Intramolecular Competition Experiments on Sulphide *vs.* Thiocarbonyl Oxidation. Evidence for Electronic and Steric Deactivation of Thiocarbonyl Groups

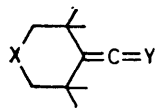
Ernst Schaumann,* Bettina Lange, and Karin Reinholdt

Institut für Organische Chemie und Biochemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, West Germany

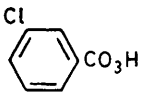
Addition of *m*-chloroperbenzoic acid (**6**) to the thiane-derived thioketene (**1**) or the thioketone (**8**) leads to selective oxidation of their respective sulphide groups.

Oxidation by hydrogen peroxide or peracids to give *S*-oxides is a characteristic reaction of sulphides and thiocarbonyl compounds.[1,2] Relatively little is known, however, about the relative ease of oxidation of a sulphide and a thiocarbonyl sulphur in the same molecule. If the two groups interact by resonance as in dithiocarboxylates[2] or in thiaxanthione,[3] the thiocarbonyl group is attacked first by the oxidant. The same preference has been reported for oxidation of a compound with isolated sulphide and thiocarbonyl groups.[4] We report here reactions that oppose the trend shown in these results.

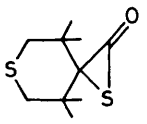
The thioketene (**1**) contains non-interacting sulphide and thiocarbonyl groups.[5] With the peracid (**6**) (1 equiv.) in



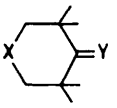
(1) X = Y = S
(2) X = SO, Y = S
(3) X = S, Y = SO
(4) X = SO_2, Y = S
(5) X = SO_2, Y = SO



(6)



(7)

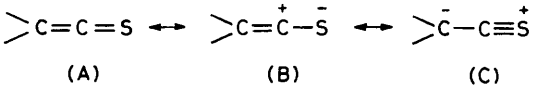


(8) X = Y = S
(9) X = SO, Y = S
(10) X = S, Y = SO
(11) X = Y = SO
(12) X = SO_2, Y = S
(13) X = SO_2, Y = SO

diethyl ether at 0 °C, (1) was oxidized in a smooth reaction to give a purple monoxide, 84% isolated, m.p. 71—72 °C. This was given the sulphoxide structure (2),†‡ with an unchanged thioketene group, by comparison of its spectroscopic data with that of (1)‡ No trace of the isomer (3) was detected. Only one diastereoisomer of (2) was isolated, probably with the oxygen in the axial position.[6]

The same oxidation procedure quantitatively converted (2) into the pink sulphone (4),†‡ m.p. 152—155 °C. Oxidation of the thioketene moiety in (1) was eventually achieved with an excess of (6) (3.5 equiv.) (diethyl ether, 20 °C) to afford the *S,S,S'*-trioxide (5),†‡ 75% isolated, m.p. 170 °C (decomp.), whose spectroscopic data matched those of previously studied thioketene *S*-oxides.[7]

In contrast to the behaviour of (6), nitrones such as 3,3,5,5-tetramethyl-1-pyrroline 1-oxide attack the thioketene group in (1) to give the α-thiolactone (7)† [80%, m.p. 104—111 °C (decomp.)] a reaction analogous to those of other sterically hindered thioketenes.[8] When refluxed in CCl_4, (7) gave a trace of a ketene *via* desulphurization, but the main reaction pathway was decarbonylation to give the thioketone (8),[9] which also offered an opportunity to test the relative reactivities of distinct sulphide and thiocarbonyl groups in the same molecule toward peracids. Thus, with (6) (1 equiv.) in CH_2Cl_2–CCl_4 at 20 °C, (8) reacted to give a diastereoisomerically pure pink sulphoxide (9)† in 91% yield whose structure was suggested by its u.v. data [λ_{max} (hexane) 545 (ε 10), 233 nm (ε 7600)] and the AB system of the four ring protons that occurs in the ^{1}H n.m.r. spectrum [δ ($CDCl_3$) 3.08, 3.55; J_{AB} 13 Hz]. For the alternative structure (10) there would be no electronic transitions in the visible region and no equivalence of the ring protons in the 2- and 6-positions. Repeating our oxidation procedure with (9) gave a mixture of (11)†‡ (19%, m.p. 138—140 °C), (12)†‡ (12%, m.p. 134—136 °C), and (13)†‡ (12%, m.p. 184—186 °C). Unchanged (9) was also present.



(A) (B) (C)

From molecular models, steric arguments to account for the selective sulphide oxidation in (1) can be discarded. However, a reasonable explanation can be derived from consideration of the canonical structure (C) of the thioketene in (1), which has some importance according to ^{13}C n.m.r. and *X*-ray data.[10] Structure (C) has diminished electron density at the thione sulphur and consequently, attack here by the electrophilic peracid (6) becomes less favourable compared to attack at the ring sulphur in (1) or even at the sulphoxide group in (2). The thione group in (8) is situated much closer to the ring methyl groups than that in (1), and the resulting steric screening accounts for the observed oxidation of the relatively unhindered ring sulphur. As sulphoxides are generally oxidized more slowly than sulphides,[11] the thione group can compete with the sulphoxide moiety in the oxidation of (9) to give a mixture of (11), (12), and (13). Thus, the relative reactivities of different sulphur functional groups toward (6) strongly depend on the electronic and steric environment.

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† Satisfactory microanalytical data were obtained for all new compounds.

‡ Selected spectroscopic data. Compound (2): i.r. (KBr) ν(C=C=S) 1750s, ν(S=O) 1030s cm^{-1}; ^{13}C n.m.r. ($CDCl_3$) δ 94.3 (*C*=C=S), 262.3 p.p.m. (C=S); u.v. (2,2,4-trimethylpentane) λ_{max} 568 (ε 11), 237 nm (ε 4320). Compound (1): i.r. (film) ν(C=C=S) 1740s cm^{-1}; ^{13}C n.m.r. ($CDCl_3$) δ 96.2 (*C*=C=S), 266.4 p.p.m. (C=S); u.v. (2,2,4-trimethylpentane) λ_{max} 573 (ε 12), 238 nm (ε 3970). Compound (4): i.r. (KBr) ν(C=C=S) 1750s, ν(SO_2) 1305s, 1100s cm^{-1}; ^{13}C n.m.r. ($CDCl_3$) δ 93.9 (*C*=C=S), 261.1 p.p.m. (C=S); u.v. (2,2,4-trimethylpentane) λ_{max} 565 (ε 12), 237 nm (ε 3640). Compound (5): i.r. (KBr) ν(CCSO) 1720w, ν(SO_2, SO) 1320, 1130, 1085s cm^{-1}; ^{13}C n.m.r. ($CDCl_3$) δ 147.5 (*C*=C=S), 229.5 p.p.m. (C=SO); u.v. (MeCN) λ_{max} 249 nm (ε 340). Compound (11): i.r. (KBr) 1080s, 1045s, 1025s, 1020s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 1.47, 1.83 (2 × s, 3H each), 1.63 (s, 6H), 2.74 and 3.25, 2.95 and 3.28 (AB systems, 2H each, J_{AB} 14 Hz). Compound (12): i.r. (KBr) 1305s, 1125s, 1115s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 1.52 (s, 12H), 3.42 (s, 4H). Compound (13): i.r. (KBr) 1310s, 1300s, 1110s, 1045m, 1030s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 1.58, 1.78 (2 × s, 6H each), 3.18, 3.27 (2 × s, 2H each).

References

1 S. Oae, 'Organic Chemistry of Sulfur,' Plenum Press, New York and London, 1977.
2 B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 1.
3 B. Zwanenburg, L. Thijs, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 577.
4 T. Karakasa and S. Motoki, *Tetrahedron Lett.*, 1979, 3961.
5 E. Schaumann, *Chem. Ber.*, 1982, **115**, 2755.
6 C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, 1964, **86**, 2935; J. C. Martin and J. J. Uebel, *ibid.*, p. 2936; J. B. Lambert and R. G. Keske, *J. Org. Chem.*, 1966, **31**, 3429.
7 E. Schaumann and W.-R. Klein, *Tetrahedron Lett.*, 1977, 3457.
8 E. Schaumann and U. Behrens, *Angew. Chem.*, 1977, **89**, 750; *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 722.
9 W. Rüger, Ph.D. Thesis, University of Hamburg, 1981; A. Krebs, W. Rüger, B. Ziegenhagen, M. Hebold, I. Hardtke, R. Müller, M. Schütz, and M. Wietzke, *Chem. Ber.*, submitted for publication.
10 E. Schaumann, S. Harto, and G. Adiwidjaja, *Chem. Ber.*, 1979, **112**, 2698.
11 B. Plesničar, in 'Oxidation in Organic Chemistry,' part c, ed. W. S. Trahanovsky, Academic Press, New York, 1978, p. 280.