Ring Opening of Persubstituted 4*H*-Thiopyran 1-Oxide During Chlorination

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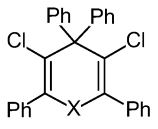
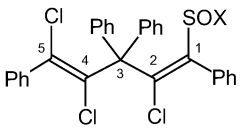
Chlorination of 3,5-dichloro-2,4,4,6-tetraphenyl-4*H*-thiopyran 1-oxide **3** (Cl_2 in CS_2, 20 °C) followed by alcoholysis (EtOH, MeOH) gives ethyl or methyl (1*E*,4*E*)-1,4,5-trichloro-1,3,3,5-tetraphenylpenta-1,4-diene-1-sulfinates **5** and **6**, respectively; the structure of **5** has been determined by X-ray analysis.

Molecular design variations of photochromic 2,4,4,6-tetraphenyl-4*H*-thiopyrans with excess of chlorine have resulted in an unexpected carbocyclization.[1] A more detailed investigation led us to establish the following reaction steps for the corresponding 3,5-dichloro intermediates: **1** + Cl_2 → **2**, **2** + H_2O → **3**. The oxygenation **1** + H_2O_2 → **3** was also accomplished. Attempts at chlorination of the final 3,5-dichloro-2,4,4,6-tetraphenyl-4*H*-thiopyran 1-oxide **3** with chlorine in carbon disulfide at 20 °C gave a new unstable tetrachloro derivative, which on treatment with ethanol or methanol could be converted to stable trichloro derivatives $C_{31}H_{25}Cl_3O_2S$ [m.p. 185–186 °C, 63% yield, *m*/*z* 566.0643 ($M^{+\cdot}$, 0.5%), calc. 566.0641 for $C_{31}H_{25}{}^{35}Cl_3O_2{}^{32}S$] and $C_{30}H_{23}Cl_3O_2S$ [m.p. 207–208 °C, 65% yield, *m*/*z* 552.0480 ($M^{+\cdot}$, 0.5%), calc. 552.0484 for $C_{30}H_{23}{}^{35}Cl_3O_2{}^{32}S$], respectively.†



1 X = S
2 X = SCl_2
3 X = SO



4 X = Cl
5 X = EtO
6 X = MeO

Besides the signals of an ethoxy moiety, the NMR spectra of the former substance confirm the presence of four phenyl groups. The molecule lacks the symmetry observed with **1** and **3**. It contains nine quaternary carbons (one sp^3 and eight sp^2); two carbons of the latter group are pure singlets in the proton-coupled ^{13}C NMR spectra (*i.e.* there are no protons in their vicinity). The ethoxy group is not attached to a carbon. As the MS and NMR data‡ were not sufficient for structure elucidation, the structure of **5** was determined by X-ray structure analysis as ethyl (1*E*,4*E*)-trichloro-1,3,3,5-tetraphenylpenta-1,4-diene-2-sulfinate (Fig. 1).§ The product of methanolysis exhibits similar mass and NMR spectra¶ so that it was assigned the structure of methyl (1*E*,4*E*)-1,3,3,5-tetraphenylpenta-1,4-diene-2-sulfinate **6**.

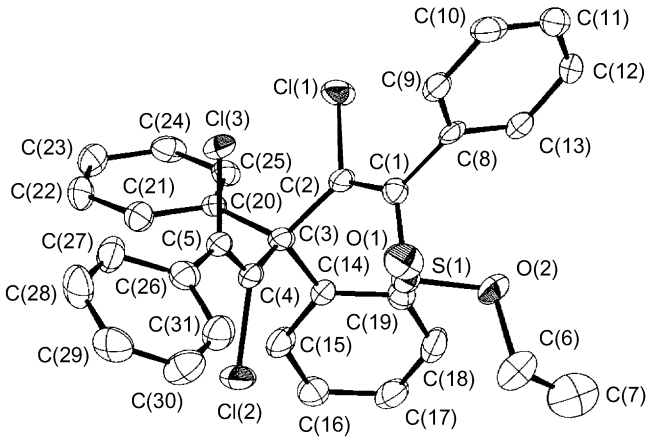


Fig. 1 Molecular structure of **5**. Selected bond lengths (Å): S(1)–O(1) 1.42(1), S(1)–O(2) 1.63(1), S(1)–C(1) 1.79(2), av. C–Cl 1.77, O(2)–C(6) 1.51(2), C(1)–C(2) 1.31(2), C(1)–C(8) 1.52(2), C(2)–C(3) 1.58(2), C(6)–C(7) 1.43(2), av. C_{ar}–C_{ar} 1.37. Bond angles (°): O(2)–S(1)–O(1) 108.9(7), C(1)–S(1)–O(1) 104.8(7), C(1)–S(1)–O(2) 94.0(7), C(6)–O(2)–S(1) 107.3(13), C(2)–C(1)–S(1) 121.9(12), C(8)–C(1)–S(1) 115.3(10), C(1)–C(2)–Cl(1) 117.8(12), C(3)–C(2)–Cl(1) 116.6(11).

Our results suggest that the primary product of chlorination is the sulfinic acid chloride **4**. The reaction described is the first example of probably general and stereospecific

† All reactions were monitored by HPLC: Separon™ SGXC18 (3 × 150 mm, 0.4 cm^3 min^{-1}), size of particles 5 μm (Tessek, Czech Republic) in MeOH. High resolution EI MS measurements were carried out by the peak-matching method using the Ultramark 1600F (PCR Inc., Gainesville, Fl, USA) as an internal standard on a Finnigan MAT 90 instrument (Finnigan MAT, Bremen, FRG), ionizing energy 70 eV, source temperature 250 °C, direct inlet.

‡ *Spectroscopic data for* **5**: ^1H NMR (399.95 MHz, $CDCl_3$, $SiMe_4$, 25 °C) δ_H 1.164 (3H, t, 7.1), 3.682 (1H, dq, 9.9, 7.1), 3.759 (1H, dq, 9.9, 7.1), 7.318–7.486 (14H, m), 7.486 (2H, m, *ortho*-), 7.544 (2H, m, *ortho*-), 7.622 (2H, m, *ortho*-). ^{13}C NMR (100.58 MHz, $CDCl_3$, $SiMe_4$, 25 °C) δ_C 15.60q, 64.43t, 127.13d (2C, *meta*-), 127.20d (2C, *meta*-), 127.71d (*para*-), 127.78d (2C, *meta*-), 127.80d (*para*-), 128.35d (2C, *meta*-), 128.51d (*para*-), 128.55d (2C, *ortho*-), 128.91d (*para*-), 130.84d (2C, *ortho*-), 131.21d (2C, *ortho*-), 131.40s, 131.50d (2C, *ortho*-), 134.06s, 134.13s, 139.61s, 141.07s, 141.96s, 144.88s, 147.47s.

§ *Crystal data for* **5**: $C_{31}H_{25}Cl_3O_2S$, M = 567.9, monoclinic, space group $P2_1/n$, a = 13.581(7) Å, b = 11.822(8) Å, c = 17.12(1) Å, β = 91.84(5)°, U = 2747(3) $Å^3$, Z = 4, D_{calc} = 1.373 g cm^{-3}, $F(000)$ = 1176, μ = 0.43 mm^{-1}. Intensities of 2537 observed unique reflections [$I_0 \geq 1.96\sigma(I_0)$] were measured with an ENRAF NONIUS-CAD4 diffractometer (298 K, graphite monochromated Mo-Kα radiation, λ = 0.71073 Å, ω/2θ scan mode, 2θ > 44°). The structure was solved by direct methods and anisotropically refined by full-matrix least-squares. Hydrogen atoms were placed in geometrically expected positions and included in the refinement in the riding motion approximation with $U_{iso} = U_{eq}$ of attached atoms. The final agreement factors are R = 10.8% and R_w = 12.3%, where $w = 1/\sigma^2(F_0)$. The calculations were perfomed using the CRYSTALS[5] and SHELXS86[6] programs. Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, *Mendeleev Commun.*, issue 1, 1994.

¶ *Spectroscopic data for* **6**: ^1H NMR (399.95, $CDCl_3$, $SiMe_4$, 25 °C) δ_H 3.429 (3H, s), 7.344–7.492 (14H, m), 7.724 (2H, m, *ortho*-), 7.554 (2H, m, *ortho*-), 7.629 (2H, m, *ortho*-). ^{13}C NMR (100.58 MHz, $CDCl_3$, $SiMe_4$, 25 °C) δ_C 54.62q, 65.60s, 127.18d (2C, *meta*-), 127.27d (2C, *meta*-), 127.77d (*para*-), 127.85d (2C, *meta*-), 128.35d (2C, *meta*-), 128.54d (2C, *ortho*-), 128.63d (*para*-), 128.94d (*para*-), 130.80d (2C, *ortho*-), 131.15d (2C, *ortho*-), 131.15s, 131.41d (2C, *ortho*-), 134.03s, 134.10s, 139.55s, 141.16s, 141.66s, 145.38s, 147.35s.

splittings of unsaturated *S*-oxides as well as a quite new transformation in thiopyran chemistry.[2] Similar but less selective chlorinations have received relatively little attention for some saturated sulfoxides.[3,4]

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