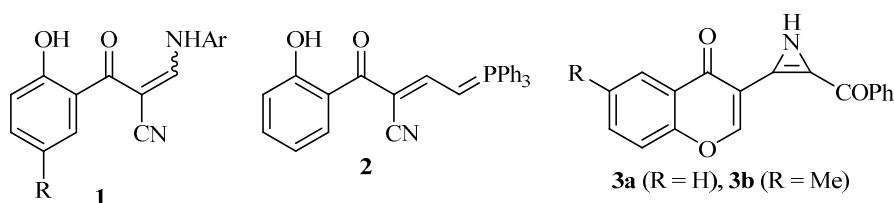


REACTION OF 3-CYANOCHROMONES WITH PYRIDINIUM PHENACYLIDE

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The reaction of 3-cyanochromones with *N*- and *C*-nucleophiles begins with an attack at C-2 atom with subsequent opening of the γ -pyrone ring and recyclization at the C=O or C \equiv N groups [1-3]. Nucleophilic 1,2-addition at the cyano group usually does not occur [1], while the reactions with aromatic amines [4] and methylenetriphenylphosphorane (Ph₃P=CH₂) [5] terminate at the stage of open products **1** and **2**. Since the assumption of a number of workers of possible addition of nucleophiles at the cyano group was subsequently shown to be incorrect [1], the reports in the literature on the synthesis of azirines **3a,b** from the corresponding 3-cyanochromones **4a,b** and pyridinium phenacylide [6] are cast in doubt and require verification.



We have found that 3-cyanochromone **4a** and 3-cyano-6-methylchromone **4b** react with phenacylpyridinium bromide in the presence of one or two equivalents of potassium carbonate in acetone at reflux over 8 h, analogously to phosphorus ylide Ph₃P=CH₂, i.e., through Michael addition of pyridinium phenacylide formed *in situ* with subsequent opening of the pyrone ring to give highly stable ylides **5a,b** in 72-77% yield. The structure of these ylides was confirmed by IR, ¹H NMR, and ¹³C NMR spectroscopy. Heating ylide **5a** at reflux in glacial acetic acid for 2 h gives the starting 3-cyanochromone **4a**. Under conditions described for the preparation of azirines **3a,b** using four equivalents of potassium carbonate [6], we isolated only a complex, intractable mixture. Products of addition at the CN group, namely, azirines **3a,b**, could not be detected despite variation of the conditions. 1,3-Dipolar cycloaddition at the double bond of the pyrone ring leading to indolizines [7] was also not observed.

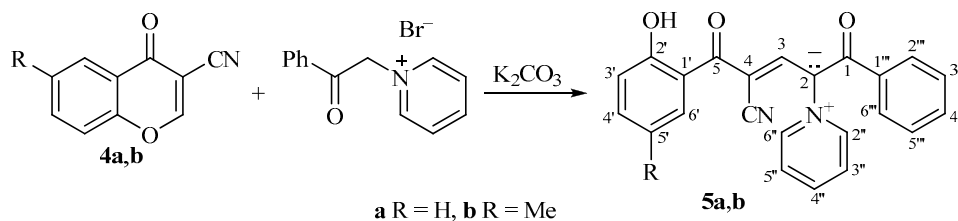
The signals in the ¹H and ¹³C NMR spectra were assigned on the basis of 2D ¹H-¹³C HSQC, HMBC, and ¹H-¹H COSY experiments in the case of betaine **5a**. The most informative cross peaks in the 2D HMBC spectrum in DMSO-d₆ are H-6'/C-5, H-3'/C-5, H-3/C-5, H-3/C-4, and H-3/CN. The singlet for H-3 proton is

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found at 7.85 ppm, while the broadened signal for the phenol proton is at 9.80-10.80 ppm. The upfield doublet for H-6' proton points to an absence of intramolecular hydrogen bonding in the salicyloyl fragment, which results in phenyl ring deviation from the molecular plane [4]. The IR spectra of betaines **5a,b** show absorption bands for the C≡N group at 2172-2183 cm⁻¹ and two C=O groups at 1608-1580 cm⁻¹, indicating extensive delocalization of negative charge (for comparison, this band is at 1661 cm⁻¹ for the chromone **4a** and 1614 cm⁻¹ for the ylide **2** [5]).

The IR spectra were recorded on a Bruker Alpha spectrometer with an ATR attachment (ZnSe crystal). The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance II spectrometer (400 and 100 MHz, respectively) in DMSO-d₆ with TMS as internal standard. The elemental analysis was carried out on an automatic PE 2400 analyzer. The melting points were determined on an FP 62 instrument.



4-Cyano-5-(2-hydroxyphenyl)-1,5-dioxo-2-(pyridinium-1-yl)-1-phenylpent-3-en-2-ide (5a). A mixture of 3-cyanochromone **4a** (300 mg, 1.75 mmol), phenacylpyridinium bromide (490 mg, 1.76 mmol), and anhydrous potassium carbonate (490 mg, 3.50 mmol) in dry acetone (100 ml) was heated at reflux for 8 h. The orange precipitate formed was filtered off, washed with acetone and water, and dried. Yield 480 mg (72%). Yellow crystals; mp 215-216°C (decomp.). IR spectrum, ν , cm⁻¹: 2172, 1608, 1581, 1564, 1512, 1481. ¹H NMR spectrum, δ , ppm (J , Hz): 6.72 (1H, t, J = 7.5, H-5'); 6.80 (1H, d, J = 8.2, H-3'); 7.16 (1H, td, J = 7.6, J = 1.5, H-4'); 7.23 (1H, d, J = 7.5, H-6'); 7.42-7.57 (3H, m, H-3'',4'',5''); 7.58-7.62 (2H, m, H-2'',6''); 7.85 (1H, s, H-3); 8.23 (2H, t, J = 7.2, H-3'',5''); 8.69 (1H, t, J = 8.0, H-4''); 9.05 (2H, d, J = 5.3, H-2'',6''); 9.80-10.80 (1H, br. s, OH). ¹³C NMR spectrum, δ , ppm: 116.4 (C-3'); 118.3 (C-5'); 119.0 (CN); 121.1 (C-2); 123.0 (C-4); 125.8 (C-1'); 127.8 (C-3'',5''); 128.2 (C-2'',6''); 128.3 (C-3'',5''); 128.5 (C-6'); 130.5 (C-4''); 131.1 (C-4'); 138.5 (C-1''); 144.0 (C-3); 146.2 (C-4''); 149.1 (C-2'',6''); 155.8 (C-2'); 185.8 (C-1); 189.4 (C-5). Found, %: C 72.82; H 4.34; N 7.34. C₂₃H₁₆N₂O₃·0.5H₂O. Calculated, %: C 73.20; H 4.54; N 7.42.

4-Cyano-5-(2-hydroxy-5-methylphenyl)-1,5-dioxo-1-phenyl-2-(pyridinium-1-yl)pent-3-en-2-ide (5b) was obtained analogously to betaine **5a**. Yield 0.88 g (77%). Yellow crystals; mp 209-211°C (decomp.). IR spectrum, ν , cm⁻¹: 2183, 1605, 1580, 1564, 1514, 1494, 1473. ¹H NMR spectrum, δ , ppm (J , Hz): 2.17 (3H, s, CH₃); 6.66 (1H, d, J = 8.2, H-3'); 6.99 (1H, d, J = 8.2, H-4'); 7.30 (1H, s, H-6'); 7.43-7.53 (3H, m, H-3'',4'',5''); 7.62 (2H, d, J = 6.5, H-2'',6''); 7.99 (1H, s, H-3); 8.23 (2H, t, J = 6.7, H-3'',5''); 8.68 (1H, t, J = 7.8, H-4''); 8.97 (2H, d, J = 5.3, H-2'',6''); 10.65 (1H, br. s, OH). Found, %: C 73.90; H 4.55; N 7.12. C₂₄H₁₈N₂O₃·0.5H₂O. Calculated, %: C 73.64; H 4.89; N 7.16.

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