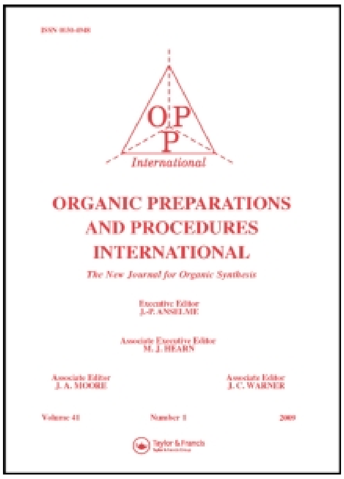

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THIOCHROMONE 1-OXIDE

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THIOCHROMONE 1-OXIDE

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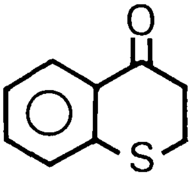
In connection with our continuing photochemical investigation of sulfoxides[1] in the thiochroman-4-one(I) series, we recently needed to prepare thiochromone 1-oxide(III). Curiously, although the analogous sulfide(II) and sulfone(IV) were first reported and characterized fifty years ago,[2] the sulfoxide member of this series has not been reported.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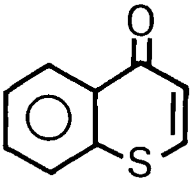
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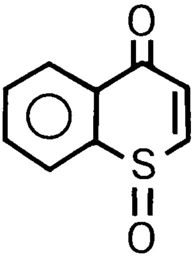
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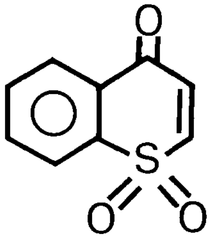
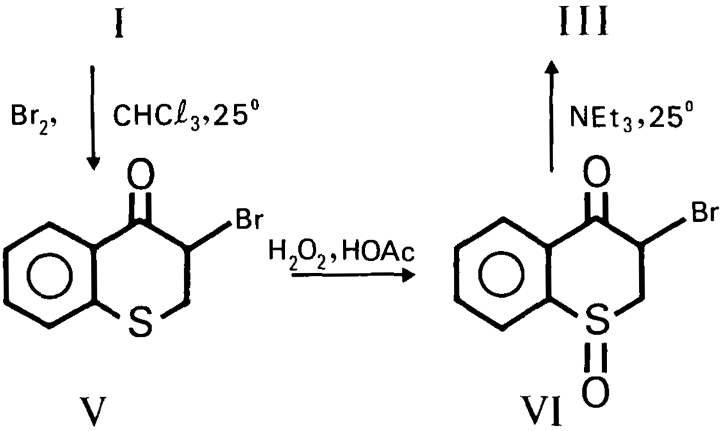
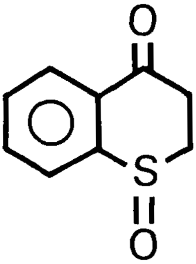

IV

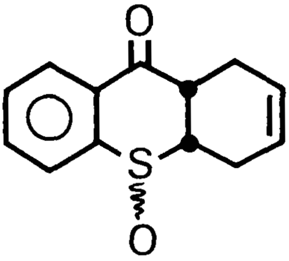
The consistent failure of our attempts to obtain III by the oxidation of thiochromone with standard reagents such as m-chloroperbenzoic acid, peracetic acid, iodobenzene dichloride, and sodium periodate provided a clue to the problem. Since the most common result of these oxidation reactions is the formation of a mixture of sulfide and sulfone, even when only one equivalent of the oxidant was present, the sulfoxide must clearly be much more susceptible to further oxidation than is usually the case, for example, in the analogous thiochroman-4-one derivatives. We have successfully avoided this difficulty by oxidation of the known 3-bromothiochroman-4-one[2](V) to the hitherto unknown sulfoxide(VI) and dehydrobromination of this compound with triethylamine.



Attempts to carry out the dehydrobromination of VI with pyridine were unsuccesful, as were attempts to obtain thiochromone1-oxide by the dehydrogenation of thiochroman-4-one 1-oxide(VII) with triphenylmethyl perchlorate[3] or DDQ.[4] Thiochromone 1-oxide readily forms a Diels-Alder adduct(VIII)with 1,3-butadiene. Our investigations of the chemical and photochemical reactivity of the title compound are continuing.



VII



VIII

EXPERIMENTAL

3-Bromothiochroman-4-one(V). - 3-Bromothiochroman-4-one was prepared from I (Aldrich Chemical Co., Inc.) in 93% yield, by bromination in chloroform according to the procedure of Arndt;[2] mp.(hexane-benzene) 74-75°, lit.[2] mp. 76-77°; ν_{max}^{Nujol} 1665 cm^{-1}; $\delta(CDCl_3)$ 3.47 (2H, AB part of ABX system), 4.89 (1H, X part of ABX system) [J_{AX} = 4Hz, J_{BX} = 8Hz, J_{AB} = 14Hz], 7.15(m,3H), 8.03(dd,1H, J = 8Hz, 2Hz) ppm.

3-Bromothiochroman-4-one 1-oxide(VI). - 3-Bromothiochroman-4-one 1-oxide was prepared from V in 85% yield by the hydrogen peroxide-acetic acid procedure previously described;[5] mp. 159-160° (chloroform); ν_{max}^{Nujol} 1690, 1040 cm^{-1}; $\delta(CDCl_3)$ 3.92 (d, 2H, J = 6Hz) 5.54(t, 1H, J = 6Hz), 7.73 (m, 3H), 8.15 (m,1H) ppm.[6]

Anal. Calcd. for $C_9H_7BrO_2S$: C,41.72; H,2.72; Br 30.82; S,12.35.
Found : C,41.80; H,2.78; Br 31.22; S,12.45.

Thiochromone 1-oxide(III). - Triethylamine (0.43 ml.) was added slowly to a solution of 3-bromothiochroman-4-one 1-oxide (0.87g.) in methylene chloride (30 ml) and the mixture stirred for 1.5 hr at 25°. The solution was washed once with water, dried (Na_2SO_4) and evaporated without heating. Purification by repeated crystallization from benzene-petroleum ether (bp. 40-50°) gave thiochromone 1-oxide as pale yellow crystals, mp. 127-129° (52%); ν_{max}^{Nujol} 1665, 1045, 1030 cm^{-1}; $\delta(CDCl_3)$ 6.70 (d, 1H, J = 11Hz), 7.82(d, 1H, J = 11Hz), 7.60-8.35(m,4H) ppm; m/e = 178(M^+), 162, 152, 150 and 136. Calculated for $C_9H_6O_2S$: 178.0088. Found: 178.0084.

Anal. Calcd. for $C_9H_6O_2S$: C,60.66; H,3.39; S,17.99.
Found : C,60.23; H,3.40; S,17.74.

Diels-Alder Adduct(VIII) from Reaction of III with 1,3-Butadiene. - 1,3-Butadiene was bubbled through a solution of thiochromone 1-oxide(0.2g.) in chloroform(10 ml) for 30 min while the mixture was stirred. The solution was sealed in a stainless steel vessel and heated for 3 h at 75°. After cooling the solvent was evaporated. The residue on repeated crystallizations from benzene and petroleum ether (40°-50°) gave white crystals (0.125g, 45%), mp. 131-132°; ν_{max}^{KBr} 1680, 1650, 1055, 1050 cm^{-1}; $\delta(CDC\ell_3)$ 2.14 (m, 2H), 3.09 (m, 2H), 3.90 (m, 2H), 5.60 (t, 2H, J = 2Hz), 7.13-8.13 (m, 4H) ppm; m/e = 232 (M^+), 152, 136.

Anal. Calcd. for $C_{13}H_{12}O_2S$: C,67.21; H,5.21; S,13.77.
Found : C,66.77; H,5.15; S,13.70.

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6. The much simpler nmr spectrum of VI is presumably due to the accidental magnetic equivalence of the C-2 protons.

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