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A MODIFICATION OF THE PECHMANN REACTION

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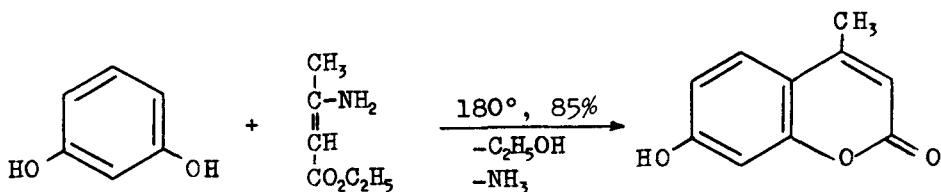
A MODIFICATION OF THE PECHMANN REACTION

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The condensation of β -ketoic esters with phenols in the presence of concentrated sulfuric acid yields coumarin derivatives. Other condensing agents that have been used are AlCl_3 , POCl_3 , ZnCl_2 , H_3PO_4 , HCl , and P_2O_5 . This reaction, which is commonly known as the Pechmann reaction¹, has found extensive application and has been used for the synthesis of several naturally occurring coumarins.

We have now found that enamine derivatives of β -ketoic acids condense smoothly at elevated temperatures with phenolic compounds without any catalyst. Thus the condensation between resorcinol, the most frequently used phenolic compound in the Pechmann reaction, and ethyl β -aminocrotonate takes place at about 180° yielding 7-hydroxy-4-methyl-coumarin.



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We have used the present procedure successfully with a number of phenolic heterocycles², where the usual Pechmann conditions gave only very poor results.

Experimental

7-Hydroxy-4-methyl-coumarin (4-Methylumbelliferone)³

A mixture of 11.0 g. (0.1 mole) of resorcinol and 12.9 g. (0.1 mole) of ethyl β -aminocrotonate was heated under nitrogen in an oil bath at 190° under a short (10 cm.) air condenser for 30-35 min.⁴ Ethanol and ammonia were liberated during the first 20-25 min. The resulting oily reaction mixture crystallized when it was digested with dil. methanol. The yield was 15 g. (85%) of nearly pure coumarin, as shown by TLC. One recrystallization from ethanol yielded a product which melted at 185°, and did not depress the melting point of an authentic sample³.

References

1. S. Sethna and R. Phadke, "The Pechmann Reaction" in Organic Reactions, Vol. 7, 1-58 (1953).
2. T. Kappe et al., unpublished results.
The heterocyclic compounds include: 4-hydroxy-coumarin, 4-hydroxy- α -pyrones, 4-hydroxy- α -pyridones, and 2-hydroxy-quinolizin-4-ones.
3. A. Russel and J. R. Frye, Organic Syntheses, Vol. 21, 22 (1941); Coll. Vol. III, 281 (1955).
4. With high melting heterocyclic compounds we have used successfully nitrobenzene as reaction medium.

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