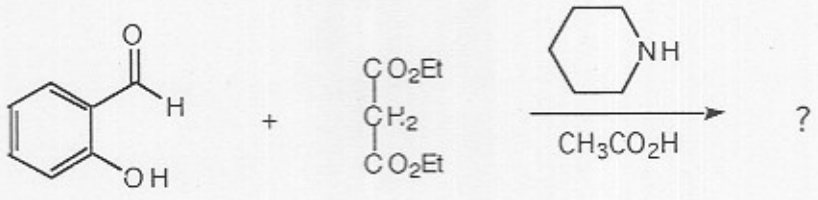
MYSTERY REACTION

REACTION OF SALICYLALDEHYDE WITH DIETHYL MALONATE

The Reaction



salicylaldehyde diethyl malonate

Introduction

The starting materials for this experiment are the phenolic aldehyde **salicylaldehyde** and the diester **diethyl malonate**. Two other organic compounds, the cyclic secondary amine **piperidine** and **acetic acid**, are present in such small quantities that they appear to be catalytic reagents, one acting as a base, the other as an acid. Under these conditions, what can be expected to happen? Solubility tests and spectra provide the principal evidence for structure determination.

Experimental Procedure

In a dry 100-mL round-bottom flask place 3.5 mL of salicylaldehyde (d = 1.146 g/mL), 5.5 mL of diethyl malonate (d = 1.055 g/mL), 20 mL of absolute ethanol, 0.4 mL of piperidine, one drop of glacial acetic acid, and a boiling chip. Heat the mixture to reflux, using a water-cooled condenser fitted with a calcium chloride drying tube or cotton plug at the top to protect from atmospheric moisture. Reflux the solution for two hours. Transfer the solution to an Erlenmeyer flask, add 30 mL of water, and cool the solution in an ice bath. After crystallization is complete, filter the crystals by suction and wash them twice with 3-mL portions of ice-cold 50% aqueous ethanol.

Allow the crystals to dry and determine the weight and melting point. If time permits, recrystallize the solid from ethanol-water to obtain a pure sample (the reported melting point is 92-94 °C). Turn in your final product to the instructor.

Structure Determination

1. Test the solubility of the product in dilute aqueous NaOH, $NaHCO_3$, and HCl. What conclusions can you draw about the presence or absence of the original functional groups?

2. Obtain IR and NMR spectra of the mystery product, either by running them yourself or from the instructor. What conclusions about functional groups present can you draw from the IR spectrum? In the NMR spectrum, pay particular attention to the integration as well as to the evidence for any changes in functional groups.

Writeup

Your ~~notebook writeup~~ lab report should include:

1. Experimental procedure, weight of product, melting point, and percent yield.
2. Concise summary of the evidence and arguments (both chemical and spectroscopic) used in assigning the structure.
3. The mechanism of formation of the product.