2,2,8,8-Tetramethyl-3,4,5,6-nonatetraene (2b; $R^1 = t\text{-}C_4H_9$, $R^2 = H$). Chromatography gave 1.16 g of **2b** (yield 66%): IR ($CDCl_3$) 2070 cm^{-1}; ^1H NMR (CCl_4) δ 1.11 (s, 18 H), 5.52 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 111.3 ($C^1 + C^5$), 170.7 ($C^2 + C^4$), 123.1 (C^3); mass spectrum, m/e 176($M^{+\cdot}$).

2,7,7-Trimethyl-2,3,4,5-octatetraene (2c; $R^1 = R^2 = CH_3$). Chromatography gave 1.05 g of **2c** (yield 70%): IR (CCl_4) 2075 cm^{-1}; ^1H NMR (CCl_4) δ 1.11 (s, 9 H), 1.89 (d, 6 H), 5.53 (m, 1 H, $^7J(H^a,CH_3)$ = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 112.0 (C^1), 170.0 (C^2), 119.8 (C^3), 171.3 (C^4), 106.1 (C^5); mass spectrum, m/e 148($M^{+\cdot}$); UV (*n*-pentane) λ_{max} 220 nm ($\epsilon \simeq 40\,000$), 250 (9000).

2,2,7-Trimethyl-3,4,5,6-nonatetraene (2d; $R^1 = C_2H_5$, $R^2 = CH_3$). Chromatography gave 0.97 g of **2d** (yield 60%): IR ($CDCl_3$) 2068 cm^{-1}; ^1H NMR (CCl_4) δ 1.12 (s, 9 H), 1.09 (t, 3 H), 1.90 (d, 3 H), 2.18 (m, 2 H), 5.66 (m, 1 H, $^7J(H^a,R^2)$ = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 111.7 (C^1), 169.8 (C^2), 121.4 (C^3), 170.6 (C^4), 112.3 (C^5); mass spectrum, m/e 162($M^{+\cdot}$); UV (*n*-pentane) λ_{max} 224 nm ($\epsilon \simeq 90\,000$), 250 ($\simeq 20\,000$).

2,2,7,8-Tetramethyl-3,4,5,6-nonatetraene (2e; $R^1 = i\text{-}C_3H_7$, $R^2 = CH_3$). Chromatography gave 1.41 g of **2e** (yield 80%): IR ($CDCl_3$) 2068 cm^{-1}; ^1H NMR (CCl_4) δ 1.11 (s, 9 H), 1.08 (d, 6 H), 1.89 (dd, 3 H), 2.33 (m, 1 H), 5.60 (m, 1 H, $^7J(H^a,R^2)$ = 2.3 Hz); ^{13}C NMR ($CDCl_3$) δ 111.4 (C^1), 169.8 (C^2), 121.7 (C^3), 170.0 (C^4), 116.3 (C^5); mass spectrum, m/e 176 ($M^{+\cdot}$).

2,2,3,8,8-Pentamethyl-3,4,5,6-nonatetraene (2f; $R^1 = t\text{-}C_4H_9$, $R^2 = CH_3$). Chromatography gave 1.33 g of **2f** (yield 70%): IR ($CDCl_3$) 2070 cm^{-1}; ^1H NMR (CCl_4) δ 1.10 (s, 9 H), 1.11 (s, 9 H), 1.89 (d, 3 H), 5.51 (q, 1 H, $^7J(H^a,R^2)$ = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 111.0 (C^1), 169.8 (C^2), 121.6 (C^3), 170.2 (C^4), 119.0 (C^5); mass spectrum, m/e 190($M^{+\cdot}$); UV (*n*-pentane) λ_{max} 223 nm ($\epsilon \simeq 60\,000$), 248 ($\simeq 12\,000$).

1,1-Tetramethylene-6,6-dimethyl-1,2,3,4-heptatetraene (2g; $R^1 = R^2 = -(CH_2)_4-$). Chromatography gave 1.13 g of **2g** (yield 65%): IR (CCl_4) 2062 cm^{-1}; ^1H NMR (CCl_4) δ 1.10 (s, 9 H), 1.60–1.90 (m, 4 H), 2.40–2.70 (m, 2 H), 5.51 (m, 1 H, $^7J(H^a,CH_2)$ = 3.5 Hz); ^{13}C NMR ($CDCl_3$) δ 112.0 (C^1), 169.7 (C^2), 121.8 (C^3), 166.7 (C^4), 115.3 (C^5); mass spectrum, m/e 174 ($M^{+\cdot}$).

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Registry No. **1a**, 79919-23-6; **1b**, 79919-24-7; **1c**, 79919-25-8; **1d**, 79919-26-9; **1e**, 79919-27-0; **1f**, 79919-28-1; **1g**, 79919-29-2; **2a**, 78601-72-6; **2b**, 78601-71-5; **2c**, 78601-74-8; **2d**, 78601-75-9; **2e**, 78601-76-0; **2f**, 78601-77-1; **2g**, 78601-73-7; *tert*-butyl silver, 71451-70-2.

3′,3′-Dichloro-3-methylene-4-thiochromanone: A Novel Product from Carbon Tetrachloride

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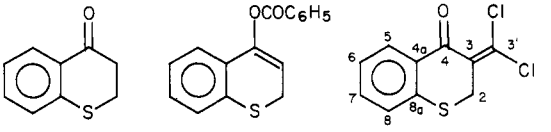
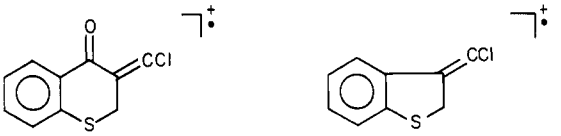
As part of our continuing investigation of the photochemical behavior of the enol acetate of 4-thiochromanone 1,[1] we recently attempted to synthesize the analogous enol benzoate 2. One of the procedures which we attempted called for refluxing 4-thiochromanone with benzoic anhydride in carbon tetrachloride solution, in the presence of a trace of 60% perchloric acid.[2] The reaction, as followed by TLC, appeared to be very slow, but after 7 days little starting material remained. Routine (aqueous) workup afforded the crude product, after thorough washing with 10% sodium hydrogen carbonate.

The major product obtained appeared to be the expected enol benzoate,[3] 2 (27%), accompanied by the starting ketone, but the early fractions after chromatography on silica gel contained a yellow oil 3 (22%), which showed no vinylic proton in the ^1H NMR and had a sharp singlet at δ 4.06 and bands in the IR at 1670 and 1595 cm^{-1}. The remaining signals in the ^1H NMR spectrum (see the Experimental Section) were characteristic of 4-thiochromanone or a simple derivative.

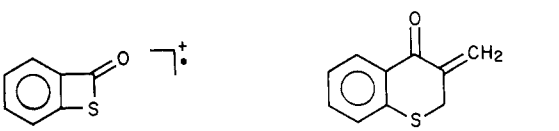


1 2 3

The mass spectrum of compound 3 showed peaks at 244, 246, and 248 with the relative intensities 100, 72, 12, strongly indicative of a dichloro compound with the molecular formula $C_{10}H_6Cl_2OS$. This was subsequently confirmed by a high-resolution mass spectral measurement. Other features of the mass spectrum included the appearance of fragment ions at m/z 209 and 181, tentatively identified as 4 and 5, respectively, while the base peak appeared at m/z 136. This ion we believe is 6 and further confirms the 4-thiochromanone structural feature, as we had shown earlier[4] that 4-thiochromanones normally fragment by a retro-Diels–Alder process, with loss of C-2 and C-3.



4 (m/z 209) 5 (m/z 181)



6 (m/z 136) 7

The structure of 3 could now be assigned with confidence as 3′,3′-dichloro-3-methylene-4-thiochromanone. Final confirmation came from the ^{13}C NMR spectrum, which revealed the 10 expected signals and multiplicities at δ 182.5 (s, C-4), 141.0 (s, C-8a), 133.4 (d, C-7), 131.3 (s, C-3), 130.4 (d, C-5), 129.8 (s, C-4a), 128.3 (s, C-3′), 127.5 (d, C-8), 125.6 (d, C-6), 32.45 (t, C-2). The aromatic signals were in close agreement with those previously assigned to a large number of simple 4-thiochromanone derivatives.[5] The signal at δ 32.45 for C-2 is at remarkably high field for a methylene group flanked by both a carbon–carbon double bond and a sulfur atom. We attribute this to a field effect of one of the two chlorine atoms. The failure of the compound to crystallize is also surprising and possibly indicates considerable distortion from planarity in the β,β-dichloro enone system. Other physical properties of compound 3 may be found in the Experimental Section.

As a chemical proof of structure 3, we attempted to reduce 3 to the parent 3-methylene-4-thiochromanone (7), which is apparently not known. Several attempts with

(1) Still, I. W. J.; Leong, T. S. *Tetrahedron Lett.* **1979**, 3613.
(2) House, H. O.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1971**, 36, 2361.
(3) The enol benzoate is rather unstable and reverts to the starting ketone under a variety of conditions. Spectral data are given in the Experimental Section.
(4) Harrison, A. G.; Thomas, M. T.; Still, I. W. J. *Org. Mass Spectrom.* **1970**, 3, 899.
(5) Chauhan, M. S.; Still, I. W. J. *Can. J. Chem.* **1975**, 53, 2880.

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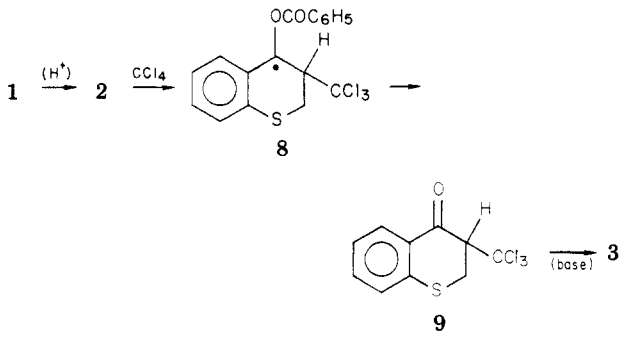
Scheme I



tri-*n*-butyltin hydride under quite forcing conditions all failed, although some evidence of reduction to the monochloro analogue of **3** was found. Likewise, attempts to synthesize **7** starting from 4-thiochromanone and paraformaldehyde, using a recent literature procedure,[6] were also without success.

The question of the mechanism of this unusual reaction is not finally resolved, but certain possibilities can be excluded. The intervention of dichlorocarbene is ruled out here, since no reaction was observed between 4-thiochromanone and dichlorocarbene generated from the thermal decomposition of sodium trichloroacetate.

When **1** was refluxed in carbon tetrachloride in the presence of benzoyl peroxide (radical catalyst), but in the absence of strong acid, no trace of **3** was found. Likewise, when the original experiment was repeated entirely in the dark, none of the dichloro compound was produced. When benzoic anhydride was omitted from the otherwise identical reaction conditions, again none of compound **3** was formed. The cumulative evidence suggests to us the following mechanistic scheme (Scheme I). Strong acid catalysis produces a sufficient concentration of the enol form of **1** or, more likely, the enol benzoate **2**, which then undergoes a free-radical addition with the solvent to form the intermediate **8**. Free-radical additions of both chloroform and carbon tetrachloride with various olefins have been studied mechanistically[7] and the addition of carbon tetrachloride has also been successfully applied recently in a synthesis of chrysanthemic acid derivatives.[8] Loss of a benzoyl radical would be expected to give **9**. Finally, **9** would undergo loss of HCl, perhaps during the workup, to produce compound **3**. Unfortunately, the original target molecule, the enol benzoate **2**, could not be isolated in sufficiently pure form to verify its intermediacy in the reaction with carbon tetrachloride.

This transformation affords an interesting demonstration of the reactivity of even a relatively inert organic solvent under conditions which appear almost tailored to ensure nonparticipation by solvent molecules.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer 298 grating spectrophotometer, UV spectra on a Unicam SP-800 instrument, and ^{1}H NMR spectra on a Varian EM-360 spectrometer. Natural abundance, proton-decoupled ^{13}C NMR spectra were obtained on the Bruker WH-400 instrument at the Southwestern Ontario NMR Centre in Guelph. Routine mass spectral data were obtained on a Bell and Howell 21-490 instrument and the accurate mass measurements on the AEI MS-902. Elemental analyses were performed by Microanalysis Laboratories Ltd., Markham, Ontario L3R 3R6.

Isolation of 3',3'-Dichloro-3-methylene-4-thiochromanone (3). 4-Thiochromanone (3.28 g., 20 mmol) and benzoic anhydride (19.30 g, 85 mmol) were refluxed in carbon tetrachloride (70 mL) containing 2 drops of 60% perchloric acid for 7 days. After cooling, the reaction mixture was poured into cold 10% sodium hydrogen carbonate solution, the organic layer was separated, and the aqueous phase was reextracted several times with ether. The combined organic layer was washed several times with 10% sodium hydrogen carbonate (until no more benzoic acid precipitated on acidification with HCl) and finally with water and dried (Na_2SO_4). Evaporation gave a crude mixture[9] (14.62 g), which was chromatographed on silica gel. Elution with carbon tetrachloride gave a yellow oil (0.55 g, 22%), after correction for recovered **1** (1.62 g, 49%). The oil was purified by short-path distillation: bp 180–185 °C (bath temperature) (10 mm); IR (liquid film) ν 1670 (C=O), 1595 cm^{-1}; UV (MeOH) λ_{max} 249 nm (ϵ 12900), 279 (12600); ^{1}H NMR ($CDCl_3$) δ 4.06 (2, s), 7.20 (3, m), 8.15 (1, m); ^{13}C NMR ($CDCl_3$) δ 182.5, 141.0, 133.4, 131.3, 130.4, 129.8, 128.3, 127.5, 125.6, 32.45; mass spectrum, *m/z* (relative intensity) 246 (42), 244 (57), 209 (45), 181 (57), 136 (100), 108 (52); mass measurement calcd for $C_{10}H_6Cl_2OS$ 243.9516, found 243.9499. Anal. Calcd for $C_{10}H_6Cl_2OS$: C, 48.98; H, 2.45; Cl, 28.95; S, 13.08. Found: C, 49.82; H, 2.96; Cl, 28.63; S, 14.11.

The expected enol benzoate **2** (27%, estimated by NMR) proved to be unstable to the chromatographic conditions employed. however, the original mixture contains a product which, from the spectral characteristics noted below, appears to be **2**. IR ($CHCl_3$) ν 1758 (ester C=O); ^{1}H NMR δ ($CDCl_3$) 3.58 (2, d, J = 5.7 Hz, -CH_2-), 5.79 (1, t, J = 5.7 Hz, =CH-), 6.9–7.7 (7, m, *arom*), 8.0–8.3 (2, m, *ortho* to C=O).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. The ^{13}C NMR spectrum was obtained at the Southwestern Ontario NMR Centre funded by a Major Installation Grant from NSERC.

Registry No. 1, 3528-17-4; 2, 79971-39-4; 3, 79971-40-7; benzoic anhydride, 93-97-0; carbon tetrachloride, 56-23-5.

(6) Paquette, L. A.; Han, Y.-K. *J. Am. Chem .Soc.* **1981**, 103, 1831.
(7) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 1887, 3921.
(8) Nakada, Y.; Endo, R.; Muramatsu, S.; Ide, J.; Yura, Y. *Bull. Chem. Soc. Jpn.* **1979**, 52, 1511.
(9) This mixture contained substantial amounts of unreacted benzoic anhydride.

Regio- and Stereospecific Synthesis of Acetylenic Thio Enol Ethers Occurring in the Genus *Anthemis*

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It has been shown by Bohlmann et al.[1a] that plants of the genus *Anthemis* contain a variety of compounds with the thio enyne fragment **1**. It is well established that this

1

structural element with cis geometry around the double bond is formed exclusively in the ring-opening of 3-thienyllithium derivatives.[2] This suggested to us that the

(1) (a) Bohlmann, F.; Burkhardt, T.; Zdero, C. "Naturally Occurring Acetylenes"; Academic Press: New York 1973; p 381. (b) *Ibid.*, p 506.
(2) Frejd, T.; Karlsson, O.; Gronowitz, S. *J. Org. Chem.* **1981**, *46*, 3132. Gronowitz, S.; Frejd, T. *J. Heterocycl. Compd. (Engl. Transl.)* **1978**, 353 and references cited therein.

0022-3263/82/1947-0374$01.25/0