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LETTERS TO THE EDITOR

NEW APPROACH TO THE SYNTHESIS OF 3-ARYLCOUMARINS. REACTION OF 3-ACYL- AND 3-ETHOXYCARBONYL-COUMARINS WITH HYDRAZIDE OF *p*-NITROPHENYLACETIC ACID

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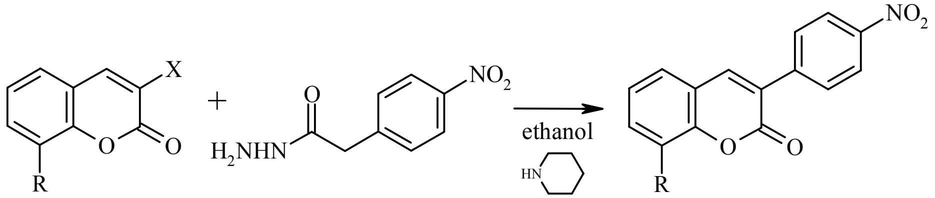
3-Arylcoumarins are usually obtained by the cyclization of mono- or *ortho*-substituted benzenes such as phenols or salicylaldehydes with compounds containing phenyl substituent along with active methylene group [1, 2]. The use of coumarins themselves as starting compounds for the preparation of 3-arylcoumarins is much rarer. The reaction of coumarins with phenyldiazonium salts to give 3-arylcoumarins has been reported [3].

We have found that the synthesis of 3-arylcoumarins containing electron-withdrawing substituents in the aryl ring may be accomplished by the reaction of 3-acylcoumarins or 3-ethoxycarbonylcoumarin with derivatives of phenylacetic acid hydrazides under Michael reaction conditions. For example, the reaction of 3-acetyl-, 3-benzoyl- and 3-ethoxycarbonylcoumarins **1a-d** with hydrazide of *p*-nitrophenylacetic acid (**2**) gave the corresponding 3-(*p*-nitrophenyl)coumarins **3a** and **3b**.



1a–d **2** **3a,b**

1 **a** X = COPh, R = OMe, **b** X = COMe, R = H, **c** X = COPh, R = H, **d** X = COOEt, R = H;
3 **a** R = OMe, **b** R = H

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The conversion of coumarins **1a-d** into 3-(*p*-nitrophenyl)coumarins **3a** and **3b** was carried out in ethanol at 18-20°C in the presence of catalytic amounts of piperidine. Thus, one drop of piperidine was added to mixture of 3-benzoyl-8-methoxycoumarin (**1a**) (0.07 g, 0.25 mmol) and hydrazide **2** (0.05 g, 0.25 mmol) in ethanol (15 ml) and stirred for 24 h at room temperature. The precipitate formed was filtered off and washed with ethanol (5 ml) to give pale yellow crystalline 3-(*p*-nitrophenyl)coumarin **3a** (0.05 g, 67%); mp 295-296°C (DMF). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm: 3.95 (3H, s, OCH_3); 7.36 (3H, s, arom); 8.02 (2H, d, arom); 8.34 (2H, d, arom); 8.43 (1H, s, 4-CH). IR spectrum, ν, cm^{-1}: 1702, 1610, 1575, 1568. Found, %: C 64.72; H 3.84; N 5.01; M$^+$ 297. $C_{16}H_{11}NO_5$. Calculated, %: C 64.64; H 3.70; N. 4.71; M 297.

Under analogous conditions, coumarins **1b-d** were converted to 3-(*p*-nitrophenyl)coumarin **3b** by reaction with hydrazide **2**. The reaction of **1b** gave **3b** in 20% yield. The reaction of **1c** gave **3b** in 71% yield. The reaction of **1d** gave **3b** in 60% yield. Coumarin **3b** was obtained as fine light yellow crystals; mp 259-261°C (DMF) (262°C [2]), M$^+$ 267. $C_{15}H_9NO_4$. Calculated: M 267. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm: 7.38-7.84 (4H, m, arom); 8.02 (2H, d, arom); 8.34 (2H, d, arom). IR spectrum, ν, cm^{-1}: 1709, 1688, 1606, 1596.

The preparation of 3-(*p*-nitrophenyl)coumarins **3a** and **3b** is a typical one-pot procedure involving several steps and carried out analogously to the conversion of 3-acylcoumarins into 3-cyanocoumarins described in our previous works [4, 5]. Evidence for this hypothesis was found in the detection of peaks characteristic of 3-phenyl-5-pyrazolone (160 $[M]^{+\cdot}$, 131 $[M - HCO]^{+\cdot}$, 118 $[M - CH_2CO]^{+\cdot}$, 103 $[PhCN]^{+\cdot}$) in the mass spectrum from the reaction mixture of **1c** and **2**. 3-Phenyl-5-pyrazolone is formed during this conversion by the reaction of hydrazine and ethyl benzoylacetate, which is lost during the recyclization of the coumarin ring.

This method for the synthesis of 3-(*p*-nitrophenyl)coumarins may be considered as an alternative supplementing the known methods for the preparation of such compounds.

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