

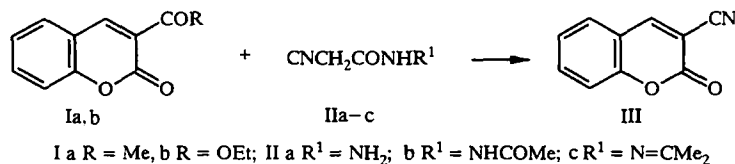
LETTERS TO THE EDITOR

UNUSUAL "REPLACEMENT" OF CARBONYL CONTAINING FUNCTIONS AT POSITION 3 OF COUMARIN BY A CYANO GROUP

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The reaction of coumarins containing electron acceptor groups at position 3 (CN, CO₂Et, COMe, COPh, etc.) with compounds containing active methylene groups, in particular cyanoacetamide and ethyl cyanoacetate, under Michael reaction conditions leads to the formation to 4-substituted derivatives of 3,4-dihydrocoumarin [1]. Further reactions of these compounds gave tricyclic compounds containing an α -pyrone ring [2] or substituted β -(*o*-hydroxyphenyl)propionic acids [3].

We have observed that the reaction of 3-acetyl(3-ethoxycarbonyl)coumarins Ia-b with cyanoacetylhydrazine and its N-acetyl- and N-propionyl-derivatives IIa-c under Michael conditions gave an unexpected result. The reaction product was 3-cyanocoumarin (III), in yields of 32-63% depending on the structure of the starting material.



Starting materials, yield of 3-cyanocoumarin in %. Ia, IIa, 38; Ia, IIb, 55; Ia, IIc, 44; Ib, IIa, 32; Ib, IIb, 63; Ib, IIc, 43.

The 3-cyanocoumarin product had a melting point and spectroscopic properties identical with those reported in the literature [4, 5]. Its IR spectrum contained bands at 2225 and 1740 cm⁻¹.

Conversion of compounds Ia and b into 3-cyanocoumarin was carried out with equimolar amounts of the starting materials in ethanol with a catalytic amount of piperidine at 18-20°C for 40-60 min.

This conversion is apparently the result of a series of consecutive reactions, including the formation of 4-substituted 3,4-dihydrocoumarins with subsequent opening and recyclization of an α -pyrone ring accompanied by elimination of a molecule of hydrazine or its derivative and loss of a molecule ethyl acetoacetate or ethyl malonate. In fact, the mass spectra of the reaction products contain peaks of ions with *m/z* corresponding to the molecular masses of products from the reaction of hydrazine with the coumarin starting material and with ethyl acetoacetate and ethyl malonate, respectively.

The preparation of 3-cyanocoumarin from compounds Ia and b may be considered as an alternative route for its synthesis.

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