyer flask using a filter funnel and was cooled in an ice bath, after which it was acidified by adding concentrated HCl drop-wise until it reached a pH value of around 1 and no more precipitate was formed. Litmus paper was used to keep track of the acidity of the mixture. Litmus paper initially has a blue color and turns pink when it comes into contact with an acidic substance.

The reaction mixture was cooled for an additional 5 minutes in an ice bath so that the precipitation could be completed. Finally, the product was filtered out using suction filtration and the crystals were washed with cold water, after which they were left to dry. The mass of carboxylate product obtained was 1.93 g and the measured melting point was 109.5°C. However, a percentage yield of 191.47% was calculated, meaning that an error was committed at some point in the experiment.

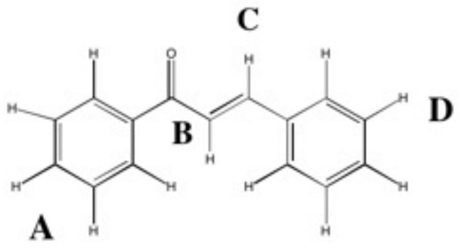
Possible error sources could have been not drying the product enough, resulting in some water remaining between the crystals and contributing to extra mass, causing a higher percentage yield than wanted. Another error source could have been not weighing the product properly and/or accurately. This would lead to inaccurate data for the mass of the product,

^{1}H NMR Analysis

1. The aldol product contains a carbonyl (RC=O) functional group and a CH_2, whereas the condensation product contains a carbonyl (RC=O) functional group and a double bond, and no CH_2, where the two ketones attached to each other.



Aldol product



Condensation product

<u>Table for the aldol product:</u>

Signal	Chemical shift	Integration	Multiplicity	Comments/ideas
A	6.5 – 8.0	5H	m	Aromatic ring with 5 hydrogens, next to a C=O
B	2.1 – 2.5	2H	d	-CH_2- next to a C=O
C	variable	1H	t	CH next to a
D	2.3 – 2.7	5H	m	Aromatic ring with 5 hydrogens, next to a -CH-

Table for the condensation product:

Signal	**Chemical shift**	**Integration**	**Multiplicity**	**Comments/ideas**
A	6.5 – 8.0	5H	m	Aromatic ring with 5 hydrogens, next to a C=O
B	4.5 – 7.0	1H	d	CH next to a CH
C	4.5 – 7.0	1H	d	CH next to a CH
D	2.3 – 2.7	5H	m	Aromatic ring with 5 hydrogens, next to a -CH-

2. Molecular formula of unknown: **$C_8H_8O_2$**

Degree of unsaturation = (2C + 2 + N – H – X)/2 = (2 x 8 + 2 – 8)/2
Degree of unsaturation = 5

The large, broad peak at 3147 cm^{-1} corresponds to C-H bonds with an sp^2 carbon. And the strong, sharp peak at 1645 cm^{-1} corresponds to a carbonyl functional group ($R_2C=O$).

Signal	Chemical shift	Integration	Multiplicity	Comments
A	8.5	1H	s	-CH(=O)
B	7.9	2H	d	Aromatic H, next to 1H
C	7.0	2H	d	Aromatic H, next to 1H
D	2.6	3H	s	CH_3- next to an oxygen

Thus, one possible structure of the unknown would be: