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AN UNUSUAL REARRANGEMENT ON PHOTOLYSIS OF THE ENOL ACETATE OF 4-THIOCHROMANONE

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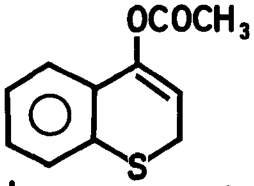
Summary: The enol acetate from 4-thiochromanone on photolysis undergoes ring opening, apparently involving a novel (1,5)-acyl migration from oxygen to sulfur, to give 1-(2-acetylthiophenyl)propen-1-one.

As part of a synthetic investigation of thiochromanone compounds, we recently synthesized the enol acetate **1** derived from 4-thiochromanone. There has been considerable research interest in the photochemistry of enol esters, as evidenced by two relatively recent reviews,[1,2] while Padwa and his collaborators[3,4] have conducted extensive studies of the photochemical behavior of enol derivatives in a series of chromanones and isochromanones. Partly from our interest in comparing the photochemical behavior of a formally analogous enol acetate in the thiochromanone series and partly from our observation that compound **1** rather rapidly decomposed on exposure to sunlight, we have examined the photolysis of the latter compound and now wish to report a rather unusual rearrangement.

Compound **1**[5] was prepared in 78% yield by the procedure used for the enol acetate from 4-chromanone.[6] The enol acetate ($\lambda_{max}^{CH_3CN}$ 243(19000); 330(1350) nm) was irradiated[7] under nitrogen in acetonitrile for 70 hours. The resulting product,[8] after chromatography on silica gel and elution with dichloromethane, afforded a pale yellow liquid (47%, bp 80-85°/0.01 mm) with strong bands in the infrared (neat liquid) at 1725, 1702 and 1665 cm^{-1} and ^1H NMR ($CDCl_3$)δ2.33 (3H,s), 5.95 (1H, dd, J=2, 10 Hz), 6.32 (1H, dd J=2, 18 Hz), 6.70 (1H, dd, J=10, 18 Hz), 7.40-7.63 (4H,m) ppm. These spectral characteristics, in particular the striking similarity between the NMR spectrum of our photoproduct and that reported recently for 1-phenylpropen-1-one **2**,[9] combined with the observation of a molecular ion peak at m/e = 206 in the mass spectrum, strongly indicated that the product was 1-(2-acetylthiophenyl)propen-1-one, **3**.



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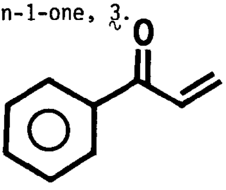

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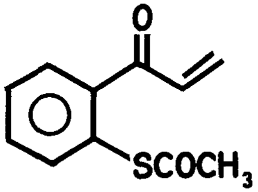

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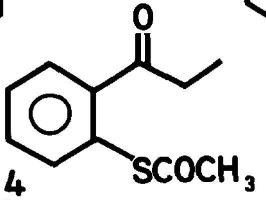

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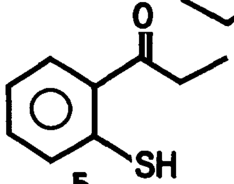

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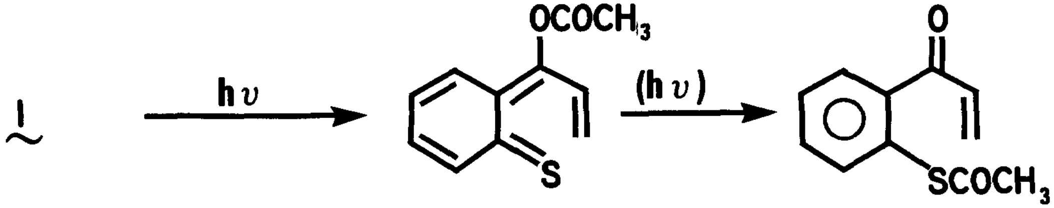
As expected for a vinyl ketone derivative, 3 proved difficult to obtain rigorously pure (as indicated by TLC) and was thus converted by catalytic hydrogenation into the saturated analogue 4, in 66% yield. High resolution mass spectral analysis established the molecular formula $C_{11}H_{12}O_2S$ for this compound, while the ^{1}H NMR ($CDCl_3$) δ1.17 (3H, t, J=7 Hz), 2.37 (3H, s), 2.88 (2H, q, J=7 Hz), 7.37-7.67 (4H, m) and ^{13}C NMR ($CDCl_3$) δ204.0, 193.1, 143.6, 136.6, 130.8, 129.4, 127.8, 125.8, 35.1, 30.2, 8.1 ppm spectral data were in excellent agreement with analogous data obtained for the model compounds propiophenone and phenyl thioacetate, thus confirming our assignment of structure. Further evidence on this point was supplied by the mild hydrolysis of 4[10] to a mixture of the thiol 5 and the analogous disulfide. Finally the unambiguous synthesis of 4 by a simple route completes our proof of structure of this compound, and hence confirms 3 as the structure of the photoproduct.



As indicated in the scheme above, the photo-rearrangement may be considered as proceeding <u>via</u> an initial (6π-) electrocylic ring opening[3,4] followed by a formal 1,5-acyl migration from oxygen to sulfur. To our knowledge, excluding the photo-Fries rearrangement of enol esters, such a 1,5-acyl shift has been reported only once previously,[11] and never for a migration to another heteroatom (sulfur, in this case). Further evidence on the nature of this process, and on the excited state responsible for this interesting photoreaction, is currently being sought.

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References and Notes

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