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New Reactions of Thione *S*-(*tert*-Alkylimides)

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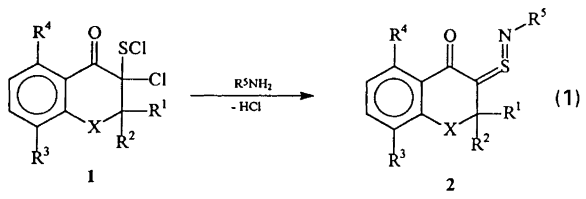
Two new α-chloro sulfenyl chlorides **1**, four new 2-thioxo-1-tetralone *S*-imides **2** (X=CH_2), and one new 3-thioxochroman-4-one *S*-imide **2** (X=O) have been prepared and characterized by comprehensive spectroscopy and, in one case, an X-ray crystal structure determination. Pyrolysis of **2** leads to the corresponding 1,2,4-trithiolanes **3** after extensive sulfur scrambling. Addition of arenethiols to **2** (R^5=*t*-Bu), but not **2** (R^5=1-adamantyl), leads to the corresponding adducts **13** with an unusual dithioacetal structure. Ozonolysis of **2** gives the corresponding α-diketones such as **16**.

In the present study we wished to continue our investigation of the chemistry of thiocarbonyl *S*-(*tert*-alkylimides).[1] As pointed out previously, thiocarbonyl *S*-imides stabilized by a bulky alkyl group on nitrogen, as in **2**, can be clearly distinguished in their chemical behavior from those with a stabilizing electron acceptor substituent on nitrogen.[1] With the known, but little used, **2a**[2] as the starting point we prepared the new compounds **2b**, **2c$_1$**, **2c$_2$**, **2d**, and **2e** from the corresponding α-chloro sulfenyl chlorides **1** in order to evaluate the relative merits of *tert*-butyl and 1-adamantyl, respectively, as R^5 of **2** and to expand the scope of the known **2** chemistry. The expected (*E*)-configuration of **2** was verified by a single crystal X-ray structure determination of **2d**, cf. Fig. 1 and Table 1.



(1)

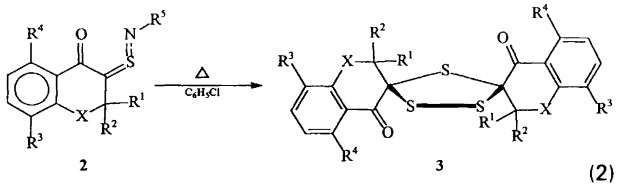
1

2

a, X = CH_2, R^1 = R^2 = R^3 = R^4 = Me
b, X = CH_2, R^1 = R^3 = R^4 = Me, R^2 = Et
c, X = CH_2, R^1 = R^2 = Et, R^3 = R^4 = Me
d, X = CH_2, R^1 = Me, R^2 = Et, R^3 = R^4 = H
d, X = O, R^1 + R^2 = $(CH_2)_5$, R^3 = R^4 = H

a, X = CH_2, R^1 = R^2 = R^3 = R^4 = Me, R^5 = *t*-Bu
b, X = CH_2, R^1 = R^3 = R^4 = Me R^2 = Et, R^5 = *t*-Bu
c$_1$, X = CH_2, R^1 = R^2 = Et, R^3 = R^4 = Me, R^5 = *t*-Bu
c$_2$, X = CH_2, R^1 = R^2 = Et, R^3 = R^4 = Me, R^5 = 1-adamantyl
d, X = CH_2, R^1 = Me, R^2 = Et, R^3 = R^4 = H, R^5 = *t*-Bu
e, X = O, R^1 + R^2 = $(CH_2)_5$, R^3 = R^4 = H, R^5 = 1-adamantyl

The pyrolysis of **2** did not, at least in our hands, yield the corresponding imines **6** as isolable products, but rather led to extensive sulfur scrambling and formation of the trithiolanes **3**. We assume that **3** are formed by [2+3] cycloaddition of the corresponding thioketone **8** and thiosulfine **11** which are both formed according to eqns. (3)–(10). This chemistry, which to the best of our knowledge is unprecedented for isolable thiocarbonyl *S*-imides, is closely related to Mloston's[3] experience with transient thione *S*-imides formed from thioketones and aryl azides. We have previously encountered **3** as cycloaddition products of thiosulfines generated in a less circuitous manner, i.e. by 'unzipping' of the corresponding acetyl α-chloroalkyl disulfides.[4]



(2)

2 **3**

a, X = CH_2, R^1 = R^2 = R^3 = R^4 = Me, R^5 = *t*-Bu
e, X = O, R^1 + R^2 = $(CH_2)_5$, R^3 = R^4 = H, R^5 = 1-adamantyl

a, X = CH_2, R^1 = R^2 = R^3 = R^4 = Me
e, X = O, R^1 + R^2 = $(CH_2)_5$, R^3 = R^4 = H

Attempts to desulfurize **2** by reaction with tributylphosphine or triphenylphosphine failed to yield well-defined products.

It has previously been found in our laboratory that

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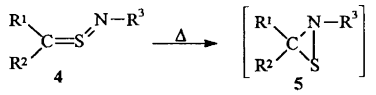
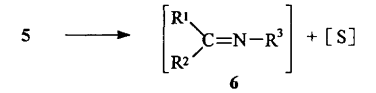
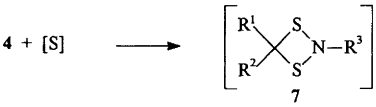


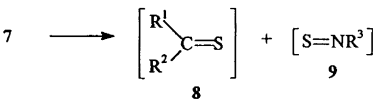
(3)



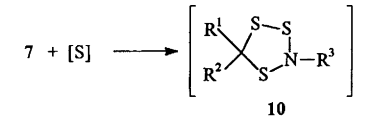
(4)



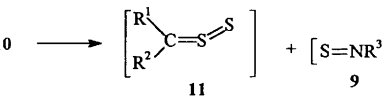
(5)



(6)

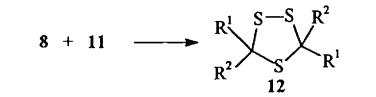


(7)



(8)

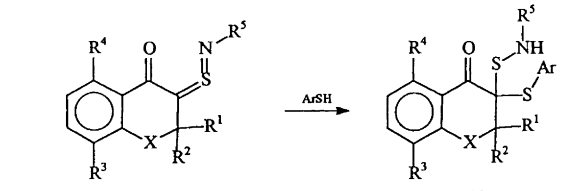
(9)



(10)

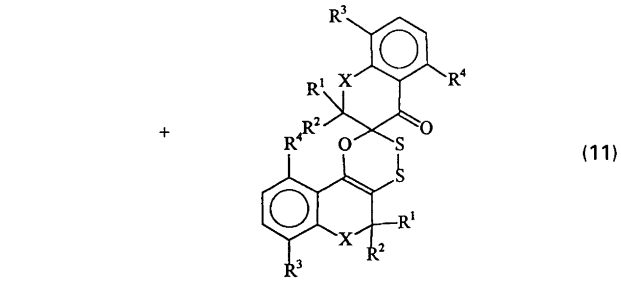
thiocarbonyl *S*-(*tert*-butylimides) add carbanions in a carbophilic manner to form the corresponding sulfenamides.[5] We now find that **2** ($R^5 = t$-Bu), but not **2** (R^5 = 1-adamantyl), smoothly adds arenethiols in a carbophilic 1,3-fashion to form the remarkably stable sulfenamides **13** with an unprecedented amino capped dithioacetal function. In one case a trace of the corresponding thioketone [2+4] dimer **14a**,[6] known from previous work with the elusive corresponding α-thioxo ketones, could be observed. The formation of **14** can be regarded as indicative of a competing thiophilic attack of the nucleophile with the formation of a hypervalent sulfur species where subsequent ligand coupling leads to the elimination of the corresponding arenesulfenamide and unmasking of the thiocarbonyl group.

Thus, while both a *tert*-butyl and a 1-adamantyl group are well suited as R^5 to make the corresponding **2** shelf stable the latter in addition strongly reduces, by extreme steric hindrance, the electrophilic properties of the sulfur(IV) cumulene system of **2**. On the other hand, no corresponding difference is apparent in the pyrolyses of **2a** and **2e**.



a, X = CH_2, $R^1 = R^2 = R^3 = R^4$ = Me
b, X = CH_2, $R^1 = R^3 = R^4$ = Me, R^2 = Et, $R^5 = t$-Bu

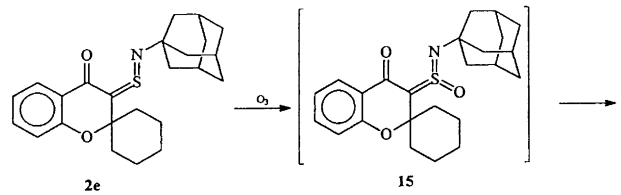
a_1, X = CH_2, $R^1 = R^2 = R^3 = R^4$ = Me, $R^5 = t$-Bu, Ar = Ph
a_2, X = CH_2, $R^1 = R^2 = R^3 = R^4$ = Me, $R^5 = t$-Bu, Ar = 4-MeC_6H_4
b, X = CH_2, $R^1 = R^2 = R^3 = R^4$ = Me, $R^5 = t$-Bu, Ar = 4-MeC_6H_4



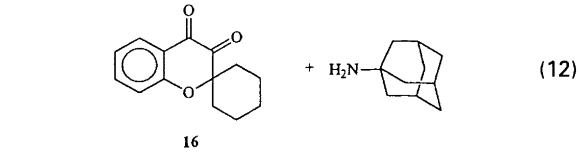
(11)

a, X = CH_2, $R^1 = R^2 = R^3 = R^4$ = Me

Ozonization of **2e** leads, albeit in poor yield, to the new dione **16**. We were unable to observe the hypothetical intermediate **15** which might be formed in the first step of the reaction sequence (12). The dione **16** could be prepared independently by selenium dioxide oxidation of the corresponding ketone **17**, cf. eqn. (13).



(12)



(13)

Experimental

NMR spectra were taken for samples in $CDCl_3$ with TMS as an internal standard with a Bruker AC 250 or Bruker AM 500 apparatus. EI (70 eV) mass spectra were recorded on a Finnigan SSQ 710 quadrupole mass spectrometer by direct inlet. FAB mass spectra were obtained with a Kratos MS50 RF instrument with 3-nitrobenzyl alcohol as the matrix and 9 keV Xe atoms. IR spectra were obtained with a Perkin Elmer 1600 Series FTIR instrument for neat samples (liquids) or KBr wafers (solids). The elemental analyses were performed by the Microanalytical Laboratory of the Department of Physical Chemistry, University of Vienna, A-1090 Vienna, Austria. All column chromatographic separations were carried out with Merck Silica Gel 60 (particle size 0.063–0.200 mm). The single crystals for the X-ray work were obtained by slow evaporation of the corresponding hexane–ether (5:1) eluate from the column chromatographic separation. Compounds **1a**,[4] **1d**,[4] **1e**,[4] and **2a**[2] were prepared according to literature procedures.

α-Chloro sulfenyl chlorides **1**. A general procedure for the synthesis of tetralone derivatives[6] was followed.

(2RS,3RS)-2-Chloro-3-ethyl-1,2,3,4-tetrahydro-3,5,8-trimethyl-1-oxonaphthalene-2-sulfenyl chloride **1b**. Ethyl α-cyano-β-ethyl-β-methylacrylate[7] (28.5 g, 0.17 mol), dissolved in 75 ml dry ether, was added over 45 min at room temperature to a Grignard solution prepared from 35 ml (0.20 mol) 2,5-dimethylbenzyl chloride and 5.3 g (0.20 mol) magnesium turnings in 30 ml dry ether. When the spontaneous reflux had subsided the mixture was stirred and heated to reflux for another 1 h. The reaction mixture was cooled and poured onto 200 g cracked ice and then acidified with 20% sulfuric acid. After the usual work-up the combined ether phases were washed successively with 75 ml water and 75 ml saturated brine, filtered through a layer of anhydrous sodium sulfate, evaporated, and the residue distilled *in vacuo*. Yield of *ethyl 3-(2,5-dimethylbenzyl)-2-cyano-3-methylpentanoate* 34.0 g (84%), b.p. 155–160 °C/0.5 mmHg (bath temperature 200–210 °C). IR (neat): $\nu_{C\equiv N}$ 2244, $\nu_{C=O}$ 1736 cm^{-1}. ^1H NMR (250 MHz): δ 0.89–1.05 (6 H, m, 3-Me, 5-Me), 1.31 (3 H, t, CH_3CH_2O), 1.51–1.71 (2 H, m, 4-CH_2), 2.15 (2 H, q, 3-CH_2), 2.22 (3 H, s, 2′-Me), 2.29 (3 H, s, 5′-Me), 2.88 (1 H, s, 2-CH), 4.19 (2 H, q, CH_3CH_2O), 6.89–7.09 (3 H, m, 3 ArH). MS (EI): *m/z* (%) 287 (*M*, 2), 119 (C_9H_{11}, 100). Found: C, 77.61, H, 8.95, N, 4.22; calc. for $C_{18}H_{25}NO_2$ (287.38): C, 75.22, H, 8.76, N, 4.87%.

Ethyl 3-(2,5-dimethylbenzyl)-2-cyano-3-methylpentanoate (37.0 g, 0.14 mol) was mixed with a solution of 12.0 g (0.20 mol) potassium hydroxide in 60 ml ethylene glycol and heated under reflux for 3 h (the reflux condenser was attached with a rubber stopper). The cooled reaction mixture was diluted with 100 ml water and then extracted successively with 60, 25, and 25 ml ether. The combined ether extracts were washed with 25 ml water and 25 ml saturated brine and then filtered through a layer of anhydrous sodium sulfate. The solvent was evaporated off and the residue distilled *in vacuo*. This yielded 17.5 g (85%) *3-(2,5-dimethylbenzyl)-3-methylpentanenitrile*, b.p. 120–122 °C/0.5 mmHg. IR (neat): $\nu_{C\equiv N}$ 2245 cm^{-1}. ^1H NMR (60 MHz): δ 0.97 (6 H, t, 3-Me, 5-Me), 1.35–1.73 (2 H, m, 4-CH_2), 2.26 (2 H, s, 2-CH_2), 2.34 (6 H, s, 2′-Me, 5′-Me), 2.66 (1 H, d, $ArCH_aH_b$), 2.77 (1 H, d, $ArCH_aH_b$), 7.01–7.27 (3 H, m, 3 ArH); MS (EI): *m/z* (%) 215 (*M*, 10), 119 (C_9H_{11}, 100). Found: C, 83.94, H, 9.90, N 6.26; calc. for $C_{15}H_{21}N$ (215.32): C, 83.66, H, 9.83, N, 6.50%.

This nitrile was converted (by 6 h reflux heating of a mixture with a 3-molar excess of KOH and ethylene glycol and subsequent conventional work-up) into *3-(2,5-dimethylbenzyl)-3-methylpentanoic acid*, b.p. 165–170 °C/1.0 mmHg, yield 69%. IR (neat): ν_{OH} 3252–3648, $\nu_{C=O}$ 1717 cm^{-1}. ^1H NMR (250 MHz): δ 0.95 (3 H, t, 5-Me), 0.99 (3 H, s, 3-Me), 1.35–1.65 (2 H, m, CH_3CH_2), 2.22 (1 H, d, 2-CH_aH_b), 2.29 (6 H, s, 2′-Me, 5′-Me), 2.35 (1 H, d, 2-CH_aH_b), 2.69 (1 H, d, $ArCH_aH_b$), 2.72 (1 H, d, $ArCH_aH_b$), 6.88–6.98 (2 H, m, 2 ArH). MS (CI): *m/z* (%) 252 ($M+NH_4^+$, 100), 234 [$(M+NH_4^+)-H_2O$, 38]. Found: C, 77.04, H, 9.50; calc. for $C_{15}H_{22}O_2$ (234.33): C, 76.87, H, 9.46.

Polyphosphoric acid (PPA) (11 g) was heated, on a steam bath, to 90 °C. Then it was removed from the steam bath and 4.6 g (0.02 mol) 3-(2,5-dimethylbenzyl)-3-methylpentanoic acid, preheated to 65 °C, added in a single portion, and the reaction mixture stirred for 3 min. It was then placed on a steam bath and another 7.5 g PPA added. Stirring was continued for 30 min, and the temperature was maintained at 90 °C. After being cooled to room temperature the reaction mixture was poured, with stirring, into ice–water. A viscous brown oil precipitated and soon changed color to yellowish green. Subsequently, the crude product was extracted with ether (three times) and the combined ether extracts successively washed with 60 ml water, 2 × 10 ml 5% aqueous NaOH, 60 ml water, 10 ml 3% aqueous acetic acid, and 5 ml water. The organic phase was dried over magnesium sulfate, filtered, and evaporated. The residue was vacuum distilled to yield 3.15 g (73%) *(RS)-3-ethyl-1,2,3,4-tetrahydro-3,5,8-trimethylnaphthalen-1-one*, b.p. 130–135 °C/1.0 mmHg. IR (neat): $\nu_{C=O}$ 1682 cm^{-1}. ^1H NMR (250 MHz): δ 0.85 (3 H, t, CH_3CH_2), 0.99 (3 H, s, 3-Me), 1.39 (2 H, q, CH_3CH_2), 2.19 (3 H, s, 5-Me), 2.33 (1 H, d, 2-CH_aH_b), 2.42 (1 H, d, 2-CH_aH_b), 2.55 (1 H, d, 4-CH_aH_b), 2.58 (3 H, s, 8-Me), 2.69 (1 H, d, 4-CH_aH_b), 6.91 (1 H, d, ArH), 7.12 (1 H, d, ArH). ^{13}C NMR (63 MHz): δ 7.61 (CH_3CH_2), 19.33 (3-CH_3), 22.69 (5-CH_3), 24.10 (8-CH_3), 33.09 (CH_3CH_2), 34.63 (C-3), 38.95 (C-4), 51.39 (C-2), 129.21, 130.14, 133.53, 133.75, 137.63, 141.07 (C-4a, C-5, C-6, C-7, C-8, C-8a), 200.24 (C-1). MS (CI): *m/z* (%) 217 ($M+H^+$, 100), 145 ($C_{10}H_9O$, 20). Found C, 83.07; H, 9.21; calc. for $C_{15}H_{20}O$ (216.31): C, 83.28; H, 9.32.

(*RS*)-3-Ethyl-1,2,3,4-tetrahydro-3,5,8-trimethylnaph-

thalen-1-one (2.16 g, 0.10 mol) was, according to a general procedure,[8] dissolved in 37 ml thionyl chloride. The temperature rose to 35 °C and a brisk evolution of gas started after 2 min. The reaction mixture was allowed to stand for another 3 h. The volatiles were removed on a rotary evaporator to leave crude **1b** (yield 65%) which was recrystallized from ligroin (b.p. 80–100 °C). Yield 60%, m.p. 95–97 °C. According to the NMR spectra both diastereomers were present. IR: $\nu_{C=O}$ 1696 cm^{-1}. ^1H NMR (250 MHz): δ 0.82 (3 H, t, CH_3CH_2), 1.08 (3 H, t, CH_3CH_2), 1.19 (3 H, s, 3-Me), 1.39 (3 H, s, 3-Me), 1.41–1.52 (1 H, m, $CH_3CH_aH_b$), 1.62–1.75 (1 H, m, $CH_3CH_aH_b$), 1.79–1.95 (1 H, m, $CH_3CH_aH_b$), 2.08–2.27 (1 H, m, $CH_3CH_aH_b$), 2.29 (3 H, s, 5-Me), 2.29 (3 H, s, 5-Me), 2.61 (3 H, s, 8-Me), 2.61 (3 H, s, 8-Me), 2.81 (1 H, d, 4-CH_aH_b), 2.88 (1 H, d, 4-CH_aH_b), 2.98 (1 H, d, 4-CH_aH_b), 3.09 (1 H, d, 4-CH_aH_b), 7.07 (1 H, d, ArH), 7.10 (1 H, d, ArH), 7.28 (1 H, d, ArH), 7.29 (1 H, d, ArH). ^{13}C NMR (125 MHz): δ 7.96 (3-CH_3CH_2), 8.04 (3-CH_3CH_2), 19.32 (3-Me), 19.37 (3-Me), 20.80 (5-Me), 20.80 (5-Me), 22.38 (8-Me), 22.59 (8-Me), 27.66 (3-CH_3CH_2), 31.26 (3-CH_3CH_2), 36.20 (C-4), 38.14 (C-4), 46.01 (C-3), 46.31 (C-3), 95.94 (C-2), 96.84 (C-2), 128.07 (C-4a), 128.33 (C-4a), 130.41 (C-5), 130.53 (C-5), 133.64 (C-6), 133.89 (C-6), 134.61 (C-7), 134.61 (C-7), 137.86 (C-8), 137.89 (C-8), 140.14 (C-8a), 140.41 (C-8a), 187.09 (C-1), 188.11 (C-1). MS (CI): *m/z* (%) 334 ($M+NH_4^+$, 3), 317 (*M*, 4), 281 ($M-Cl$, 4), 266 ($M-CH_3Cl$, 10), 247 ($M-Cl_2$, 100). Found: C, 57.35; H, 5.87; Cl, 22.05; S, 9.99; calc. for $C_{15}H_{18}Cl_2OS$ (317.26): C, 56.78; H, 5.72; Cl, 22.35; S, 10.10%.

(RS)-2-Chloro-3,3-diethyl-1,2,3,4-tetrahydro-5,8-dimethyl-1-oxonaphthalene-2-sulfenyl chloride **1c**. With the same methodology as used above, but starting from ethyl α-cyano-β,β-diethylacrylate[9] we obtained the following new compounds.

Ethyl 3-(2,5-dimethylbenzyl)-2-cyano-3-ethylpentanoate, yield 69%, b.p. 162–167 °C/0.8 mmHg (bath temperature 200–210 °C). IR (neat): $\nu_{C\equiv N}$ 2240, $\nu_{C=O}$ 1730 cm^{-1}. ^1H NMR (60 MHz): δ 0.70–1.09 (6 H, m, 3-CH_3CH_2, 5-Me), 1.35 (3 H, t, CH_3CH_2O), 1.41–1.98 (4 H, m, 3-CH_3CH_2, 4-CH_2), 2.30 (6 H, s, 2′-Me, 5′-Me), 2.92 (2 H, s, $ArCH_2$), 3.62 (1 H, s, 2-CH), 4.28 (2 H, q, CH_3CH_2O), 6.65–7.11 (3 H, m, 3 ArH). MS (EI): *m/z* (%) 301 (*M*, 0.2), 119 (C_9H_{11}, 100). Found: C, 77.68, H, 8.82, N, 4.66; calc. for $C_{18}H_{25}NO_2$ (301.41): C, 75.70, H, 9.03, N, 4.64%.

3-(2,5-Dimethylbenzyl)-3-ethylpentanenitrile, yield 83%, b.p. 120–125 °C/0.5 mmHg. IR (neat): $\nu_{C\equiv N}$ 2250 cm^{-1}. ^1H NMR (250 MHz): δ 0.85 (6 H, t, 3-CH_3CH_2, 5-Me), 1.25–1.62 (4 H, m, 3-CH_3CH_2, 4-CH_2), 2.11 (2 H, s, 2-CH_2), 2.25 (6 H, s, 2′-Me, 5′-Me), 2.65 (2 H, s, $ArCH_2$), 6.81–7.02 (3 H, m, 3 ArH). MS (EI): *m/z* (%) 229 (*M*, 10), 119 (C_9H_{11}, 100). Found: C, 83.56, H, 9.89, N 5.96; calc. for $C_{16}H_{23}N$ (229.34): C, 83.78, H, 10.10, N, 6.10%.

3-(2,5-Dimethylbenzyl)-3-ethylpentanoic acid, b.p. 175–180 °C/1.0 mmHg, yield 86%. IR (neat): ν_{OH} 3248–3650, $\nu_{C=O}$ 1715 cm^{-1}. ^1H NMR (250 MHz): δ 0.89 (6 H, t, 3-CH_3CH_2, 5-Me), 1.41–1.57 (4 H, m, 3-CH_3CH_2, 4-CH_2), 2.25 (8 H, s, 2′-Me, 5′-Me, 2-CH_2), 2.71 (2 H, s, $ArCH_2$), 6.88 (1 H, d, ArH), 7.01 (1 H, d, ArH). MS (CI): *m/z* (%) 248 (*M*, 12), 120 (C_9H_{12}, 100). Found: C, 76.34, H, 8.92; calc. for $C_{16}H_{24}O_2$ (248.35): C, 77.48, H, 9.75%. This somewhat unsatisfactory analysis was deemed acceptable in the light of the correct spectral data and the satisfactory data for the preceding as well as the subsequent step of our reaction sequence.

3,3-Diethyl-1,2,3,4-tetrahydro-5,8-dimethylnaphthalen-1-one, yield 73%, b.p. 162–165 °C/3.0 mmHg, yield 87%. IR (neat): $\nu_{C=O}$ 1678 cm^{-1}. ^1H NMR (250 MHz): δ 0.85 (6 H, t, 2×CH_3CH_2), 1.39 (4 H, q, 2×CH_3CH_2), 2.27 (3 H, s, 5-Me), 2.45 (2 H, s, 2-CH_2), 2.59 (3 H, s, 8-Me), 2.67 (2 H, s, 4-CH_2), 6.95 (1 H, d, ArH), 7.15 (1 H, d, ArH). ^{13}C NMR (125 MHz): δ 7.30 (2×CH_3CH_2), 19.54 (5-CH_3), 22.81 (8-CH_3), 28.56 (CH_3CH_2), 28.70 (CH_3CH_2), 36.88 (C-3), 37.37 (C-4), 47.92 (C-2), 129.38, 130.67, 133.74, 133.96, 137.87, 141.21 (C-4a, C-5, C-6, C-7, C-8, C-8a), 201.70 (C-1). MS (EI): *m/z* (%) 230 (*M*, 35), 159 ($C_{11}H_{11}O$, 50), 146 ($C_{10}H_{10}O$, 100). Found C, 83.31; H, 9.88; calc. for $C_{16}H_{22}O$ (230.34): C, 83.42; H, 9.62.

1c: Yield 34%, m.p. 81–83 °C (from toluene–ligroin, b.p. 80–100 °C). IR: $\nu_{C=O}$ 1702 cm^{-1}. ^1H NMR (500 MHz): δ 0.82 (3 H, t, CH_3CH_2), 1.15 (3 H, t, CH_3CH_2), 1.49–1.59 (1 H, m, $CH_3CH_aH_b$), 1.77–1.85 (1 H, m, $CH_3CH_aH_b$), 1.88–1.97 (1 H, m, $CH_3CH_aH_b$), 2.02–2.11 (1 H, m, $CH_3CH_aH_b$), 2.30 (3 H, s, 5-Me), 2.62 (3 H, s, 8-Me), 2.89 (1 H, d, 4-CH_aH_b), 3.03 (1 H, d, 4-CH_aH_b), 7.09 (1 H, d, ArH), 7.28 (1 H, d, ArH). ^{13}C NMR (125 MHz): δ 9.39 (2×CH_3CH_2), 19.24 (5-CH_3), 22.42 (8-CH_3), 27.47 (CH_3CH_2), 30.61 (CH_3CH_2), 35.24 (C-4), 48.49 (C-3), 96.54 (C-2), 128.34, 130.33, 133.39, 134.46, 138.03, 140.18 (C-4a, C-5, C-6, C-7, C-8, C-8a), 186.87 (C-1); MS (CI, FAB): *m/z* (%) 331 ($M+H^+$, 100). Found: C, 58.13; H, 6.15; Cl, 21.10; S, 9.77; calc. for $C_{16}H_{20}Cl_2OS$ (331.29): C, 58.00; H, 6.08; Cl, 21.40; S, 9.67%.

Thione S-*imides* **2**. A general procedure for the conversion of α-chloralkanesulfenyl chlorides into thiocarbonyl *S*-(*tert*-alkylimides)[2] was followed. Sulfenyl chloride **1** (0.01 mol) was dissolved in 30 ml $CHCl_3$, cooled to 5 °C, and 6.0 ml (0.03 mol) *tert*-butylamine were added in one portion to the stirred solution. After another 15 min of stirring the reaction mixture was poured onto ice, the organic phase was separated and dried over K_2CO_3, the solvent evaporated off, and the residue triturated with petroleum ether (b.p. 40–60 °C) at −30 °C until solidification.

(E)-3-Ethyl-1,2,3,4-tetrahydro-3,5,8-trimethyl-2-thioxonaphthalen-1-one S-(tert-*butylimide*) **2b**. M.p. 100–103 °C (from petroleum ether b.p. 40–60 °C), yield 19%; IR: $\nu_{C=O}$ 1675 cm^{-1}. ^1H NMR (500 MHz): δ 0.85

(3 H, t, CH_3CH_2), 1.39 [9 H, s, $C(CH_3)_3$], 1.41 (3 H, s, 3-Me), 1.55–1.72 (2 H, m, CH_3CH_2), 2.25 (3 H, s, 5-Me), 2.55 (3 H, s, 8-Me), 2.92 (1 H, d, 4-CH_aH_b), 3.10 (1 H, d, 4-CH_aH_b), 7.09 (1 H, d, ArH), 7.31 (1 H, d, ArH). ^{13}C NMR (125 MHz): δ 9.45 (CH_3CH_2), 19.49 (3-CH_3), 22.03 (5-CH_3), 22.70 (8-CH_3), 29.01 (CH_3CH_2), 31.75 [$C(CH_3)_3$], 37.25 (C-4), 44.68 (C-3), 62.78 [$C(CH_3)_3$], 129.89, 131.43, 132.89, 133.39, 136.81, 139.71 (C-4a, C-5, C-6, C-7, C-8, C-8a), 151.34 (C-2), 187.76 (C-1). MS (CI, FAB): *m/z* (%) 318 ($M+H^+$, 40), 260 ($M-C_4H_9$, 20), 245 ($M+H^+-C_4H_{10}N$, 65), 215 ($C_{12}H_9NOS$, 100). Found: C, 71.98; H, 8.64; N, 4.32; S, 10.24; calc. for $C_{19}H_{27}NOS$ (317.47): C, 71.87; H, 8.57; N, 4.41; S, 10.09%.

(E)-3,3-Diethyl-1,2,3,4-tetrahydro-5,8-dimethyl-2-thioxonaphthalen-1-one S-(tert-*butylimide)* **2c$_1$**. M.p. 93–95 °C (from petroleum ether b.p. 40–60 °C), yield 17%. IR: $\nu_{C=O}$ 1690 cm^{-1}. ^{1}H NMR (250 MHz): δ 0.75–0.90 (6 H, m, 2×CH_3CH_2), 1.36 (9 H, s, CMe_3), 1.51–1.79 (2 H, m, CH_3CH_2), 2.29 (3 H, s, 5-Me), 2.35–2.49 (2 H, m, CH_3CH_2), 2.56 (3 H, s, 8-Me), 3.01 (2 H, s, 4-CH_2), 7.05 (1 H, d, ArH), 7.19 (1 H, d, ArH). ^{13}C NMR (50 MHz): δ 9.47 (2×CH_3CH_2), 19.44 (5-CH_3), 22.21 (8-CH_3), 28.26 (2×CH_3CH_2), 31.62 [$C(CH_3)_3$], 33.44 (C-4), 48.85 (C-3), 62.76 [$C(CH_3)_3$], 129.83, 131.35, 132.71, 133.48, 137.06, 140.32 (C-4a, C-5, C-6, C-7, C-8, C-8a), 149.88 (C-2), 188.64 (C-1). MS (CI, FAB): *m/z* (%) 332 ($M+H^+$, 41), 300 ($M+H^+-S$, 5), 274 ($M+H^+-C_2H_5$, 10), 259 ($M+H^+-C_4H_{10}$, 80), 229 ($C_{14}H_{13}NOS$, 100). Found: C, 72.43; H, 9.19; N, 4.29; S, 9.49; calc. for $C_{20}H_{29}NOS$ (331.49): C, 72.45; H, 8.81; N, 4.22; S, 9.67%.

(RS)-(E)-3,3-Diethyl-1,2,3,4-tetrahydro-5,8-dimethyl-2-thioxonaphthalen-1-one S-*(1-adamantylimide)* **2c$_2$**. M.p. 116–119 °C (from petroleum ether b.p. 40–60 °C), yield 30%. IR: $\nu_{C=O}$ 1689 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.75–0.99 (6 H, m, 2×CH_3CH_2), 1.52–1.62 (2 H, m, CH_3CH_2), 1.67–2.19 (15 H, m, 1-adamantyl), 2.30 (3 H, s, 5-Me), 2.38–2.48 (2 H, m, CH_3CH_2), 2.57 (3 H, s, 8-Me), 2.72 (2 H, s, 4-CH_2), 6.98 (1 H, d, ArH), 7.18 (1 H, d, ArH). ^{13}C NMR (125 MHz): δ 9.45 (2×CH_3CH_2), 19.56 (5-CH_3), 22.42 (8-CH_3), 28.17 (2×CH_3CH_2), 33.39 (C-4), 29.93 (C-3′, C-5′, C-7′), 36.12 (C-4′, C-6′, C-10′), 45.34 (C-2′, C-8′, C-9′), 48.71 (C-3), 63.35 (C-1′), 129.74, 131.27, 132.61, 133.34, 136.95, 140.22 (C-4a, C-5, C-6, C-7, C-8, C-8a), 150.04 (C-2), 187.94 (C-1). MS (CI, FAB): *m/z* (%) 410 ($M+H^+$, 13), 135 ($C_{10}H_{15}$, 100). Found: C, 76.42; H, 8.91; N, 3.42; S, 7.74; calc. for $C_{26}H_{35}NOS$ (409.60): C, 76.23; H, 8.61; N, 3.41; S, 7.82%.

(E)-3-Ethyl-1,2,3,4-tetrahydro-3-methyl-2-thioxonaphthalen-1-one S-(tert-*butylimide)* **2d**. M.p. 78–80 °C (from petroleum ether b.p. 40–60 °C), yield 17%. IR: $\nu_{C=O}$ 1689 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.88 (3 H, t, CH_3CH_2), 0.99 (9 H, s, CMe_3), 1.29 (3 H, s, 3-Me), 1.39–1.75 (2 H, m, CH_3CH_2), 2.91–3.09 (2 H, m, 4-CH_2), 7.15–7.25 (1 H, m, ArH), 7.31–7.35 (1 H, m, ArH), 7.38–7.45 (1 H, m, ArH), 7.47–7.55 (1 H, m, ArH). ^{13}C NMR (125 MHz): δ 7.81 (CH_3CH_2), 22.05 (3-CH_3), 27.57 [$C(CH_3)_3$], 30.82 (CH_3CH_2), 40.71 (C-4), 45.66 (C-3), 54.13 [$C(CH_3)_3$], 129.26, 131.34, 132.72, 133.15, 135.16, 139.38, (C-4a, C-5, C-6, C-7, C-8, C-8a), 142.23 (C-2), 185.61 (C-1). MS (EI): *m/z* (%) 289 (*M*, 9), 218 ($M-C_4H_9N$, 10), 200 ($C_{13}H_{14}NO$, 20), 57 (C_4H_9, 100). While our X-ray crystal structure determination (cf. Fig. 1 and Table 1) leaves no doubt about **2d**'s identity we were unable to obtain satisfactory elemental analyses which must be due to an inhomogeneity of our crystal crop. When the synthesis was repeated the crude product appeared as an oil which withstood our attempts at crystallization and/or chromatographic purification.

(E)-3′-Thioxospiro[cyclohexane-1,2′-chroman]-4′-one S-*(1-adamantylimide)* **2e**. M.p. 143–145 °C (from petroleum ether b.p. 40–60 °C), yield 17.5%. IR: $\nu_{C=O}$ 1617 cm^{-1}. ^{1}H NMR (250 MHz): δ 1.21–2.19 (21 H, m), 2.17 (2 H, s), 2.85–3.02 (2 H, m), 6.92–7.19 (2 H, m, 2 ArH), 7.42–7.52 (1 H, m, ArH), 7.88 (1 H, dd, ArH). ^{13}C NMR (125 MHz): δ 21.21 (C-3+C-5), 24.69 (C-4), 29.91 (C-3″, C-5″, C-7″), 30.04 (C-2, C-6), 36.02 (C-4″, C-6″, C-10″), 45.23 (C-2″, C-8″, C-9″), 64.51 (C-1″), 85.44 (C-2′), 118.09 (C-8′), 121.20 (C-6′), 121.37 (C-4a′), 126.25 (C-5′), 135.39 (C-7′), 143.51 (C-3′), 158.43 (C-8a′), 179.32 (C-4′). MS (CI, NH_3): *m/z* (%) 396 ($M+H^+$, 1), 364 ($M+H^+-S$, 30), 152 ($C_{10}H_{18}N$, 100). Found: C, 71.92; H, 7.56; N, 3.63; S, 8.08; calc. for $C_{24}H_{29}NO_2S$ (395.47): C, 72.88; H, 7.39; N, 3.34; S, 8.12%.

Pyrolysis of **2**. The thione *S*-imide (0.002 mol) was dissolved in 5 ml chlorobenzene and refluxed for 3 h. The solvent was evaporated off *in vacuo* and the residue was column chromatographed (eluent hexane–ether 5:1). From **2a** was obtained *trans*-1,1″,2,2″,3,3″,4,4″-octahydro-3,3,3″,3,5,5″,8,8″-octamethyldispiro[naphthalene-2,3′-[1,2,4]trithiolane-5′,2″-naphthalene]-1,1″-dione **3a**,[4] m.p. 218–220 °C, yield 20%. From **2e** was obtained *trans*-tetraspiro[cyclohexane-1,2′-chroman-3′,3″-[1,2,4]-trithiolane-5″,3‴-chroman-2‴,1⁗-cyclohexane]-4′,4‴-dione **3e**,[4] m.p. 280–282 °C, yield 20%.

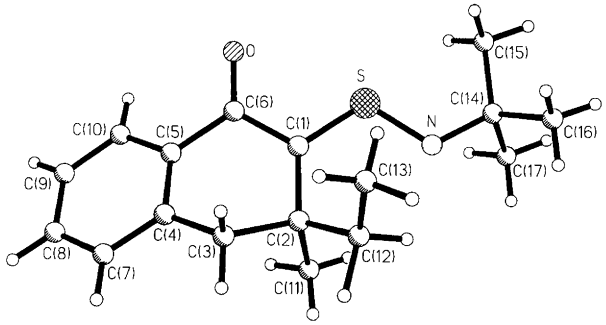


Fig. 1. Single crystal X-ray structure of **2d**.

Table 1. Crystal and experimental data for **2d**.

Formula	$C_{17}H_{23}NOS$
Formula weight	289.42
Crystal system	Tetragonal
Space group	$I4_1/a$
Unit-cell dimension:	
a/Å	18.0201(3)
b/Å	18.0201(3)
c/Å	20.1616(3)
Unit-cell volume, V/Å^3	6547.0(2)
Formula units per unit cell, Z	16
F(000)	2496
Calculated density, D_x/g cm^{-3}	1.175
Radiation	Mo Kα
Wavelength, λ/Å	0.71073
Linear absorption coefficient/mm^{-1}	0.194
Temperature, T/K	296
Crystal description	Yellow
Crystal size/mm	0.28 × 0.28 × 0.28
Intensity data collection	
Siemens SMART CCD diffractometer	
ω rotation with narrow frames	
θ-range/°	1.52–29.87
Range of h	−24–23
Range of k	−24–9
Range of l	−25–27
Measured reflections	21760
Total number of unique reflections	4305
No. of independent reflections, $[I>2\sigma(I)]$	2421
R(int)	0.1646
Corrections	Lorenz and polarization
Structure refinement:	
Minimization of	$\Sigma w(\lvert F_o\rvert^2-\lvert F_c\rvert^2)^2$
Anisotropic thermal parameters	All non-hydrogen atoms
Isotropic thermal parameters	Hydrogen atoms
No. of refined parameters	274
Weighting scheme	$[\sigma^2(F^2_o)+(0.0000P)^2+12.8727P]^{-1}$, $P=(F_o^2+2F_c^2)/3$
$R=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.0783 (obs. data)
$wR2=[\Sigma w\lvert F^2_o-F^2_c\rvert^2/\Sigma wF_o^4]^{1/2}$	0.1929 (all data)
$S=[\Sigma w(\lvert F_o\rvert^2-\lvert F_c\rvert^2)^2/(N_{obs}-N_{var})]^{1/2}$	1.212
Final $(\Delta/\sigma)_{max}$	0.057
Final $\Delta\rho_{min}$ and $\Delta\rho_{max}$/e Å^{-3}	−0.289 and 0.711

Reaction of **2a** *with benzenethiol.* To a solution of **2a** (0.60 g, 0.002 mol) in 10 ml CH_2Cl_2 was added over 5 min, with stirring, benzenethiol (0.20 ml, 0.002 mol), dissolved in 10 ml CH_2Cl_2. The volatiles were removed *in vacuo* to leave, besides a trace of **14a**[2] (identified by comparison with an authentic sample, mixed m.p. and TLC), 0.40 g (50%) *N-tert*-butyl-1,2,3,4-tetrahydro-3,3,5,8-tetramethyl-1-oxo-2-(phenylthio)naphthalene-2-sulfenamide **13a$_1$**, m.p. 133–135 °C (from petroleum ether b.p. 40–60 °C). IR: ν_{NH} 3292, $\nu_{C=O}$ 1677 cm^{-1}. ^{1}H NMR (250 MHz): δ 1.11 (9 H, CMe_3), 1.36 (3 H, s, 3-Me), 1.42 (3 H, s, 3-Me), 2.05 (3 H, s, 5-Me), 2.19 (3 H, s, 8-Me), 2.81 (1 H, d, 4-CH_aH$_b$), 2.88–3.00 (1 H, br s, NH, exchangeable with D_2O), 3.35 (1 H, d, 4-CH$_a$$H_b$), 6.88 (1 H, d, ArH), 7.05–7.29 (4 H, m, 4 ArH), 7.37 (2 H, m, 2 ArH). ^{13}C NMR (63 MHz): δ 19.61 (3-Me), 22.64 (3-Me), 25.71 (5-Me), 26.56 (8-Me), 29.72 [C(CH_3)$_3$], 42.47 (C-3), 43.39 (C-4), 54.05 [C(CH$_3$)$_3$], 128.12 (C-2, C-3′, C-5′), 128.99 (C-4a), 129.62 (C-5), 131.00 (C-6), 133.61 (C-7), 133.61 (C-8), 133.71 (C-4′), 137.16 (C-2′, C-6′), 139.22 (C-8a), 139.46 (C-1′), 193.69 (C-1). MS (EI): m/z (%) 413 (M, 5), 309 ($C_{20}H_{21}OS$, 30), 231 ($C_{14}H_{15}OS$, 10), 201 ($C_{12}H_9OS$, 100). Found: C, 69.63; H, 7.65; N, 3.49; S, 15.31; calc. for $C_{24}H_{31}NOS_2$ (413.61): C, 69.68; H, 7.55; N, 3.38; S, 15.50%.

Reaction of **2a** *with 4-methylbenzenethiol.* When **2a** was treated as above with 4-methylbenzenethiol, 75% *N-tert*-butyl-1,2,3,4-tetrahydro-3,3,5,8-tetramethyl-1-oxo-2-(4-methylphenylthio)naphthalene-2-sulfenamide **13a$_2$**, m.p. 133–135 °C (from petroleum ether b.p. 40–60 °C) was obtained. IR: ν_{NH} 3293, $\nu_{C=O}$ 1678 cm^{-1}. ^{1}H NMR (250 MHz): δ 1.12 (9 H, s, CMe_3), 1.35 (3 H, s, 3-Me), 1.47 (3 H, s, 3-Me), 2.11 (3 H, s, 5-Me), 2.30 (6 H, s, 4′-Me, 8-Me), 2.76 (1 H, d, 4-CH_aH$_b$), 2.91–3.01 (1 H, br s, NH, exchangeable with D_2O), 3.35 (1 H, d, 4-CH$_a$$H_b$), 6.87–6.97 (3 H, m, 3 ArH), 7.13–7.21 (3 H, m, 3 ArH). ^{13}C NMR (125 MHz): δ 19.53 (3-CH_3), 21.18 (4′-CH_3), 22.59 (3-CH_3), 25.74 (5-CH_3), 26.52 (8-CH_3), 29.76 [C(CH_3)$_3$], 42.35 (C-3), 43.37 (C-4), 53.96 [C(CH$_3$)$_3$], 128.87 (C-2, C-3′, C-5′), 129.58 (C-4a, C-5), 131.01 (C-6). 133.60 (C-7), 133.75 (C-8), 137.29 (C-2′, C-6′), 139.21 (C-4′), 139.30 (C-8a), 139.47 (C-1′), 193.64 (C-1). MS (CI): m/z (%) 428 (M+H$^+$, 0.6), 398 (M+H$^+$−C_2H_6, 1.2), 372 (M+H$^+$−C_4H_9, 4), 355 ($C_{21}H_{21}OS_2$, 9), 325 ($C_{19}H_{15}OS_2$, 90), 74 ($C_4H_{12}N$, 100). Found: C, 70.10; H, 7.97; N, 3.35; S, 14.60; calc. for $C_{25}H_{33}NOS_2$ (427.63): C, 70.21; H, 7.77; N, 3.27; S, 14.99%.

Reaction of **2b** *with 4-methylbenzenethiol.* When **2b** was treated as above with 4-methylbenzenethiol, 75% (2*RS*,3*RS*)-*N-tert*-butyl-3-ethyl-1,2,3,4-tetrahydro-3,5,8-tetramethyl-1-oxo-2-(4-methylphenylthio)naphthalene-2-sulfenamide **13b**, m.p. 121–123 °C (from petroleum ether b.p. 40–60 °C) was obtained. IR: ν_{NH} 3291, $\nu_{C=O}$ 1674 cm^{-1}; ^{1}H NMR (250 MHz): δ 0.81 (3 H, t, 3-CH_3CH$_2$), 1.10 (9 H, s, CMe_3), 1.36 (3 H, s, 3-Me), 2.08 (3 H, s, 5-Me), 2.23–2.43 (8 H, m, 3-CH$_3$CH_2, 4′-Me, 8-Me), 3.01 (1 H, dd, 4-CH_aH$_b$), 3.06–3.15 (1 H, br s, NH, exchangeable with D_2O), 3.21 (1 H, dd, 4-CH$_a$$H_b$), 6.89–6.98 (3 H, m, 3 ArH), 7.09–7.27 (3 H, m, 3 ArH). ^{13}C NMR (125.7 MHz): δ 8.66 (3-CH_3CH$_2$), 19.55 (3-Me), 21.19 (4′-Me), 22.03 (5-Me), 22.65 (8-Me), 29.64 (CMe_3), 30.76 (3-CH$_3$$CH_2$), 37.18 (C-4), 45.58 (C-3), 53.91 (CMe$_3$), 128.81 (C-2, C-3′, C-5′), 129.55 (C-4a), 129.69 (C-5), 130.66 (C-6), 131.34 (C-7), 133.66 (C-8), 137.46 (C-2′, C-6′), 139.20 (C-4′), 139.27 (C-8a), 139.37 (C-1′), 193.60 (C-1). MS (EI): m/z (%) 441 (M, 30), 369 (M−$C_4H_{10}N$, 30), 337 (M−$C_4H_{10}NS$, 25), 318 (M−C_7H_7S, 20), 245 ($C_{15}H_{17}OS$, 20), 213 ($C_{15}H_{17}O$, 100). Found: C, 70.53; H, 8.23; N, 3.30; S, 14.23; calc. for $C_{26}H_{35}NOS_2$ (441.66): C, 70.70; H, 7.99; N, 3.17; S, 14.52%.

Ozonization of **2e**. A stream of ozone–oxygen was passed, with stirring, through a solution of 1.60 g (0.004 mol) **2e** in 30 ml CH_2Cl_2, cooled to −78 °C. The volatiles were removed *in vacuo* and the oily residue subjected to column chromatography (eluent ether–hexane 1:1). The first fraction consisted of 0.15 g (16%) spiro[chroman-2,1′-cyclohexane]-3,4-dione **16**, m.p. 88–91 °C. IR: $\nu_{C=O}$ 1692 cm^{-1}. ^1H NMR (500 MHz): δ 1.21–1.89 (8 H, m, 4 CH_2), 1.95–2.11 (2 H, m, CH_2), 7.09–7.12 (2 H, m, 2 ArH), 7.60–7.69 (1 H, m, ArH), 7.92–7.98 (1 H, m, ArH). The ^{13}C NMR spectrum contained too many lines to be practically useful. MS (EI) *m/z* (%) 230 (*M*, 78), 202 (*M*−CO, 76), 173 ($C_{11}H_9O_2$, 100), 160 ($C_{10}H_8O_2$, 58), 147 ($C_9H_7O_2$, 80), 121 ($C_7H_5O_2$, 65). Found: C, 71.98; H, 6.47; calc. for $C_{14}H_{14}O_3$ (230.25): C, 73.02; H, 6.13%.

Spiro[chroman-2,1′-cyclohexane]-3,4-dione **16** *by* SeO_2 *oxidation of spiro[chroman-2,1-cyclohexan]-4-one* **17**. A general procedure for the SeO_2 oxidation of active methylene compounds[10] was followed. A mixture of 30 ml dioxane, 1 ml water, and 5.5 g (0.05 mol) SeO_2 was heated to 50–55 °C until it had become homogeneous. Compound **17**[11] (10.8 g, 0.05 mol) was added in one portion and the resulting mixture was refluxed with stirring for 6 h. The hot solution was decanted from the precipitated selenium and the volatiles were evaporated off *in vacuo*. The crude product was purified on a column (eluent hexane–ether 2:1) and yielded 1.80 g (16%) **16**, m.p. 86–89 °C. IR: $\nu_{C=O}$ 1682 cm^{-1}. ^1H NMR (250 MHz): δ 1.29–1.91 (8 H, m, 4 CH_2), 1.98–2.15 (2 H, m, CH_2), 6.82–6.95 (1 H, m, ArH), 6.97–7.08 (1 H, m, ArH), 7.09–7.19 (2 H, m, 2 ArH). The ^{13}C NMR spectrum contained too many lines to be practically useful. MS (EI): *m/z* (%) 230 (*M*, 80), 202 (*M*−CO, 76), 173 ($C_{11}H_9O_2$, 98), 160 ($C_{10}H_8O_2$, 60), 147 ($C_9H_7O_2$, 100), 121 ($C_7H_5O_2$, 65). Found C, 72.60; H; 6.31; calc. for $C_{14}H_{14}O_3$ (230.25): C, 73.02; H, 6.13%.

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References

1. El-Sayed, I., Abdel-Megeed, M. F., Yassin, S. M. and Senning, A. *Phosphorus, Sulfur, Silicon Relat. Elem. 86* (1994) 239.
2. Crossland, I. *Acta Chem. Scand., Ser. B 31* (1977) 890.
3. Mloston, G. and Heimgartner, H. *Helv. Chim. Acta 78* (1995) 1298.
4. Hegab, M. I., Abdel-Megeid, F. M. E., Gad, F. A., Shiba, S. A., Søtofte, I., Møller, J. and Senning, A. *Acta Chem. Scand. In press.*
5. Holm, S., Boerma, A. J., Nilsson, N. H. and Senning, A. *Chem. Ber. 109* (1976) 1069.
6. Bell, V. L. and Cromwell, N. H. *J. Org. Chem. 23* (1958) 789.
7. Cowan, M. D. and Vogel, I. A. *J. Chem. Soc.* (1940) 1528.
8. Crossland, I. *Acta Chem. Scand., Ser. B 30* (1976) 787.
9. Prout, F. S., Hartman, R. J., Huang, E. P. Y., Korpics, C. J. and Richelaar, G. R. *Org. Synth. Coll. Vol. IV* (1963) 93.
10. Riley, A. H. and Gray, R. A. *Org. Synth. Coll. Vol. II* (1943) 509.
11. Kelly, S. E. and Vanderplas, B. C. *J. Org. Chem. 56* (1991) 1325.

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