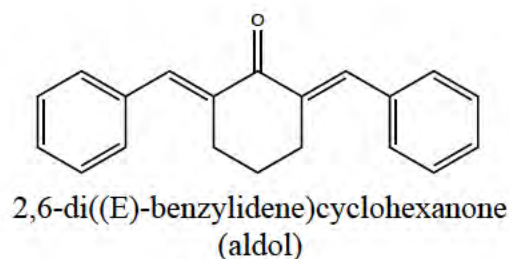
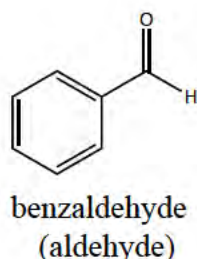
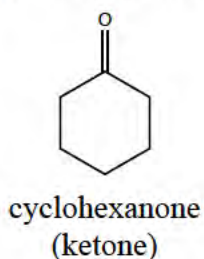
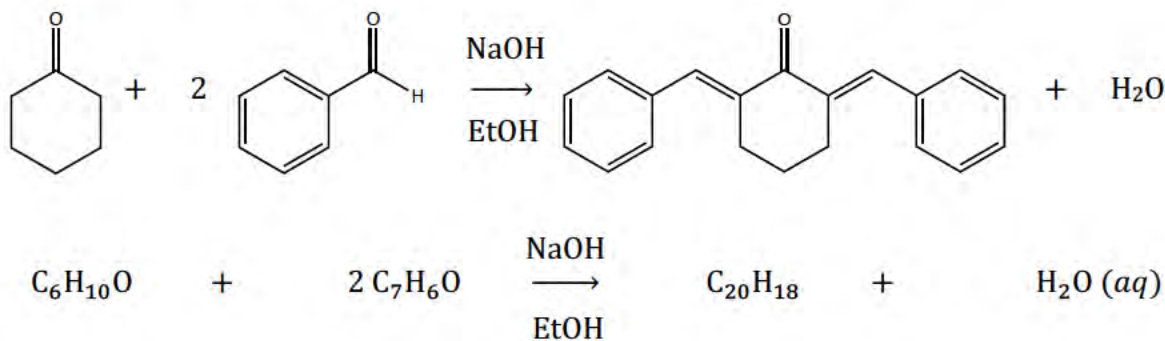


**Purpose**

To carry out a mixed aldol condensation and analyze the product by melting point,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR to determine the identity of the starting material.

**Unknown**

C1 (Assigned B1, but accidentally used a different ketone, most likely C)

**Proposed Structures****Proposed Chemical Equation****Calculations**

$$m_{\text{theoretical yield aldol}} = m_{\text{limiting reagent-cyclohexanone}} \left( \frac{1 \text{ mol}_{\text{cyclohexanone}}}{\text{MW}_{\text{cyclohexanone}}} \right) \left( \frac{\text{MW}_{\text{product}}}{1 \text{ mol}_{\text{product}}} \right)$$

$$= 0.25 \text{ g} \left( \frac{1 \text{ mol}}{98.15 \text{ g}} \right) \left( \frac{274.36 \text{ g}}{1 \text{ mol}} \right) \approx 0.70 \text{ g aldol}$$

Limiting reagent determination shown in Table 1. Calculations based on product identity being 2,6-dibenzylideneacetone as predicted.

$$m_{\text{crude}} = m_{\text{watch glass and crude}} - m_{\text{watch glass}} = 54.30 \text{ g} - 53.60 \text{ g} = 0.70 \text{ g crude}$$

$$\% \text{ yield}_{\text{crude}} = \left| \frac{m_{\text{crude}}}{m_{\text{theoretical yield crude product}}} \right| \times 100 = \left| \frac{0.70 \text{ g}}{0.70 \text{ g}} \right| \times 100 = 100. \% \text{ crude yield}$$

Not enough recrystallized product was recovered to mass (barely enough for melting point analysis), thus the recrystallization calculation uses 0 g recovered.

$$\% \text{ recovery} = \left| \frac{m_{\text{recovered recrystallized}}}{m_{\text{crude}}} \right| \times 100 = \left| \frac{0\text{g}}{0.70\text{g}} \right| \times 100 \approx 0\% \text{ recovery}$$

## Results

**Table 1** Reactant Reagent Table

<i>Reactant</i>	Molar mass (g/mol)	Density (g/ml)	Amount used	Moles used	Relative molar ratio	Stoichiometric molar ratio*
<i>Benzaldehyde</i>	106.12	1.04	1 ml	$9.80 \times 10^{-3}$	3.85	2
<i>Cyclohexanone</i>	98.15	0.948	0.25 g	$2.55 \times 10^{-3}$	1	1

Only the reactants involved in the main reaction are included for the sake of determining the limiting reagent. Catalysts, solvents, and reagents clearly in excess were deemed irrelevant and thus not included. The identity of the ketone and aldehyde, as well as the relevant calculations and stoichiometric ratios, were based on the predictions made.

The tabulated data suggests cyclohexanone was the limiting reagent in this reaction.

**Table 2** Mass and yield of products

<i>Category</i>	Mass recovered (g)	Theoretical yield (g)	Percent yield/recovery (%)
<i>Crude Product</i>	0.70	0.70	100.
<i>Recrystallization</i>	0	0.70	0

Practically no recrystallized product recovered to mass.

**Table 3** Melting points of relevant compounds

<i>Compound</i>	Melting Point (°C)	
	Experimental	Literature
<i>Crude Product</i>	101.1-114.9	—
<i>Recrystallized Product</i>	117.1-118.0	—
<i>2,6-dibenzylidenecyclohexanone</i>	—	118
<i>Dibenzylideneacetone</i>	—	113
<i>2,6-bis(4-fluorobenzylidene)cyclohexanone</i>	—	118-120

**Table 4**  $^{13}\text{C}$  NMR spectrum absorption maxima ( $\text{cm}^{-1}$ ) and peak assignments

<i>Chemical shift (ppm)</i>	Carbon identification label
22.99	$\text{sp}^3$ carbon (A)
28.44	$\text{sp}^3$ carbons (B)
128.36	aromatic $\text{sp}^2$ carbon (C)
128.57	aromatic $\text{sp}^2$ carbon (D)
130.36	aromatic $\text{sp}^2$ carbon (E)
135.94	vinyl $\text{sp}^2$ carbon (F)
136.15	aromatic allylic $\text{sp}^2$ carbon (G)
136.92	vinyl $\text{sp}^2$ carbon (H)
190.38	carbonyl (ketone) carbon (I)

Refer to spectrum for carbon identification. Difficult to specify which  $\text{sp}^2$  carbons between 128 and 137 ppm are vinyl, allylic, or aromatic.

**Table 5**  $^1\text{H}$  NMR spectrum analysis

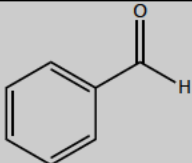
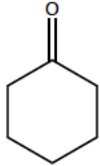
<i>Chemical Shift (ppm)</i>	<i>Relative integration</i>	<i>Multiplicity</i>	<i>Proton identification label</i>
$\approx 0.50$	$\approx 3$	triplet	1 saturated H (A)
$\approx 2.85$	$\approx 1$	doublet or triplet*	2 allylic Hs (B)
$\approx 3.15$	$\approx 3$	triplet	1 vinylic H (C)
$\approx 6.75$	$\approx 1$	singlet*	5 aromatic Hs (D)

\*difficult to discern

Refer to spectrum for proton identification and further explanation.

$^1\text{H}$  NMR spectrum results did not seem reasonable, nor did they align with any of the possible ketones or aldehydes. The presence of an integration of only 1 at a shift corresponding to an aromatic proton considering the expectation of at least 4 or 5 aromatic hydrogens (considering the symmetry the possible aldehydes which all contain benzene ring in some form).

**Table 6** Identity of starting materials

<i>Starting Material Class</i>	<i>Unknown</i>	<i>Proposed Identity</i>	<i>Proposed Structure</i>
<i>Aldehyde</i>	1	benzaldehyde	
<i>Ketone</i>	C (most likely)	cyclohexanone	

## Discussion/Conclusions

After performing a mixed aldol condensation with an unknown ketone and alcohol combination in ethanol, under basic conditions, an aldol was successfully produced. Analysis of this aldol allowed for the identification of the unknown ketone and aldehyde most likely as cyclohexanone and benzaldehyde respectively, forming the aldol, 2,6-di((E)-benzylidene)cyclohexanone. Melting point analysis revealed the aldol's melting point range 117.1-118.0 °C in the case of the recrystallized product (101.1-104.9 °C for the crude). This most closely aligned with 2,6-di((E)-benzylidene)cyclohexanone, whose melting point is 118 °C. However, dibenzylideneacetone (113 °C) and 2,6-bis(4-fluorobenzylidene)cyclohexanone (118-120 °C) could not be eliminated due to their melting point's being close to that of the crude and recrystallized respectively. While it was difficult to discern the ketone and aldehyde for certain due to the possibility of using the incorrect ketone during the experiment, cyclohexanone seemed the likeliest ketone given the most closely matching melting point as well as the knowledge that I most probably used ketone C rather than ketone B (since those were the two ketones at the station I retrieved my reagent from). By comparing the different ketones combined with aldehyde 1, it became clear that C was the cyclohexanone due to the number of carbon peaks (the number of carbons increased by 1 from A to B to C to D when the aldehyde was kept constant, coinciding with ketones which also differed by 1 carbon each). The 8 carbon environments in the  $^{13}\text{C}$  NMR corresponded to the mixture of benzaldehyde with cyclohexanone.  $^1\text{H}$  NMR served little purpose in confirming or disproving this prediction since it matched no possible products. There was clearly an issue with the spectrum since only 1 proton appeared in the region where aromatic protons would be

expected. Using the predicted reagents, a balanced equation was proposed wherein 1 cyclohexanone reacted with 2 benzaldehydes to form 1 2,6-di((E)-benzylidene)cyclohexanone and water under the reaction conditions. This balanced chemical equation allowed for the determination of the limiting reagent, cyclohexanone, as well as the percent yield of crude 100.0%. Since practically no recrystallized product was able to be recovered (only enough to perform melting point analysis, but not enough to even mass), percent recovery was 0%.

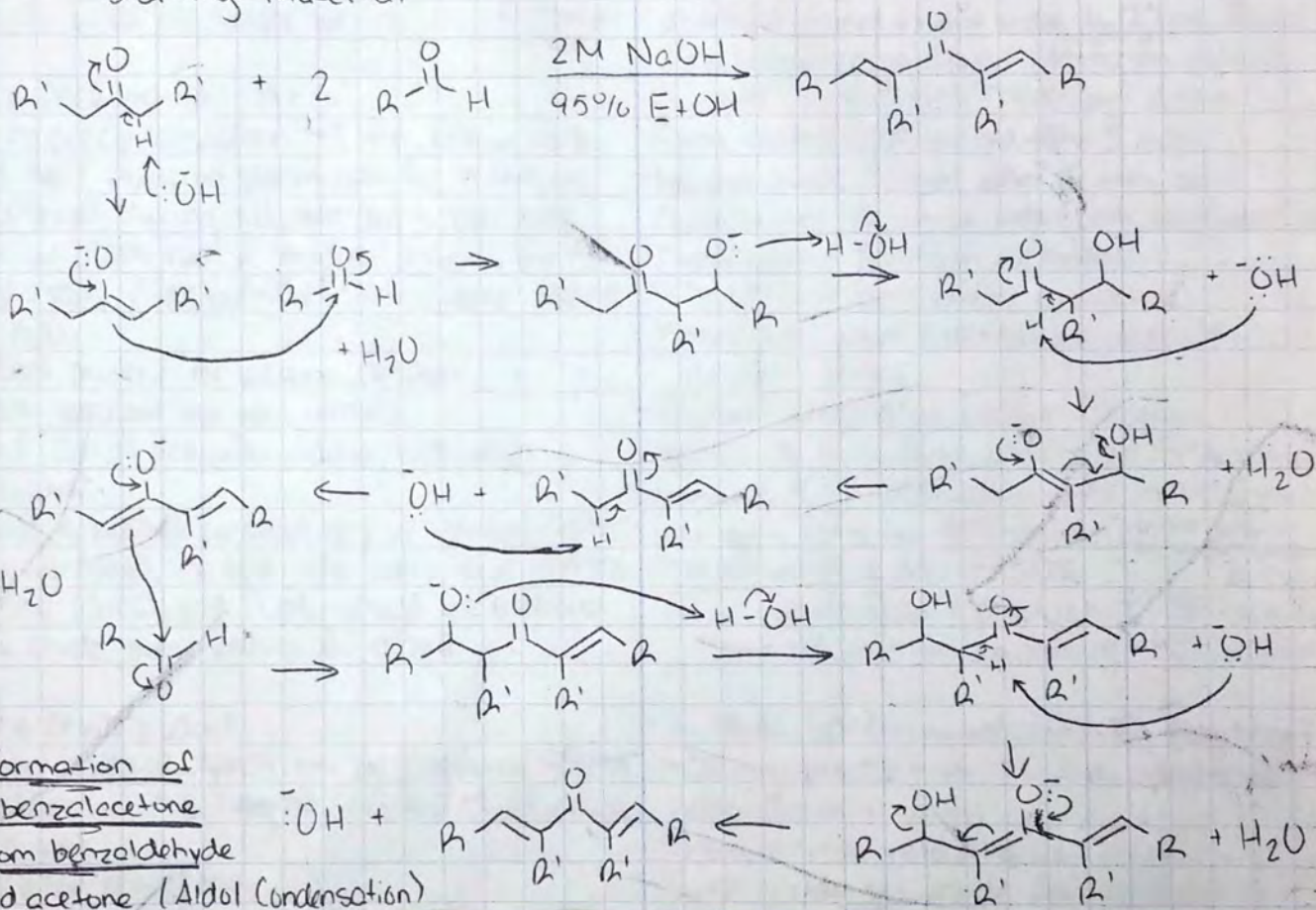
## References

*Experiment 6 Aldol Condensation, Chemistry 52 Laboratory.* Department of Chemistry, Dartmouth College, 2019.

*Sigmaaldrich.com. (2019).* Sigma Aldrich, 2019.

Exp. No. 6	Experiment/Subject Mixed Aldol Condensation	Date 8/8/19
Name Matthew Fam	Lab Partner	Locker/Desk No. Course & Section No.

Purpose: To carry out a mixed aldol condensation and analyze the product by melting point, <sup>1</sup>H NMR, and <sup>13</sup>C NMR to determine the identity of the starting material



Reagent	Mass (g)	Volume (ml)	Concentration (M)	Safety/Notes
ketone *volatile (100%)	.25	5 (2.5)		95% ethanol - highly flammable, eye irritant; fresh air, wash, rinse sodium hydroxide - corrosive, skin/eye damage; fresh air, wash, rinse acetic acid - flammable, skin/eye damage; fresh air, wash, rinse deuterated chloroform - harmful if swallowed, skin/eye irritant, toxic if inhaled, carcinogen, damages fertility and organs; fresh air, wash, rinse toluene - flammable, fatal if swallowed and enters airway, skin irritant, drowsiness, damages fertility/organs; wash, rinse, fresh air
ethanol (95%)	—	5 (2.5)		
aq sodium hydroxide	—	4	2M	
aldehyde	1.8 (4.5)	1 (unlabeled)		
4% acetic acid (in 95% ethanol)	—	.5		
deuterated chloroform	—	~0.7		
toluene	—	depends on # (Table 1)		

Signature	Date	Witness TA	Date
-----------	------	------------	------

Exp. No. 6	Experiment/Subject Mixed Aldol Condensation	Date 8/8/19	27
Name Matthew Farn	Lab Partner	Locker/Desk No.	Course & Section No.

Procedure: Add 0.25g ketone, 95% ethanol, (5 mL), 4 mL 2M aq. sodium hydroxide, and 1.0 mL aldehyde (1.8 g if aldehyde 5) in that order in 25 mL Erlenmeyer flask

Cork flask and stir 15 min. If no precipitate, after ~5 min, remove cork and heat flask on steam bath for 15 min w/ occasional stirring and then cool to room temp. Stir w/ glass rod if product prevents stir bar. Cool flask in ice bath for 5 min (whether heated or not).

Collect product by vacuum filtration. Break vacuum between washes. Wait 20-30 sec after adding each wash to vacuum

Crude is washed consecutively w/ ice-cold 95% ethanol (5 mL), ice cold 4% acetic acid in 95% ethanol (5 mL), and 5 mL ice-cold 95% ethanol. Dry crude over vacuum for 10 min

Mass crude product

Obtain <sup>1</sup>H NMR spectrum by dissolving ~50 mg product in ~0.7 mL deuterated chloroform in a vial.

Check for homogeneity. If needed, filter solution through cotton pipet filter into NMR tube.

Set aside some crude for melting point analysis. 85°C - 260°C @ 20°C ramp rate for estimate then 1-2°C ramp rate to get more exact

Recrystallize not more than 0.5g crude from toluene or 95% ethanol (refer to table 1).

Collect recrystallized product by vacuum filtration rinse w/ appropriate volume ice cold solvent, and dry over vacuum ~10-15 min

Obtain mass and melting point range dry product. Print/analyze appropriate <sup>13</sup>C NMR.

Submit recrystallized product in labelled scintillation vial (white cap)

Show excess crude to TA and dispose of in solid waste.

Observations: → Assigned B1 (may have accidentally used different ketone, most likely B or C)

• 0.25g ketone, 5 mL ethanol, 4 mL 2M aq. sodium hydroxide, and 1.0 mL aldehyde added in that order to 25 mL flask → no precipitate, so heated; orange-yellow liquid; some slightly lighter precipitate

• Flask corked and stirred 15 min

• No precipitate formed after 5 min, so flask heated 15 min on steam bath, occasional stir

• Flask cooled 5 min in ice bath → bright, yellow, clumpy precipitate → some precipitate filtered out despite ice-cold washes

• Product collected via vacuum filtration

• Washed 3 times, first w/ 5 mL ice cold 95% ethanol, then w/ 5 mL 4% acetic acid in 95% ethanol, and again w/ 5 mL 95% ethanol (broke vacuum between washes) → mass watch glass 53.60g then dried watch glass + product 54.30 10 min over vacuum) \* some set aside for mp analysis

• <sup>1</sup>H NMR spectrum obtained by dissolving ~50 mg product in ~0.7 mL deuterated chloroform in a vial

→ Homogenous yellow liquid

• Some crude set aside for mp analysis → 0.11 g used for recrystallization

• Recrystallized 0.41 g crude from toluene (as specified by table 1) → could not get recrystallization to occur → 0.26 g despite attempts to add more crude and reattempt as well as addition of other person's

→ shiny, small, yellow recrystallized product to solution.

crude 101.1°C 114.9°C recrystallized product 117.1°C 118.0°C

→ Not enough recrystallized product to mass/submit I had anyway and had just enough for mp analysis

Signature	Date	Witness/TA	Date
-----------	------	------------	------