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INTERACTION OF 6'-METHOXYCARBONYL-1,3,3-TRIMETHYL-INDOLINO-2,2'-[2H]CHROMENE WITH HYDRAZINE HYDRATE

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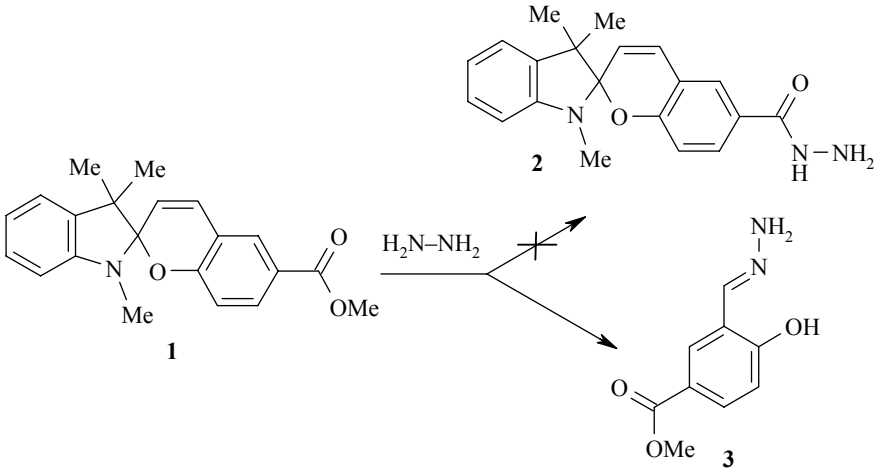
It has been shown previously that spiropyrans of the benxoxazione series, containing a [2H]chromene chelate forming hydrazon grouping in the benzo-nucleus [1] can be used as ligands to obtain complexes with transition metals [2].

It is decidedly interesting to attempt to prepare a new type of compound, namely spiropyrans **2**, which include an acid hydrazide substituent in the benzene ring of the [2H]chromene unit.



Unexpectedly the required hydrazide **2** was not formed from the reaction of the spiropyran **1** with hydrazine hydrate, but instead a solid substance was separated with a well resolved ^{1}H NMR spectrum which permitted its identification, in conjunction with its IR spectrum, as methyl 3-hydrazonomethyl-4-hydroxybenzoate (**3**).

The ^{1}H NMR spectrum of a $CDCl_3$ solution was recorded with a Varian Unity-300 (300 MHz) instrument. Proton signals were assigned relative to the residual protons of the solvent (δ 7.26 ppm). The IR spectrum of a nujol mull was measured with Specord IR-75 instrument.

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6'-Methoxycarbonyl-1,3,3-trimethylindolino-2,2'-[2H]-chromene (1) was prepared by prolonged boiling of an equimolar mixture of 1,2,3,3-tetramethylindolenium perchlorate, methyl 3-formyl-4-hydroxybenzoate, and piperidine in 2-propanol. The precipitate, which formed on cooling the reaction mixture, was filtered off and recrystallized from methanol. Mp 109°C (mp 106-108°C [3]). The ^{1}H NMR spectrum corresponded to structure **1**.

Methyl 3-hydrazonomethyl-4-hydroxybenzoate (3). A mixture of spiropyran **1** (335 mg, 1 mmol) and 100% hydrazine hydrate (55 mg, 1.1 mmol, ~ 0.05 ml) in absolute methanol was boiled for 30 min, the reaction mixture was cooled until a precipitate formed, which was filtered off. Yield 161 mg (83%); mp 193°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.89 (3H, s, OCH_3); 5.53 (2H, s, NH_2); 6.96 (1H, d, *J* = 8.6, H-5); 7.90 (1H, s, -CH=N-); 7.83-7.89 (2H, m, H-6,2); 11.61 (1H, s, OH). Signals of the protons of a *gem*-dimethyl group in position 3 of the indoline unit and the doublet signal of the protons in position 3' of the pyran ring of the [2H]chromene unit, characteristic of spiropyrans of the indoline series, were absent form the ^{1}H NMR spectrum. Found, %: C 55.53; H 5.27; N 14.25. $C_9H_{10}N_2O_5$. Calculated, %: C 55.67; H 5.19; N 14.43.

The presence in the IR spectrum of compound **3** of stretching frequencies ν_{OH} and ν_{NH} at 3374 and 3229 cm^{-1} respectively together with a strong absorption band at 1700 cm^{-1} provides a basis for the establishment of the structure methyl 3-hydrazonomethyl-4-hydroxybenzoate for compound **3**.

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