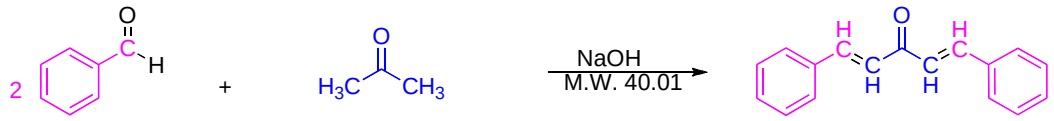
9. Aldol Reaction

M. Jones: Condensation Reactions, Aldol reaction, Chapter 17, Section 3, pgs 840-850.

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

Aldol Reaction. In the experiment, you will perform a base-catalyzed, condensation reaction using benzaldehyde and acetone (see Figure 1). A condensation reaction is one, which condenses two or more molecules to make one single compound.



Benzaldehyde
bp 178-179 °C
density 1.04 g/mL

Acetone (2-propanone)
bp 56 °C
density 0.790 g/mL

Dibenzalacetone (1,5-Diphenyl-1,4-pentadien-3-one), mp 110-112 °C

Figure 1. The overall reaction.

First let's define some different types of compounds. An aldehyde is a molecule with an R-HC=O structure. There is a carbonyl group (C=O). The carbon of the carbonyl group is flanked by a hydrogen (H) and an R group (R does not equal H). A ketone is a molecule with an $R_2C=O$. The R groups do not have to be the same. In this reaction, two molecules of benzaldehyde (aldehyde) are condensed with one molecule of acetone (ketone). Acetone acts as a nucleophile which adds to the carbonyl carbon of benzaldehyde). The first step in the reaction is to form the nucleophile, which is an enolate ion (Figure 2). This is a deprotonation step where a hydroxide ion pulls off a proton from the alpha carbon (carbon adjacent to the carbonyl carbon) to yield a resonance-stabilized enolate. The nucleophile adds to the carbonyl carbon of benzaldehyde in step 2. The resulting alkoxide

ion is protonated in step 3 to form the "true" Aldol product which has both alcohol (OH) and carbonyl (C=O) functionalities.

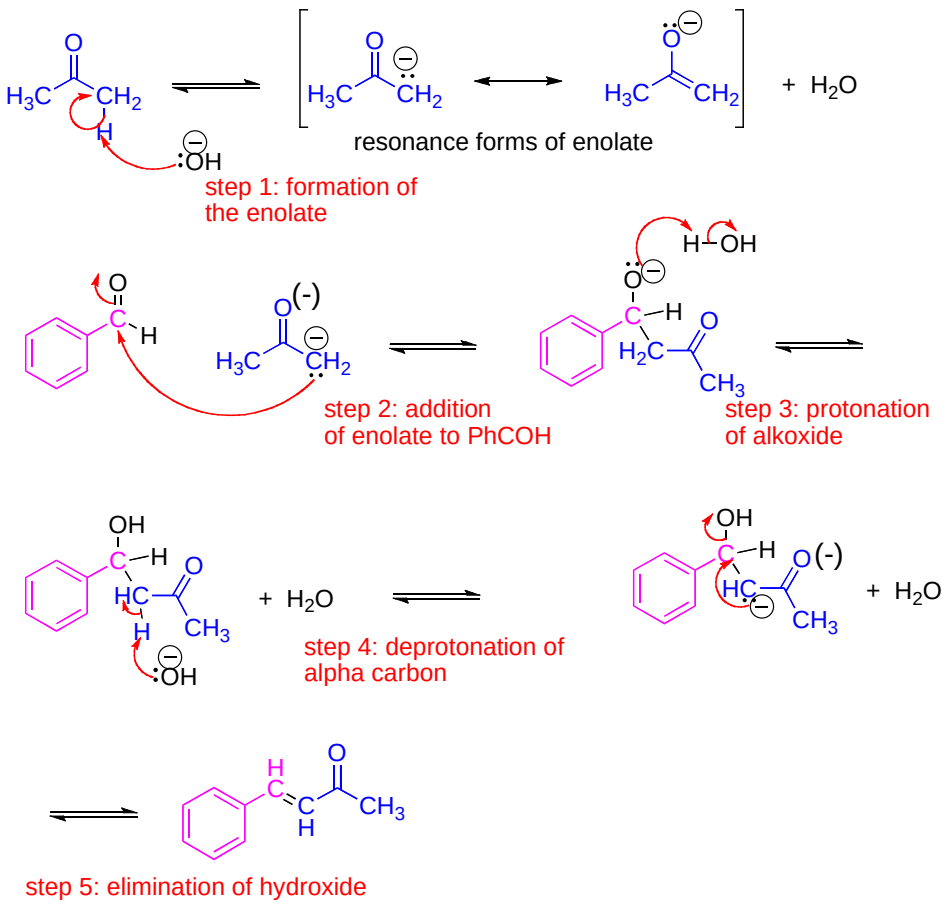


Figure 2. General reaction mechanism for the condensation of one molecule of benzaldehyde with one molecule of acetone.

With heating, this product eliminates water (dehydration) to form an *α,β*-unsaturated ketone. This happens first by a deprotonation step (step 4) with sodium hydroxide to form a resonance-stabilized carbanion. Then in step 5, a hydroxide ion is eliminated to form the *α,β*-unsaturated ketone called benzalacetone (mp 42 °C). The entire reaction sequence is repeated to condense another molecule of benzaldehyde to the second alpha carbon of acetone and form dibenzalacetone.

Cautions and tips:

- Make sure all glassware is clean.
- Before you start the experiment, start the water bath and put ethanol on ice to save time.
- If no crystals form, add a few drops of water to the solution and scratch the side of the tube with a stir rod.

Experiment

Prepare an ice water bath for the recrystallization. Combine 0.6 mL of benzaldehyde (PhCOH), 0.2 mL of acetone (CH_3COCH_3), 8 mL of ethanol (CH_3CH_2OH), and lastly 4.0 mL of 5 M aqueous sodium hydroxide solution into your reaction tube and cap the tube. Make sure to record all amounts of starting materials. Shake the tube a few times every minute for a total of 30 minutes. After that time period, remove the liquid from the crystals using a pipette. Add 10 mL of water and shake the tube. Remove the water with a pipette and wash the tube two more times with water. Collect the crystals by vacuum filtration. Recrystallize the resulting crystals using warm ethanol. Vacuum filter and wash the crystals with a cold solution of ethanol/water (70:30). Dry and weigh the crystals, take a melting point and report the percent yield.