2-Keto-4-trifluoromethyl-9-methyl-6,7,8,9-tetrahydro-2*H*-pyrano[3,2-*g*]quinoline, an Efficient, Stable Laser Dye

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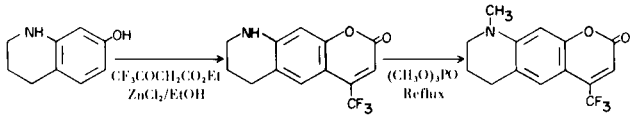
In our search for laser dyes operating at the blue-green transmission window of sea water, we have examined many 7-substituted coumarins. Such materials have been previously reported to lase (2) and were found to have lower thresholds than a number of families of compounds we examined. In attempts to improve photochemical stability (3) for device application, we have made the title compound (III), the most stable dye yet prepared within the class. Indeed stability of the flashlamp rather than of the dye becomes a limiting problem.

The preparation starting from 7-hydroxy-1,2,3,4-tetrahydroquinoline (4) (I) employs the von Pechmann condensation with ethyl 4,4,4-trifluoroacetoacetate to produce the intermediate II, itself an efficient laser dye but of lower stability than III.



I II III

Methylation of the 9-position is accomplished by means of trimethyl phosphate, a method we have used successfully in many of our preparations. Photochemical decomposition of coumarin dyes and the reasons leading to our selection of III will be reported later.

EXPERIMENTAL (5)

2-Keto-4-trifluoromethyl-6,7,8,9-tetrahydro-2*H*-pyrano[3,2-*g*]-quinoline.

7-Hydroxy-1,2,3,4-tetrahydroquinoline (2.38 g., 16 mmoles), ethyl 4,4,4-trifluoroacetoacetate (2.9 g., 16 mmoles), anhydrous zinc chloride (about 6 g.) and dry ethanol (50 ml.) were mixed and heated at reflux for 18 hours under a dry nitrogen atmosphere with stirring. A solid deposited on cooling. Filtration gave yellow crystals, 3.5 g. (76%), m.p. 229-230°; nmr (deuteriochloroform): δ 1.65-1.88 (m, 2, $CH_2CH_2CH_2$), 2.62 (t, 2, J = 6 Hz, CH_2CH_2Ar), 3.23 (t, 2, J = 6 Hz, N-CH_2CH_2), 6.23 (bs, 2, aromatics), 7.06 (bs, 1, C_3-H); ir (potassium bromide): 3450 (NH), 1720 cm^{-1} (C=O); mass spectrum: m/e 269 (M^+).

Anal. Calcd. for $C_{13}H_{10}NO_2F_3$: C, 58.00; H, 3.74; N, 5.20; F, 2.17. Found: C, 57.92; H, 3.59; N, 5.20; F, 21.17.

2-Keto-4-trifluoromethyl-9-methyl-6,7,8,9-tetrahydro-2*H*-pyrano-[3,2-*g*]quinoline.

The previous pyranoquinoline (2.5 g.) was refluxed in trimethyl phosphate (30 ml.) for four hours. Cooling gave crude product, 2.3 g. (87%), which recrystallized from acetonitrile to golden needles, m.p. 197-198°; nmr (deuteriochloroform): δ 1.86-2.10 (m, 2, $CH_2CH_2CH_2$), 2.80 (t, 2, J = 6 Hz, CH_2CH_2Ar), 3.01 (s, 3, N-CH_3), 3.41 (t, 2, J = 6 Hz, NCH_2CH_2), 6.36 and 6.44 (two s, each 1, aromatics), 7.20 (bs, 1, C_3-H); absorption max (ethanol): 257 nm (ε, 13,700), 412 nm (32,000); mass spectrum: m/e 283 (M^+).

Anal. Calcd. for $C_{14}H_{12}F_3NO_2$: C, 59.36; H, 4.24; N, 4.95; F, 20.14. Found: C, 59.46; H, 4.25; N, 5.13; F, 19.94.

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(3) E. J. Schimitschek, J. A. Trias, M. Taylor, and J. E. Celto, *IEEE J. Quantum Electron.*, QE-9, 781 (1973); E. J. Schimitschek, J. A. Trias, P. R. Hammond, and R. L. Atkins, *Optics Commun.*, 11, 352 (1974).

(4) C. J. Cavallito and T. H. Haskell, *J. Am. Chem. Soc.*, 66, 1166 (1944). Our modification of this procedure was to hydrogenate the 7-quinolinol (10 g.), in ethanol (200 ml.) in the presence of 1 g. of platinum oxide until hydrogen uptake ceased 14-16 hours. Filtration and evaporation gave crude 7-hydroxy-1,2,3,4-tetrahydroquinoline, which was used directly.

(5) Melting points are uncorrected. Combustion analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921; infrared spectra were determined by means of a Perkin Elmer 137 spectrometer, ultraviolet and visible spectra by means of a Perkin Elmer 202 spectrometer, nmr spectra by means of a Varian XL100-15 spectrometer operating at 100.1 MHz and mass spectra by means of a Hitachi Perkin Elmer RMU-6E spectrometer.