Table II. Some Data of Thiinoindolizines

compd^a	reactant	% yield^b	mp, °C	IR (KBr) ν, cm^{-1} NH	CN	CO
24	16	67	142-145 (204-205)^c	3250		1670
	18	63	142-145			
25	17	43	268-270	3250	2213	1688
26	19	57	202-205 (184-188)^c	3260		1680
27	20	56	264-267	3250	2218	1685
28	21	40	199-202 (192-196)^c	3260		1680
29	22	63	192-195 (184-187)^c	3260	2218	1687

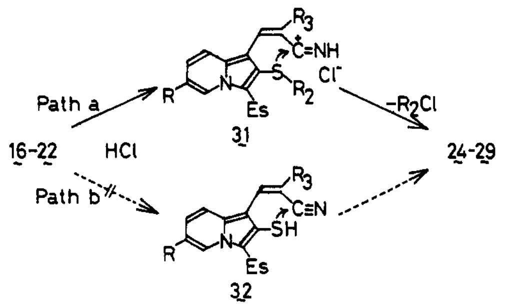
^{a} Satisfactory analytical values were reported for all compounds in the table. ^{b} After recrystallization. ^{c} Its hydrochloride.

Table III. NMR Data of Thiinoindolizines

compd	C-4	C-5	C-6	C-7		C-8	NH	COOEt^a
24	8.51 (s)	7.90 (br d)	7.50 (br t)	7.13 (dt)		9.71	9.5-10.5	1.33 (t), 1.55 (t),
	$J_{5,6} = 9.0$, $J_{6,7} = J_{7,8} = 7.0$, $J_{6,8} = 2.0$ Hz					(br d)	(br)	4.43 (q), 4.51 (q)
26	8.78 (s)	7.65 (d)	7.23 (dd)	2.41 (s)		9.39	9.5-10.5	1.41 (t), 1.47 (t),
		$J_{5,6} = 9.0$, $J_{6,8} = 2.0$ Hz				(br s)	(br)	4.34 (q), 4.40 (q)
28	8.45 (s)	7.81 (d)	7.48 (dd)	1.32 (t)	2.78 (q)	9.55	9.0-10.0	1.42 (t), 1.49 (t),
		$J_{5,6} = 9.0$, $J_{6,8} = 2.0$ Hz				(br s)	(br)	4.41 (q), 4.49 (q)

^{a} The coupling constants are 7.0 Hz.

Scheme II



path a, protonation-cyclization-elimination
path b, hydrolysis-cyclization

(ethoxymethylene)cyanoacetate **6** or (ethoxymethylene)malononitrile **7** in the presence of excess potassium carbonate in chloroform followed by the thermolyses in xylene or toluene of the resulting 2-allylidene-1,2-dihydropyridines **8-14**, according to the literature.[4] 3-Benzoylindolizine **23** was directly obtained without isolation of intermediate **15** from the reaction of picolinium salt **5**[9] with **6**. Some results and properties of new compounds **9**, **11-14**, **17**, and **19-23** are given in Table I.

Preparation of Thiino[3,2-*a*]indolizines 24-29. General Method. To concentrated hydrochloric acid (20 mL) was added 2-(alkylthio)-1-(2-cyanovinyl)indolizine (1 mmol), and the suspended solution was heated on a water bath (70-80 °C) until the indolizine was completely dissolved (ca. 1-2 h). The fluorescent blue reaction solution was then evaporated to dryness at reduced pressure, and water (20 mL) was added. The resulting solution was neutralized carefully with aqueous potassium carbonate, and the yellow substance that separated was collected by suction. Recrystallizations from chloroform gave orange needles of a thiino[3,2-*a*]indolizine derivative. The hydrochlorides of these thiinoindolizines were obtained by recrystallizations of the residue from ethanol without alkaline treatment. However, treatment of 3-benzoylindolizine **23** and 3-[2-cyano-2-(ethoxycarbonyl)-vinyl]-2-(methylthio)pyrazolo[1,5-*a*]pyridine with hydrochloric acid afforded only complex mixtures, and any significant products could not be separated from them. These results and properties are given in Tables II and III.

Registry No. **1**, 59181-95-2; **2**, 67988-75-4; **3**, 79917-93-4; **4**, 79917-94-5; **5**, 59181-92-9; **6**, 94-05-3; **7**, 123-06-8; **8**, 67988-67-4; **9**, 79917-95-6; **10**, 67988-69-6; **11**, 79917-96-7; **12**, 79917-97-8; **13**, 79917-98-9; **14**, 79917-99-0; **16**, 67988-71-0; **17**, 79918-00-6; **18**, 67988-73-2; **19**, 79918-01-7; **20**, 79918-02-8; **21**, 79918-03-9; **22**, 79918-04-0; **23**, 79918-05-1; **24**, 79918-06-2; **24**·HCl, 79918-07-3; **25**, 79918-08-4; **26**, 79918-09-5; **26**·HCl, 79918-10-8; **27**, 79918-11-9; **28**, 79918-12-0; **28**·HCl, 79918-13-1; **29**, 79918-14-2; **29**·HCl, 79918-15-3; 3-[2-cyano-2-(ethoxycarbonyl)vinyl]-2-(methylthio)pyrazolo[1,5-*a*]pyridine, 75619-88-4.

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[9] Pyridinium salts **1-5** were prepared from 2-picoline, 2,5-lutidine, and 5-ethyl-2-methylpyridine according to the literature (Tominaga, Y.; Miyake, Y.; Fujito, H.; Matsuda, Y.; Kobayashi, G. *Yakugaku Zasshi* **1977**, *97*, 927), and some properties of new salts **3** and **4** are as follows. **3**: yellow needles (ethanol), mp 141-144 °C; IR (KBr) ν 1700 cm^{-1} (CO). Anal. Calcd for $C_{14}H_{20}NO_2S_2I$: C, 39.53; H, 4.74; N, 3.29. Found: C, 39.43; H, 4.71; N, 3.32. **4**: yellow needles (ethanol), mp 146-147 C; IR (KBr) ν 1705 cm^{-1}. Anal. Calcd for $C_{15}H_{22}NO_2S_2I$: C, 41.00; H, 5.05; N, 3.19. Found: C, 41.03; H, 5.04; N, 3.19.

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tert-Butylsilver-Induced 1,5-Substitution in Some 2,4-Pentadiynyl Methanesulfinates. A Novel Route to Di- and Trisubstituted Pentatetraenes

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Received July 3, 1981

Hitherto pentatetraenes are rather unexplored compounds. Up to 1976 only six pentatetraenes had been reported, all of them being tetrasubstituted.[1] In this year the parent hydrocarbon, C_5H_4, was prepared for the first time via a retro-Diels-Alder reaction.[2] The compound was substantially contaminated with 1,3-pentadiyne, however.

Because of their unique π system, pentatetraenes may exhibit chirality. An example of a chiral tetrasubstituted pentatetraene has recently been described.[3]

At the time this work was initiated, pentatetraenes had not been synthesized via an organometal-induced 1,5-substitution in appropriate 2,4-pentadiynyl esters. In view of the observed smooth alkylsilver induced 1,5-substitution in pentenynyl sulfinates (eq 1),[4] it was anticipated that

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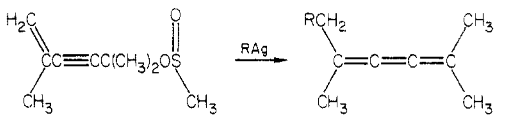
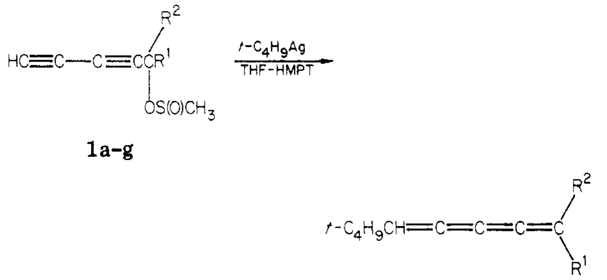
[1] Hopf, H. "The Chemistry of Ketenes, Allenes, and Related Compounds", Part 2; Patai, S., ed.; Wiley: New York, 1980; Chapter 20.
[2] Ripoll, J. L.; Thuillier, A. *Tetrahedron* **1977**, *33*, 1333.
[3] Bertsch, K.; Jochims, J. C. *Tetrahedron Lett.* **1977**, 4379.

0022-3263/82/1947-0371$01.25/0

these group 1B metal compounds could also be utilized to convert 2,4-pentadiynyl sulfinates into pentatetraenes.


(1)

The desired reaction indeed occurred when the 2,4-pentadiynyl sulfinates **1** (eq 2) were treated with *tert*-butylsilver at −30 °C in a mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPT). Via this route seven *tert*-butyl-substituted pentatetraenes have been prepared in good yields (eq 2; yield of **2** after purification by column chromatography, 60–80%; purity of **2**, ≃85–90%).


1a–g

(2)

2a–g

1a, **2a**, $R^1 = i\text{-}C_3H_7$; $R^2 = H$
1b, **2b**, $R^1 = t\text{-}C_4H_9$; $R^2 = H$
1c, **2c**, $R^1 = CH_3$; $R^2 = CH_3$
1d, **2d**, $R^1 = C_2H_5$; $R^2 = CH_3$
1e, **2e**, $R^1 = i\text{-}C_3H_7$; $R^2 = CH_3$
1f, **2f**, $R^1 = t\text{-}C_4H_9$; $R^2 = CH_3$
1g, **2g**, $R^1 = R^2 = \text{-}(CH_2)_4\text{-}$

Compounds **2**, especially **2a** and **2b**, are thermally very unstable so that it is difficult to obtain them in a reasonable purity. Furthermore, it seems that compounds **2** may undergo addition of *tert*-butylsilver. For instance, during the conversion of **1b** a small amount of a contaminant was formed with the *m/e* value 234 ($M^{+}\cdot$) in the mass spectrum. Addition of *tert*-butylsilver to **2b** in this case followed by protolysis would indeed give a compound with this molecular peak. During the reaction of **1** with *tert*-butylsilver a small excess of **1** was therefore used in order to make this addition reaction less likely.

It is worth noting in this connection that *tert*-butylsilver did not induce a substitution in **1** when the group R^1 was phenyl (R^2 = H or CH_3). Even when 2 mol equiv of the silver compound was used, no conversion of **1** could be detected. Attempts to convert the methanesulfonate analogues of **1** in these cases were also unsuccessful. The reason for this is still obscure. Unlike *tert*-butylsilver, methyl- and ethylsilver were not able to convert sulfinates **1a–g** into pentatetraenes under conditions which had been used for the *tert*-butylsilver reaction. Similar disappointing results were obtained when isopropylsilver was used. Unfortunately, we have not yet found better reaction conditions to realize the 1,5-substitution in these cases. From previous work it is known that methylsilver is highly unreactive toward various substrates. *n*-Alkylsilver and isopropylsilver, however, smoothly react with substrates like conjugated enynes[5] and the pentenynyl sulfinates already mentioned.[4] They attack in these cases the double bond. Apparently, organosilver compounds are less prone to attack a triple bond than a double one.

The pentatetraenes **2a–g** ave been characterized by NMR and IR spectroscopy. In the IR spectrum the characteristic pentatetraene stretching vibration was present (2062–2078 cm^{-1}; for the parent compound the value 2085 cm^{-1} has been reported[2]). Also the ^{13}C NMR data recorded for **2a–g** (see the Experimental Section) support the proposed structure. Because of the presence of substituents in **2a–g** the chemical shifts of the two sp^2-hybridized carbon atoms considerably differ from those recorded for the parent hydrocarbon (viz., 81.7 ppm); the C_{sp} chemical shifts very well correspond with the values 178.4 and 118.3 ppm found for the parent compound (cf. ref 2). The relatively high value found for $^7J(HC{=}C{=}C{=}C{=}CH)$ in the ^1H NMR spectrum of **2**, viz., 2.3–3.5 Hz, shows that spin transmission through the π system of **2** is efficient.

A study on stereochemical features of *tert*-butylsilver-induced 1,5-substitution in 2,4-pentadiynyl sulfinates is in progress.

Experimental Section

General Procedures. Infrared spectra were recorded on a Perkin-Elmer 457 IR spectrometer using $CDCl_3$ or CCl_4 as solvent. ^1H NMR spectra were determined on a Varian EM-390 spectrometer using CCl_4 as solvent and Me_4Si as internal standard. ^{13}C NMR spectra were determined at −20 °C on a Bruker WP-200 spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard. Mass spectra were recorded on a AEI-MS-902 mass spectrometer. All reactions were carried out in an atmosphere of dry nitrogen.

Materials. THF was distilled from $LiAlH_4$; HMPT was purified according to ref 6. *tert*-Butylmagnesium chloride was prepared in THF from *tert*-butyl chloride and magnesium; its molarity was determined by Watson's titration method.[7] Lithium bromide was dried at 220 °C in high vacuum and was used as a 2.0 M solution in THF. The sulfinates **1** were prepared from the corresponding carbinols[8] according to the procedure given in ref 9 (yields, >95%) and were used without further purification.

General Procedure for the Preparation of Pentatetraenes 2a–g. To a stirred suspension of 1.88 g of silver(I) bromide (10.0 mmol) in 45 mL of dry THF were successively added, at 25 °C, 15.0 mL of lithium bromide in THF (2.0 M) and 5.5 mL of dry HMPT to yield a clear solution. This solution was cooled to −60 °C and 10.0 mmol of $t\text{-}C_4H_9MgCl$ in 10 mL of dry THF was carefully added. Stirring was continued for 20 min at −60 °C. The resulting homogeneous solution of $t\text{-}C_4H_9Ag$ was then carefully added to a stirred solution of 11.0 mmol of sulfinates **1** in 45 mL of dry THF at −40 to −30 °C. Stirring was continued for 1 h at −30 °C. The products **2a–g** were isolated by pouring the respective reaction mixtures into a mixture of 90 mL of a saturated aqueous NH_4Cl solution containing 0.8 g of NaCN and 60 mL of pentane. After the mixture was shaken, the pentane layer was separated, dried with K_2CO_3, and concentrated in vacuo while the temperature of the residue was kept below −5 °C. The crude pentatetraenes were purified by fast column chromatography over alumina W200 neutral (activity grade, Super 11), using pentane as eluent. After evaporation of the eluent (below −5 °C) the pentatetraenes $t\text{-}C_4H_9\text{-}C^1(H^a){=}C^2{=}C^3{=}C^4{=}C^5(R^1)\text{-}R^2$ were obtained as unstable oils (purity, ≃85–90%).

2,2,8-Trimethyl-3,4,5,6-nonatetraene (2a; $R^1 = i\text{-}C_3H_7$, $R^2 = H$). Chromatography gave 1.30 g of **2a** (yield 80%): IR (CCl_4) 2078 cm^{-1}; ^1H NMR (CCl_4) δ 1.13 (s, 9 H), 1.05 (d, 6 H), 2.20–2.90 (m, 1 H), 5.50–5.70 (m, 2 H, $^7J(H^a,R^1) = 2.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 111.3 (C^1), 170.7 (C^2), 121.7 (C^3), 171.7 (C^4), 116.3 (C^5); mass spectrum, *m/e* 162 ($M^{+}\cdot$).

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(4) Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *J. Organomet. Chem.* **1980**, *192*, 275.

(5) Westmijze, H.; Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1979**, *172*, 377.

(6) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971.

(7) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(8) Shostakovskii, M. F.; Bogdanova, A. V. "The Chemistry of Diacetylenes"; Wiley; New York, 1974; Chapter 3.

(9) Vermeer, P.; Westmijze, H.; Kleijn, H.; van Dijck, L. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 56.

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 ($M^{+\cdot}$).

Acknowledgment. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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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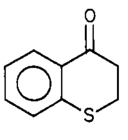
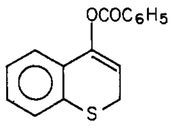
Received August 28, 1981

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.

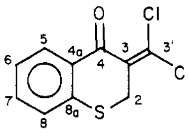
The major product obtained appeared to be the expected enol benzoate,[3] **2** (27%), accompanied by the starting ketone, but the early fractions after chromatography on silica gel contained a yellow oil **3** (22%), which showed no vinylic proton in the ^1H NMR and had a sharp singlet at δ 4.06 and 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

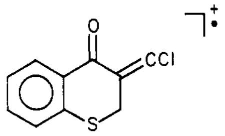


2

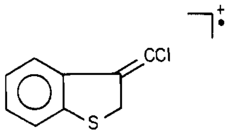


3

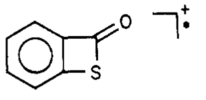
The mass spectrum of compound **3** showed peaks at 244, 246, and 248 with the relative intensities 100, 72, 12, strongly indicative of a dichloro compound with the molecular formula $C_{10}H_6Cl_2OS$. This was subsequently confirmed by a high-resolution mass spectral measurement. Other features of the 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.



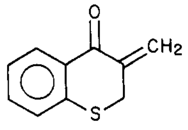
4 (*m/z* 209)



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

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[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.

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