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Quantitative photooxidation of 4-hydroxy-3-pyrazolinylcoumarins to pyrazolyl derivatives

Valery F. Traven,*[a] Ivan V. Ivanov,[a] Aleksandr S. Pavlov,[a] Aleksandr V. Manaev,[a] Irina V. Voevodina[a] and Valery A. Barachevskii[b]

[a] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation. Fax: +7 495 609 2964; e-mail: traven@muctr.edu.ru*
[b] *Photochemistry Center, Russian Academy Sciences, 119421 Moscow, Russian Federation*

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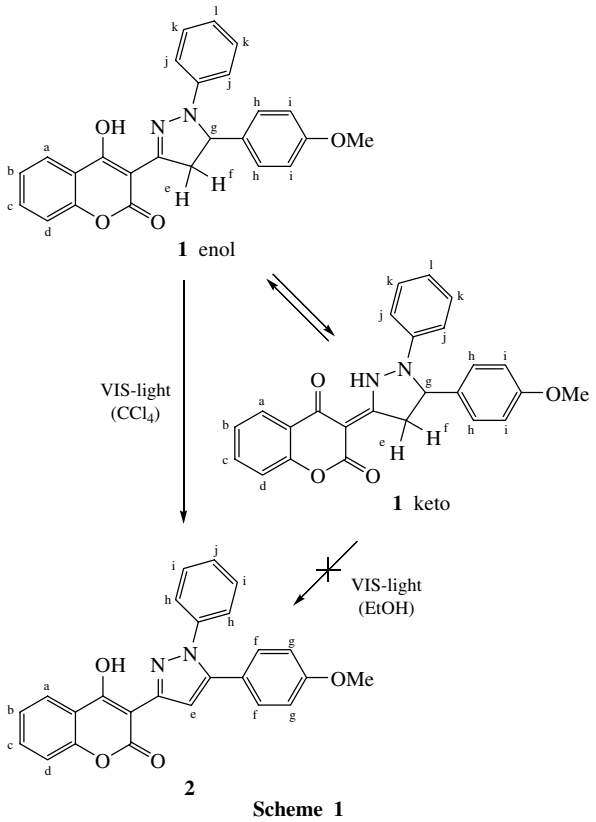
4-Hydroxy-3-pyrazolinylcoumarins undergo quantitative photooxidation to pyrazolyl derivatives under illumination with visible light at room temperature in a carbon tetrachloride solution.

In a study of the synthesis and structural transformations of 4-hydroxycoumarin derivatives,[1–4] we found that 4-hydroxy-3-pyrazolinylcoumarin **1** was photooxidised to 4-hydroxy-3-pyrazolylcoumarin **2** under very mild conditions (Scheme 1).†

We found that compound **1** (dissolved in CCl_4) changed its electronic absorption spectrum under illumination with visible light for 1 h (Figure 1).

These spectral transformations are not due to the solvatochromism of **1** since its solution in CCl_4 does not change its electronic absorption spectrum in the dark for a long time. These transformations are insensitive to oxygen, and they cannot be explained by hydroxy(hydrazono)/keto(hydrazino) tautomerism. Moreover, these transformations are irreversible.

We followed the reaction by measuring ^{1}H NMR spectra and found that the photooxidation of pyrazoline **1** to pyrazole derivative **2** occurred. The ^{1}H NMR spectra of compound **1** before and after illumination are compared in Figure 2 (curves *1* and *2*, respectively). We also prepared compound **2** by an independent way *via* the oxidation of **1** by potassium bichromate.



Scheme 1

The ^{1}H NMR spectrum of pyrazole **2** is shown in Figure 2 (curve *3*).

Pyrazoline **1** also undergoes photooxidation in other solvents. A change of CCl_4 as a solvent for acetonitrile and DMF decreased the rate of the transformation. The reaction stopped at all in an ethanol solution. This fact is due to tautomeric transformations of **1**. Figure 3 shows that a change from 100% CCl_4 to 100% DMF affected the equilibrium of tautomeric enol and keto forms of **1** (Scheme 1). Enol form is stable in nonpolar solvents (CCl_4, $CHCl_3$) since it contains a strong H-bond between 4-hydroxy and 3-hydrazono functions. Polar solvents (DMF, DMSO, EtOH) weaken the H-bond; therefore, keto form of **1** becomes significant. This suggestion is proved by ^{1}H NMR spectrum recorded in [$^2H_6$]DMSO (signals of OH and NH functions can be seen).‡

† ^{1}H NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200 MHz). Electronic absorption spectra were obtained on a PD-303 UV UV-VIS spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-500 spectrofluorimeter. Chromatomass spectra were obtained on a PE SCIEX API165 (ELSD UV254) spectrometer; column, Synergi-2u-Hydro-RP-Mercury, 20×2.0 mm. Phototransformations of **1** were studied under illumination by visible light (Camelion lamp LH30-4U).

4-Hydroxy-3-(3'-p-*anisyl-2'-phenyl-5'-pyrazolinyl)coumarin* **1**. A mixture of 4-hydroxy-3-(*p*-methoxycinnamoyl)coumarin (3 g, 0.009 mol), phenylhydrazine (3.65 ml, 0.037 mol) and 50 ml of acetic acid was refluxed for 1 h. Then, the reaction mixture was cooled until a precipitate was formed. The precipitate was filtered off, dried and recrystallised from ethanol, **1**, yellow crystals, yield 67%, mp 181–183 °C. ^{1}H NMR ($CDCl_3$) δ: 3.60 (m, 1H, H^e), 3.82 (s, 3H, OMe), 4.24 (m, 1H, H^f), 5.18 (m, 1H, H^g), 6.88 (m, 3H, H^i, H^l), 6.96 (d, 2H, H^j, ^3J 7.4 Hz), 7.25 (m, 4H, H^k, H^h), 7.37 (m, 2H, H^b, H^d), 7.60 (m, 1H, H^c), 8.06 (d, 1H, H^a, ^3J 7.7 Hz), 14.10 (s, 1H, OH). MS, *m/z*: 412 (100%). Found (%): C, 72.85; H, 4.91; N, 6.77. Calc. for $C_{25}H_{20}N_2O_4$ (%): C, 72.82; H, 4.85; N, 6.80.

4-Hydroxy-3-(3'-p-*anisyl-2'-phenyl-5'-pyrazolyl)coumarin* **2**. A mixture of **1** (0.5 g, 0.0012 mol), $K_2Cr_2O_7$ (0.14 g, 0.0005 mol) and 30 ml of acetic acid was refluxed for 0.5 h. Then, the reaction mixture was poured into water (50 ml) and ice. The precipitate was filtered off, dried and recrystallised from ethanol to give **2**, yellow crystals, yield 56%, mp 149–151 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 3.71 (s, 3H, OMe), 6.97 (d, 2H, H^g, ^3J 8.3 Hz), 7.25 (m, 3H, H^f, H^e), 7.48 (m, 7H, H^b, H^d, H^h, H^i, H^j), 7.73 (m, 1H, H^c), 7.96 (d, 1H, H^a, ^3J 8.3 Hz), 13.80 (s, 1H, OH). MS, *m/z*: 410 (75%). Found (%): C, 73.11; H, 4.26; N, 6.77. Calc. for $C_{25}H_{18}N_2O_4$ (%): C, 73.17; H, 4.39; N, 6.83.

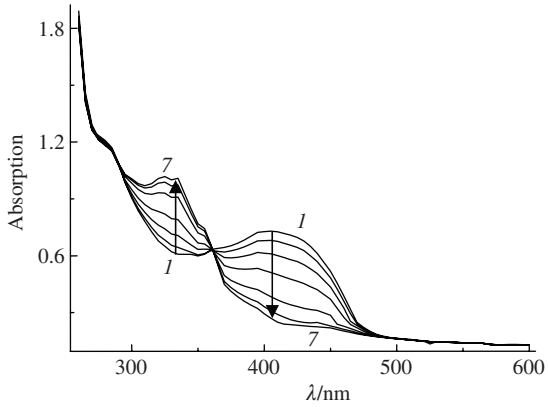


Figure 1 Electronic absorption spectra of **1** in CCl_4 under illumination with visible light for 1 h: (*1*) 1 min, (*7*) 60 min.

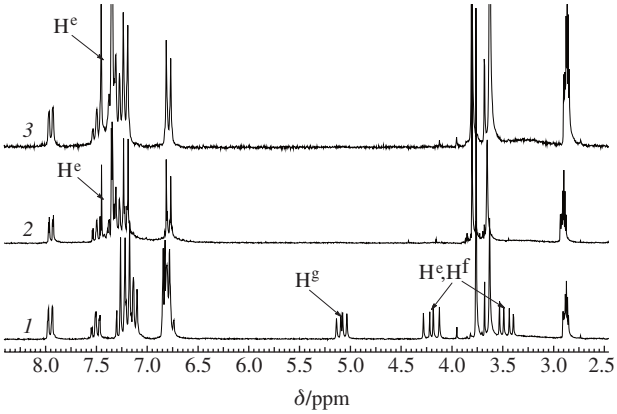


Figure 2 ^{1}H NMR spectra of compound **1** before and after illumination with visible light (curves *1* and *2*, respectively); (*3*) ^{1}H NMR spectrum of compound **2** prepared by the independent oxidation of **1** (solvent, CCl_4).

The rate of transformation also depends on the concentration of solution and the energy of illumination: under visible light, at a concentration of 10^{-5} mol dm^{-3}, compound **1** undergoes 100% phototransformation for 1 h. At concentrations of 10^{-3} mol dm^{-3}, the reaction was complete in 8 h: a solution of **1** (0.015 g, 0.036 mmol) in 30 ml of CCl_4 was illuminated by visible light for 8 h; after solvent evaporation, compound **2** was isolated: 0.0148 g (99% yield), mp 148–150 °C. The illumination of **1**

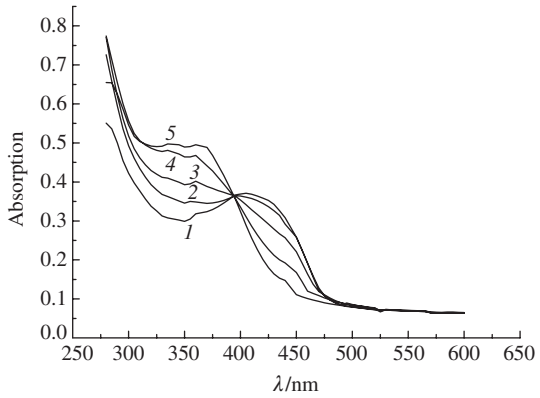


Figure 3 Electronic absorption spectra of **1** in (*1*) 100% CCl_4, (*2*) 60% CCl_4 + 40% DMF, (*3*) 40% CCl_4 + 60% DMF, (*4*) 20% CCl_4 + 80% DMF and (*5*) 100% DMF.

‡ Signals of protons H^e, H^f and H^g were assigned:[5] 3.37 (dd, 1H, H^e), 3.72 (s, 3H, OMe), 4.14 (dd, 1H, H^f), 5.38 (dd, 1H, H^g), 6.65–6.95 (m, 4H, H^h, H^k), 7.00–7.30 (m, 5H, H^i, H^j, H^l), 7.35–7.50 (m, 2H, H^b, H^d), 7.70 (t, 1H, H^c), 8.00 (d, 1H, H^a), 9.57 (s, 0.4H, NH), 13.82 (s, 0.5H, OH).

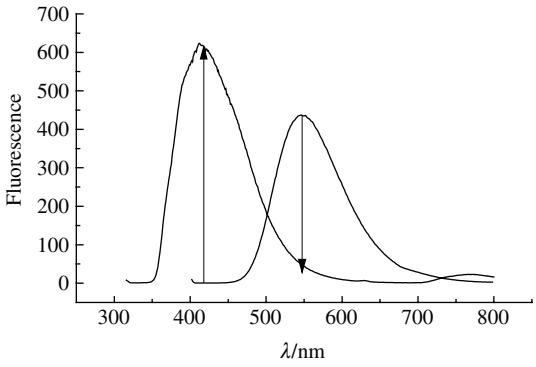


Figure 4 Fluorescence spectra of **1** before (λ_{em} 547 nm) and after (λ_{em} 423 nm) illumination with visible light (solvent, acetonitrile).

by 366 nm light at a low concentration provided its complete transformation into **2** for several minutes.

Different substituents in phenyl rings provide the same phototransformation of pyrazolinylcoumarin **1** derivatives, even though they affect much the photooxidation rate. As an example, *p*-X-substituents in the 2′-phenyl ring of compound **1** analogues and their relative photooxidation rates are listed below: NO_2, 0.02; H, 1; F, 1.81; Me, 2.51; OMe, 4.51.

The phototransformation of **1** into **2** is also followed by definite change of fluorescence spectrum. A shift of fluorescence is well seen in Figure 4. A maximum of electron emission at 547 nm is due to the fluorescence of starting **1** and a maximum at 423 nm is due to formed pyrazole **2**.

The phototransformation of **1** into **2** provides a new mild way for the aromatization of pyrazoline derivatives. The aromatization of these derivatives and their analogues, as a rule, requires strong oxidising reagents, for example, heating with potassium bichromate in acetic acid or with DDQ in toluene.[6,7] Several procedures of the photooxidation of pyrazoline derivatives have also been reported.[8,9] However, these procedures require the presence of oxygen and dyes as photosensitizers.

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