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The Microscale Laboratory

The Pechmann Reaction

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In our laboratory experiments, we often use reactions in which multiple transformations take place (1). Students may initially view such processes as complex, but they learn to apply known mechanisms in sequence to arrive at an overall mechanism for the reaction.

One reaction that uses a series of simple steps to effect a complex change in the substrate is the Pechmann reaction (2). This reaction involves three steps: hydroxalkylation, transesterification, dehydration (3), to unite a phenol and a keto-ester to produce a coumarin. Typically, extreme condensing agents such as H2SO4 or POCl3 are required for a successful reaction, leading to safety concerns and undesirable waste streams. Recently, solid acid catalysis in the Pechmann reaction has been described (4)—an improvement that makes this established, but little-known, reaction much more suitable for undergraduates.

The solid acid catalysts Amberlyst-15, H-BEA, and Filtrol are used in the reaction between resorcinol and ethyl acetocetate to generate 7-hydroxy-4-methylcoumarin:

\[ \text{H}_2\text{O} + \text{COOCH}_2\text{CH}_3 \xrightarrow{\text{Amberlyst-15}} \text{H}_2\text{COOCH}_2\text{CH}_3 \]

(A number of other ketoesters are also used in the literature references, but the yields were lower, and we have not investigated their use in our labs.) This procedure offers a reliable addition to our sequence of second-semester organic laboratory exercises. The procedure is simple, it requires only the glassware contained in a standard microscale kit, the yields are consistent, and the concept of azotropic removal of water can be introduced (by use of a Hickman still). Furthermore, the ideas of electrophilic aromatic substitution, transesterification, and elimination—all of which are covered in a typical organic chemistry curriculum—can be reinforced.

Procedure

Place 110 mg (1.0 mmol) of resorcinol, 127 µL (130 mg, 1.0 mmol) of ethyl acetocetate, 1.5 mL of toluene, and 100 mg of Amberlyst-15 into a 3-mL conical vial equipped with a spin vane. Place a Hickman still on top of the conical vial and fill the trough with toluene. Take care not to overfill the trough, which would decrease the concentration of reactants and slow down the reaction!

With stirring, heat the mixture at reflux for 90 minutes.1 Remove the system from heat, and allow it to cool.2 Add 2 mL of warm methanol to dissolve the off-white product, and filter under vacuum to separate the acid catalyst.

Remove the solvent from the filtrate in vacuo. Recrystallize the product from methanol/water to obtain 7-hydroxy-4-methylcoumarin as a white solid. Typical student yields range from 35 to 55% (approximately 60–95 mg) (lit. yield: 81% [4a]), with melting points of 180–182 °C (lit. mp: 185–186 °C [3]).

Notes

1. Reaction times were decreased from the literature value of 4 h by increasing the concentration of reactants.
2. The Hickman still may be removed at this point.

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