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# Enolate Reaction with Carbonyl Groups



Student Name

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# Part A

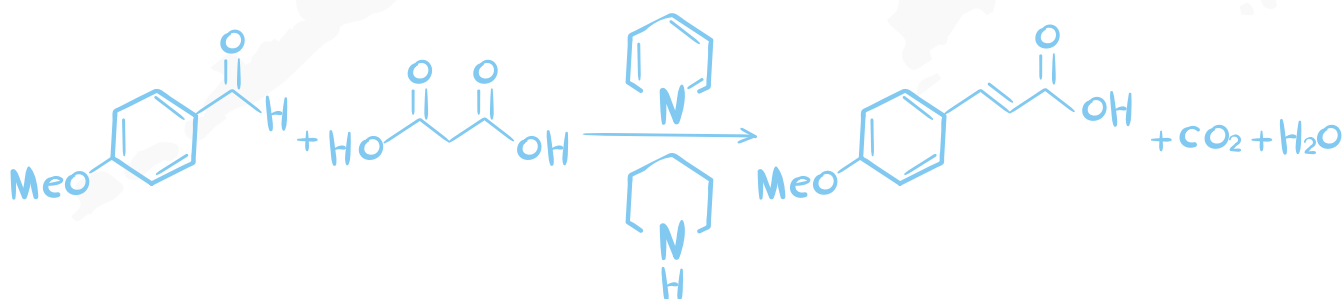


Reaction of enolate ions with Carbonyl Groups

## Aim

To prepare *trans*-*p*-methoxycinnamic acid using *p*-anisaldehyde (*p*-benzaldehyde) and malonic acid in presence of pyridine.

### a) *trans*-*p*-Methoxycinnamic acid



## Procedure

3.4 g of *p*-anisaldehyde, 6.5 g of malonic acid and 6 mL of pyridine were measured and placed in a 100mL RB flask. A reflux condenser was then connected to the flask.

The flask fitted to a condenser was placed in a fume hood. 5 drops of piperidine were then added to the mixture in the flask and the flask heated in an oil bath under reflux for 90 minutes.

At the end of 90 minutes, the flask was cooled and its content diluted using an equal volume of water. Concentrated hydrochloric acid was then poured into the contents in the flask.

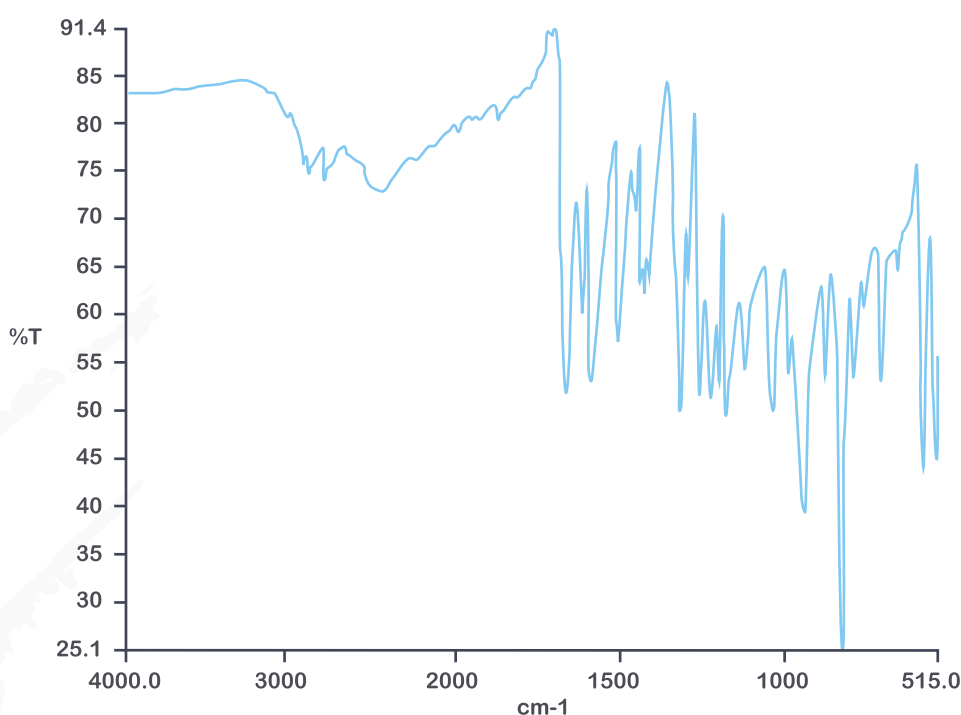
The precipitate collected after addition of concentrated hydrochloric acid was cooled and the resulting product collected by vacuum filtration. The product was then washed using cold water. The product was air dried and its crude mass measured.

After recording the mass, the product was recrystallized from ethanol and an infrared spectrum of this purified product was obtained. The infrared spectrum was then used to identify OH and carbonyl stretches.

## Results and Discussion

Bubbles were observed in the flask during heating. This was as a result of carbon dioxide production from the reaction of p-anisaldehyde and malonic acid.

1.43 g of crude product was collected; its melting point is 166 °C. The infrared spectrum of the purified p-methoxycinnamic acid obtained is as follows:



**Q1. Comment on the temperature of the reaction solution when it is heated under reflux (i.e. at its boiling point) in an oil bath at 120°C vs a Bunsen burner, with a temperature of 400°C.**

The temperature of the reaction solution heated in an oil bath with a reflux connected to it is relatively smooth and constant as compared to the one under a Bunsen burner, which keeps fluctuating.

**Q2. Why does the p-methoxycinnamic acid precipitate upon acidification?**

p-methoxycinnamic acid precipitated out because it was protonated by the concentrated acid. When concentrated hydrochloric acid, which is a stronger acid than p-methoxycinnamic acid, was added to the solution, the hydroxyl groups are protonated.

**Q3. Acquire an infrared spectrum of the purified p-methoxycinnamic acid and identify the carbonyl and OH stretches by annotating the spectrum.**

The infrared spectra of OH groups are characterized by strong absorption bands in the region around 3500 $\text{cm}^{-1}$ . This high-frequency vibration results from the small mass of hydrogen as compared to that of oxygen. The band is usually sharp at around that region. The band with increase occurs because of the formation of hydrogen bonds in the molecule.



## Part B



Condensation of an enolate ion with a carbonyl group.

### Aim

To prepare trans-p-methoxycinnamic acid using p-anisaldehyde (p-benzaldehyde) and malonic acid in presence of pyridine.

### b) Dibenzalacetone



### Procedure

3.5g of sodium hydroxide was measured and dissolved in 30mL water. The sodium hydroxide solution was then mixed with 25mL of ethanol in a 250 ml conical flask and then stirred. The contents in the flask were then placed in a water bath and maintained at a temperature of 20-25 °C.

3.3 g of benzaldehyde and 0.90 g of A.R Acetone were mixed and then divided into two portions.

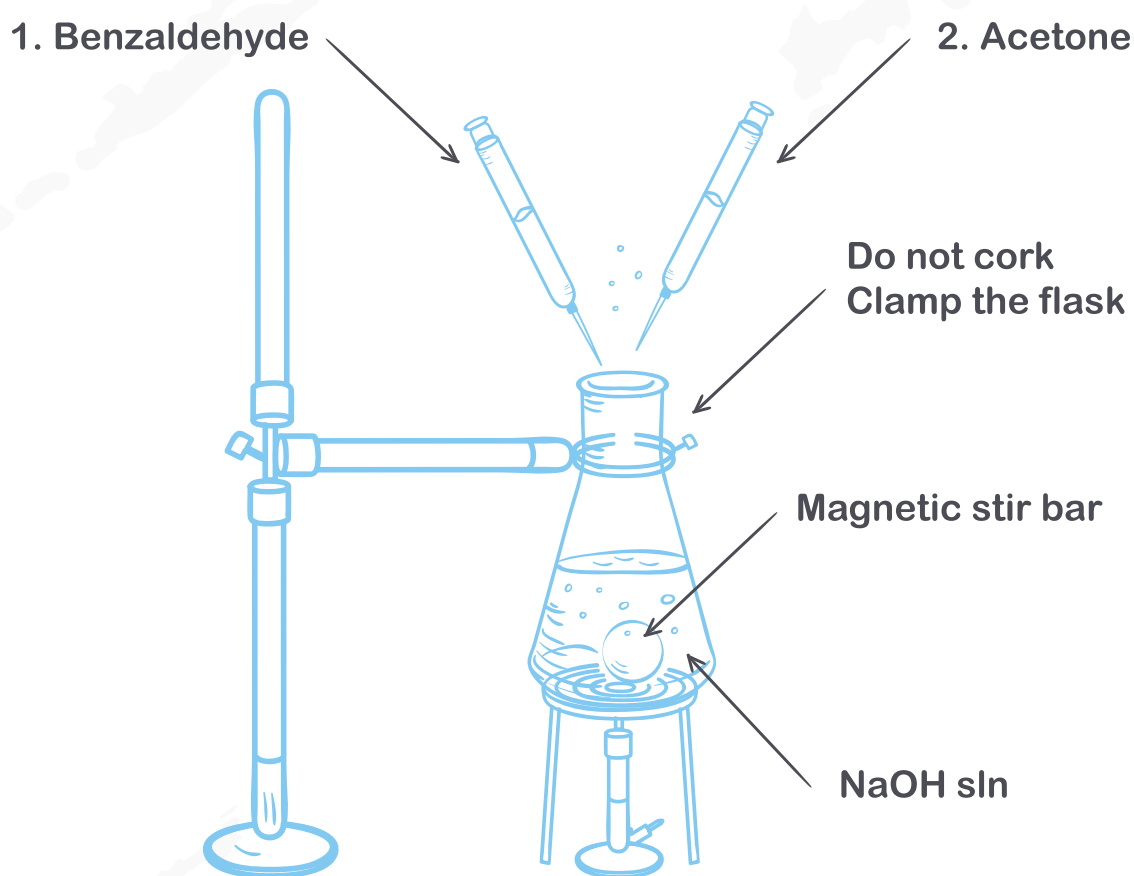
Half of the benzaldehyde-acetone mixture was added in one portion and then stirred vigorously.

After 15 minutes, the remaining half of benzaldehyde-acetone mixture

was added and stirring continued for 30 minutes.

The precipitate after stirring was collected using vacuum filtration and then washed with cold water until washing was neutral.

The crude product was then air-dried and weighed. After weighing, the crude product was recrystallized from methanol, and then was measured again.

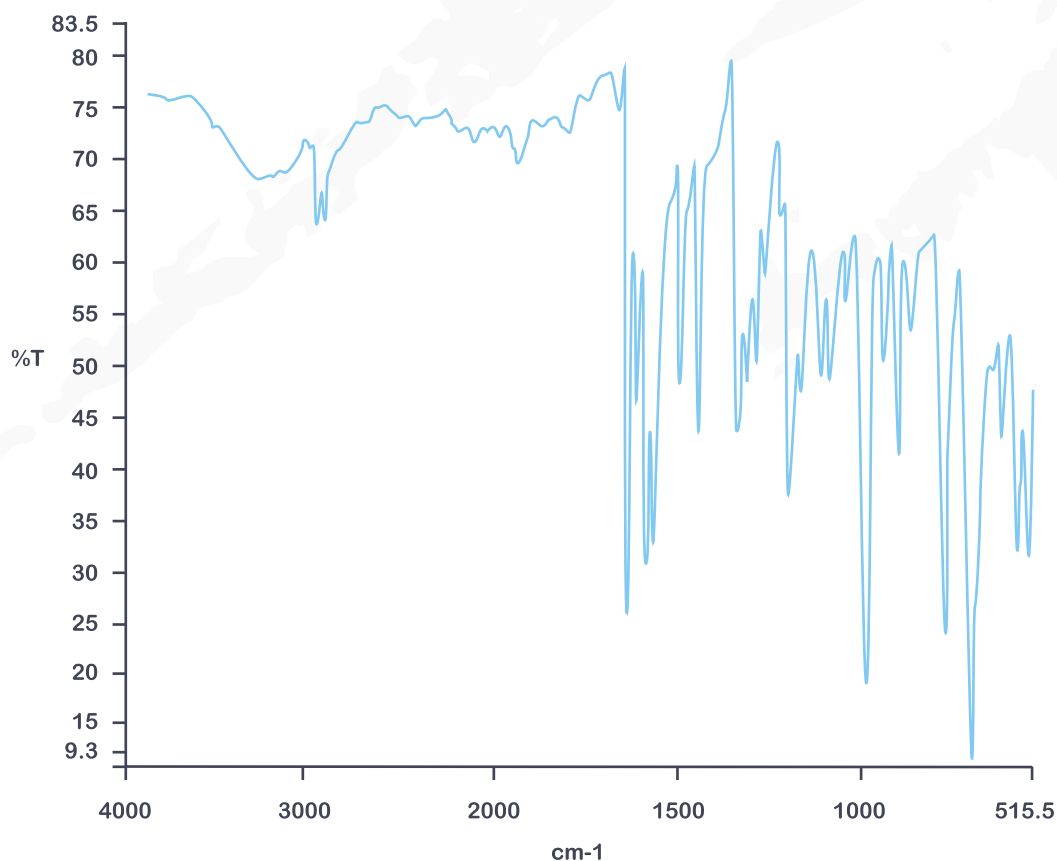


**Fig. 1.** Reaction setup

## Results and Discussions

The mass of the crude product was 6.9838 g and had a melting point of 105 °C.

Infrared spectrum of dibenzalacetone collected is as follows:



### Explain the principle of recrystallization as a purification technique.

Recrystallization is a method used to separate desired chemicals from impurities. The desired compound and the impurities are dissolved in an appropriate solvent. Either the impurities or the desired compound precipitates out of the solution while the other remains in the solution. The technique is named after the crystals, which form when precipitation occurs.



Infrared spectrum of dibenzalacetone collected is as follows:

## Why is dibenzalacetone coloured?

Dibenzalacetone is colored because of the presence of conjugate dienes ( $C=C-C=C$ ) which absorb light in the visible light spectrum giving the compound a yellow colour<sup>2</sup>.

**Acquire an infrared spectrum of the purified dibenzalacetone and identify the absorption associated with the carbonyl stretch by annotating the spectrum.**

The carbonyl group in dibenzalacetone has lower frequency in the infrared spectrum than the standard carbonyl ( $1700\text{cm}^{-1}$ ). This is because dibenzalacetone has conjugated dienes throughout the molecule making the carbonyl group a 1.5 bond due to the presence of delocalized electrons.

The reaction of benzaldehyde (aldehyde) and acetone (ketone) using sodium hydroxide as the base represents a typical aldo condensation reaction<sup>3</sup>. Acetone has hydrogen atoms on both sides making it possible to deprotonate and yield a nucleophile (enolate anion). The carbonyl group of the benzaldehyde is highly electrophilic and reacts rapidly with the enolate ion. The solvent used protonates the alkoxide that is produced resulting in a  $\alpha$ -hydroxyketone while it is dehydrated by the sodium hydroxide.