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

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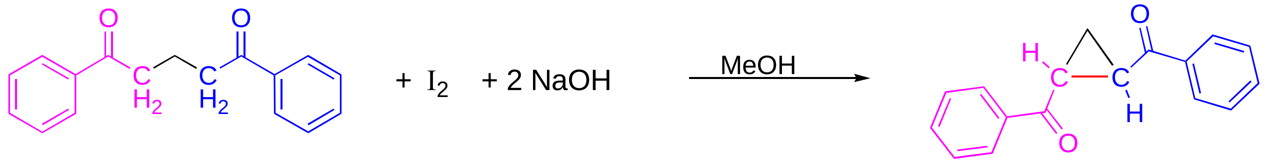
S_N2 Reaction Chapter 7 (Section 7.4) pgs 268-288
Formation of Enolates Chapter 19 (Section 19.1) pgs 932-933
Halogenation at the α-position Chapter 19 (Section 19.4a) pgs 946-950

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.

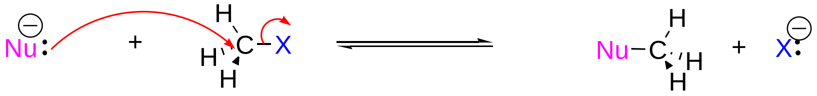


Figure 2. The general S_N2 reaction.

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.

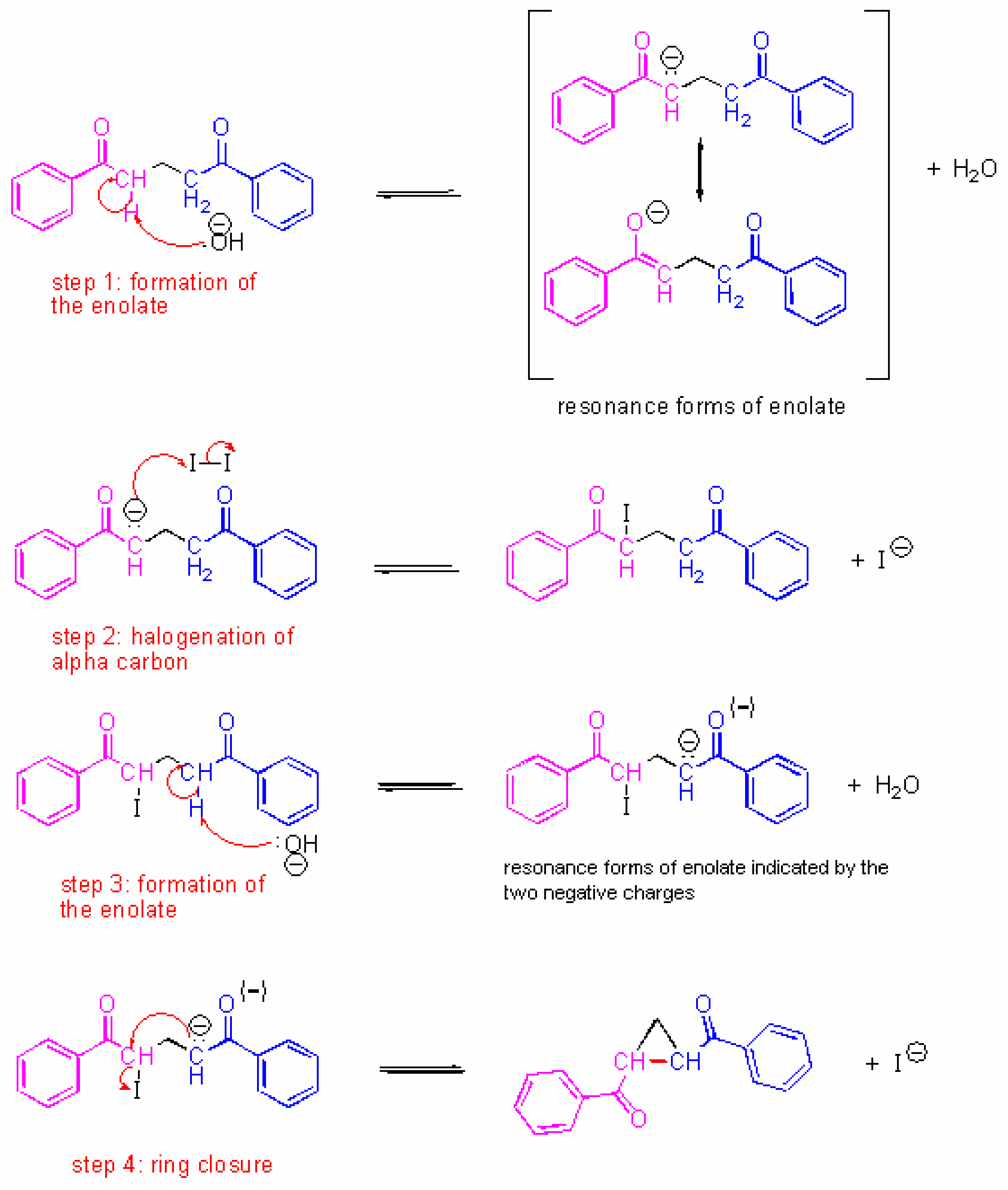


Figure 3. The reaction mechanism.

Experiment

Place 400 mg of 1,3-dibenzoylpropane into a large reaction tube. Add 5 mL of methanol and 7 mL of a 0.67 M sodium hydroxide in methanol solution. Stir the contents with a glass rod until the 1,3-dibenzoylpropane is completely dissolved [**Note: Gentle heating may help in dissolving the 1,3-dibenzoylpropane.**]. Add 2.5 mL of a 0.67 M iodine in methanol solution dropwise via a pipette. Swirl the reaction tube to mix the contents after each drop [**Note: Do not add the next drop of iodine until the previous drop has gone into solution, that is, wait until the brown color disappears.**]. After the addition of iodine is complete, place the reaction tube into a pre-heated water-bath (40–45 °C, monitor the temperature with a thermometer) and heat the reaction contents for 40 minutes, swirling the reaction tube every 5 minutes or so. After cooling to room temperature, and while stirring with a glass rod, add ice-cold water until a precipitate forms. Place the reaction tube into an ice-bath and chill for 10 to 15 minutes. Collect the precipitate via vacuum filtration and wash the solid with 3 to 4 mL of cold water. Recrystallize the solid from a methanol–water solvent pair [**Note: Do not add more than 5 drops of water or oiling will occur when cooling down to room temperature.**]. Collect the product via vacuum filtration, and wash it with a few milliliters of cold methanol. Weigh the product and record its melting point.