6. Synthesis of *trans*-1,2-dibenzoylcyclopropane

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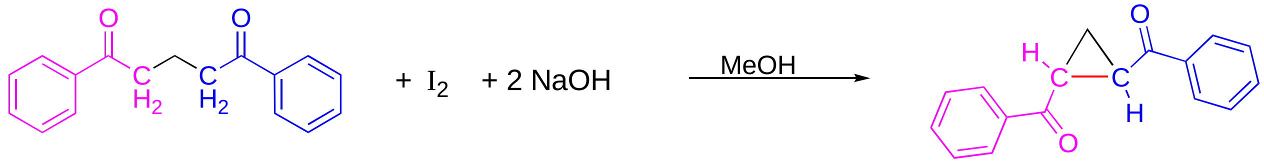
S_N2 Reaction Chapter 7 (Section 7.4) pgs 268-288
Formation of Enolates Chapter 19 (Section 19.1) pgs 932-933
Halogenation at the α-position Chapter 19 (Section 19.4a) pgs 946-950

This procedure has been adapted from the microscale procedure described in the first edition of *Experimental Organic Chemistry A Balanced Approach: Macroscale and Microscale* by Jerry R. Mohring, Christina N. Hammond, Terence C. Morrill, and Doublas C. Neckers, W.H. Freeman, New York; 1998, pgs 333-339.

Background

In this experiment, you will perform a base-catalyzed ring closure to form a cyclopropane. The overall reaction is depicted in Figure 1. There are several steps in this reaction: formation of an enolate, halogenation of the α-position, formation of a second enolate, followed by intramolecular S_N2 (ring closure).



1,3-dibenzoylpropane
(1,5-diphenyl-1,5-pentanedione)
mp 67.5 ^oC

trans-1,2-dibenzoylcyclopropane

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. Now, let's review the S_N2 reaction.

The S_N2 Reaction. S_N2 is an acronym for substitution nucleophilic bimolecular. A general mechanism for this reaction is pictured below.

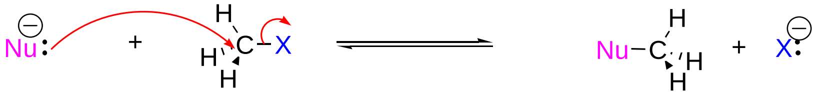


Figure 2. The general S_N2 reaction.

In this reaction, there are basically four different steps. The first step in the reaction is to form the nucleophile, which is an enolate. This is formed in a deprotonation step where hydroxide pulls off a proton on the alpha carbon (carbon adjacent to the carbonyl carbon) to yield a resonance-stabilized enolate. This nucleophile attacks an I_2 molecule resulting in a halide product (step 2).

In step 3, another enolate, another nucleophile, is generated. This nucleophile then does an intramolecular substitution reaction, which is favored entropically.

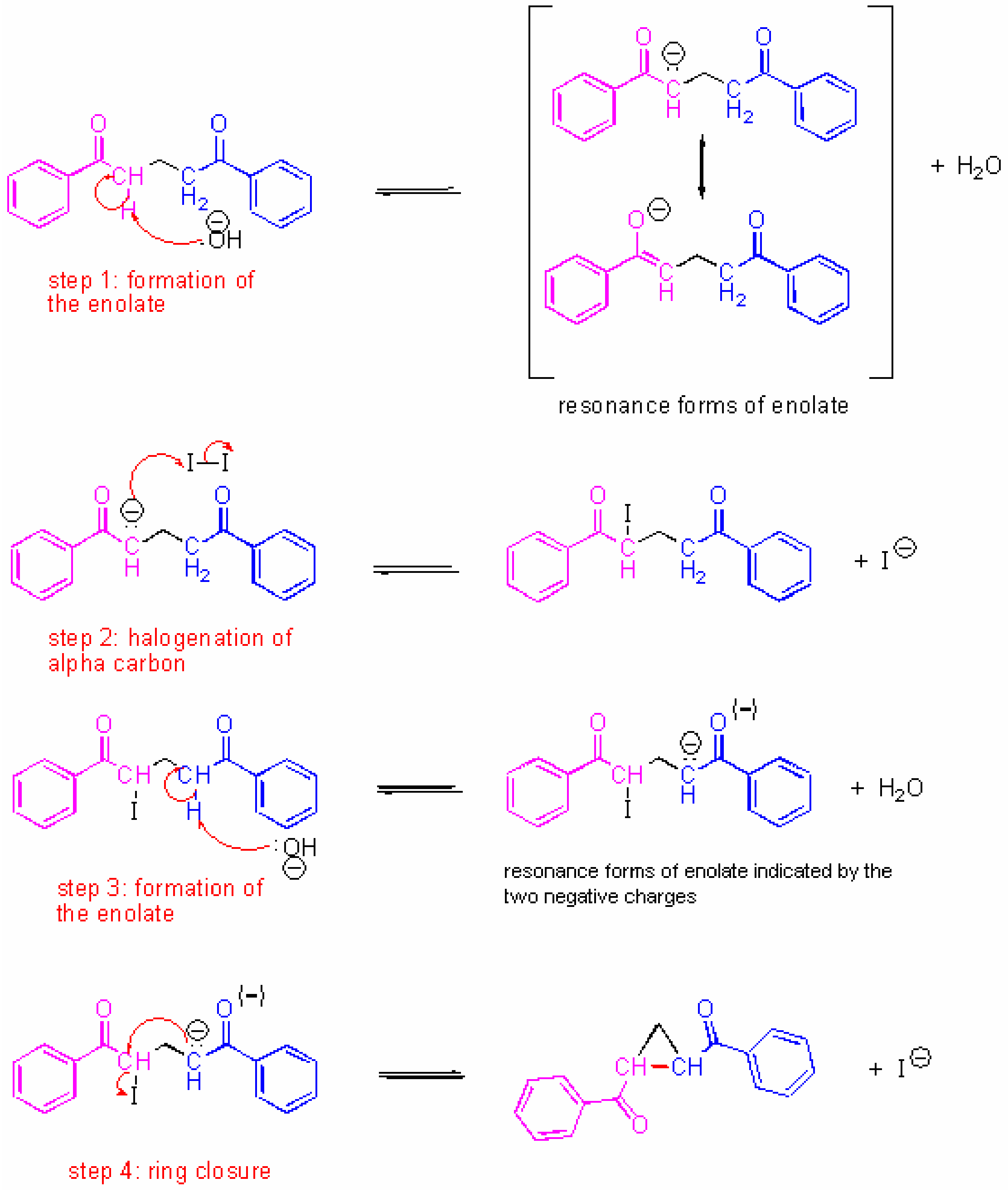


Figure 3. The reaction mechanism.

Experiment

Transfer 400 mg of 1,3-dibenzoylpropane and a boiling chip to a 25-mL round bottom flask. Add 5 mL of a 0.67 M sodium hydroxide in methanol solution. Heat the flask in a warm water bath (50-80 °C) and swirl the mixture until all of the solid has dissolved. Fit the flask with a Claisen adapter. Fit the one port directly over the flask with a rubber septum and the other port with a reflux condenser. Through the rubber septum, add 2.5 mL of a 0.67 M iodine solution in methanol dropwise via a syringe (20-gauge needle). After the iodine addition is complete, heat the reaction for an additional 40 minutes. Let the flask cool to room temperate and place it in an ice bath. Vacuum-filter the solution into a clean filter flask and collect the crystals. Wash the crystals with a half-pipette-full (about 1 mL) of water three times. Refilter any precipitate that forms inside the filter flask. Recrystallize the product from a methanol/water solvent pair. Filter, dry and weigh the final product. Record the melting point of the final product.