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SHORT COMMUNICATIONS

5,5-Dimethyl-7-thioxo-2-phenyl-5,6-dihydro-7*H*-thiochromen

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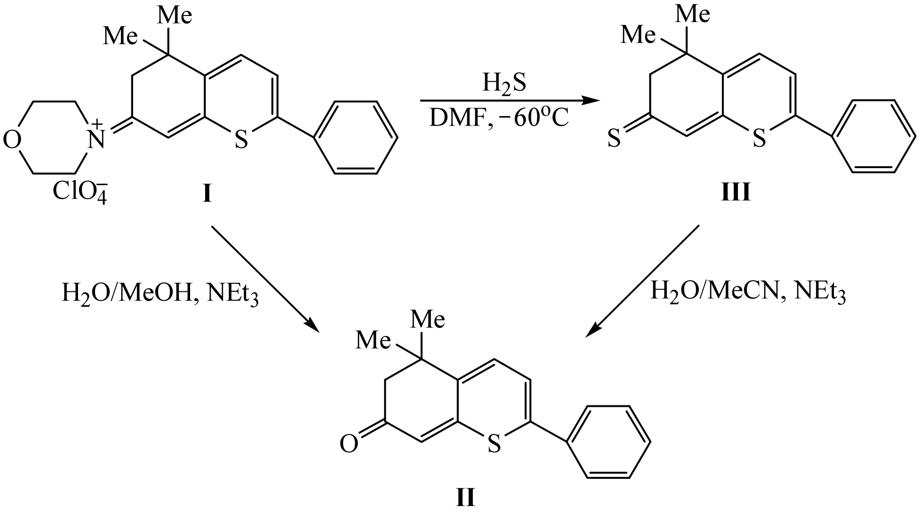
Formerly we obtained by heterocyclization of 1-*N,N*-dimethylimmonio-3-phenyl-2-propen-3-yl 5,5-di-methyl-1-morpholiniocyclo-2-hexen-3-yl sulfide diperchlorate 5,5-dimethyl-7-morpholinio-2-phenyl-5,6-dihydro-7*H*-thiochromen perchlorate (**I**). Its hydrolysis yielded 7-oxo derivative **II** [1].



In this study we reacted perchlorate **I** with the hydrogen sulfide to obtaon in a quantitative yield previously unknown 5,5-dimethyl-7-thioxo-2-phenyl-5,6-dihydro-7*H*-thiochromen (**III**). The reaction was carried out in DMF in the presence of a catalytic quantity of triethylamine at –60°C. Treating compound **III** with water afforded ketone **II**.

5,5-Dimethyl-7-thioxo-2-phenyl-5,6-dihydro-7*H*-thiochromen (III). Into a bright red solution of 0.2 g (0.46 mmol) of perchlorate **I** in 3 ml of anhydrous DMF at –60°C was passed for 10 min a flow of dry hydrogen sulfide, 0.01 ml of triethylamine was added, and the stream of hydrogen sulfide was passed at the same temperature for 3 h more (TLC monitoring on Silufol UV-254 plates, eluent chloroform–ethyl acetate, 3:1). The color of the reaction mixture changed into violet. The reaction mixture was poured on 50 g of ice–water mixture, the reaction product was extracted into chloroform, the extract was washed with ice water and dried over $MgSO_4$ at 5°C. On evaporating the solvent we obtained 0.12 g (92%) of compound **III** as a thick violet oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 s (6H, CH_3), 2.85 s (2H, CH_2), 6.87 and 6.90 d (2H, =CH–CH=), 6.89 s (1H, HC=), 7.42–7.43 m ($3H^{m,p}$ Ph), 7.54 d ($2H^o$ Ph). IR spectrum, ν, cm^{-1}: 1576, 1598 (C=C–S), 1076 (C=S). UV spectrum, λ_{max}, nm (ε): 249 (13095), 269 (10849), 331 (2998), 424 (9779), 498 (11400), 526 sh (10497). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.75 (CH_3), 37.14 (C^5), 56.96

(C^6), 118.14 (C^3), 124.24 (C^4), 128.89 (C^8), 135.64 (C^2), 142.99 (C^{10}), 150.31 (C^9), 216.88 (C^7); 126.16 ($C'_{2,6}$, Ph), 126.86 (C'_4, Ph), 129.33 ($C'_{3,5}$, Ph). Found, %: C 71.40; H 5.86; S 21.87. $C_{17}H_{16}S_2$. Calculated, %: C 71.83; H 5.63; S 22.54.

Hydrolysis of 5,5-dimethyl-7-thioxo-2-phenyl-5,6-dihydro-7*H*-thiochromen (III). A solution of 0.05 g of thione III in 6 ml of aqueous acetonitrile (1:5 v/v) in the presence of a catalytic quantity of triethyl amine was stirred for 4 h at 50–60°C. The color of the reaction mixture changed from violet to red. The reaction mixture was extracted with chloroform, the extract was washed with water and dried on Na_2SO_4. On evaporating the solvent the presence in the residue (0.03 g) of 5,5-dimethyl-7-oxo-2-phenyl-5,6-dihydro-7*H*-thiochromen (**II**) was determined by TLC (eluent chloroform–ethyl acetate, 3:1) comparing with an authentic sample.

^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400 (at operating frequencies 400.0 and 100.6 MHz respectively), internal reference HMDS. IR spectrum was recorded on a spectrophotometer Bruker IFS-25, UV spectrum on a Perkin Elmer Lambda 35 UV-Vis instrument.

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