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STEREOELECTRONIC CONTROL IN THE OXIDATION OF *GEM*-DISULPHIDES

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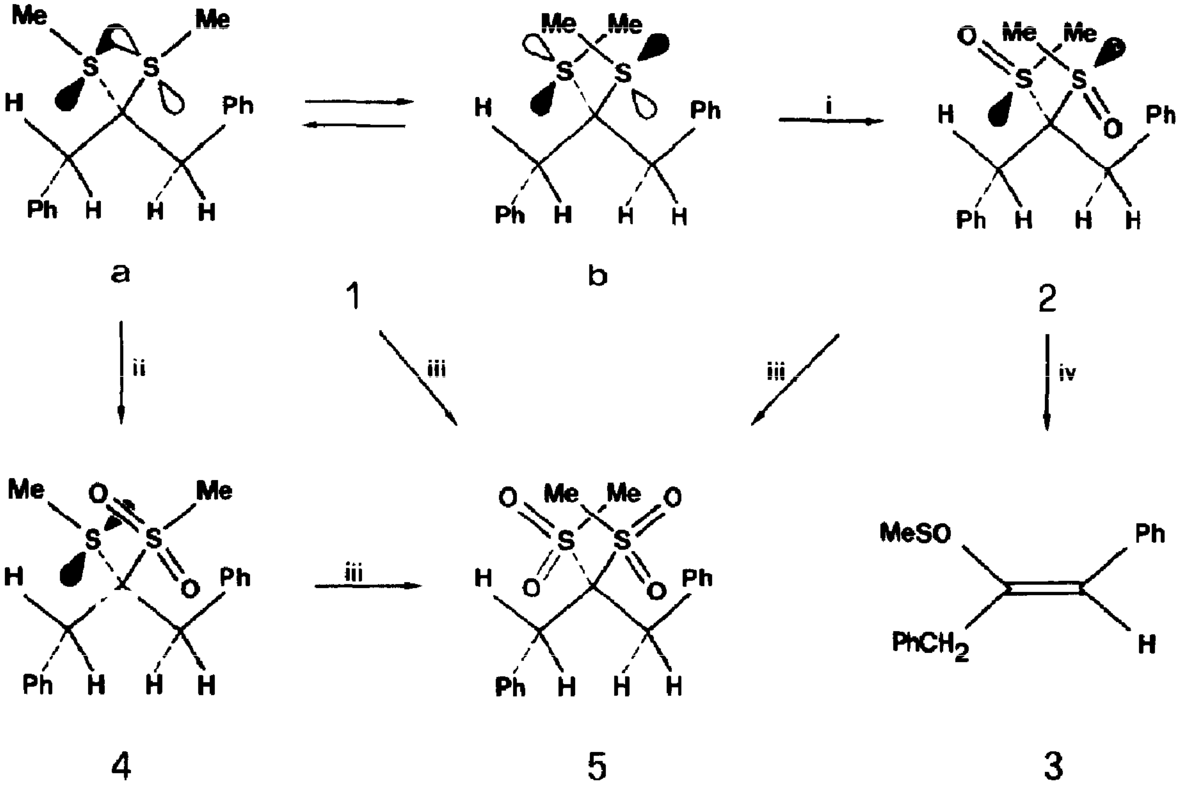
Summary — The first example of stereospecific oxidation in the gem-*disulphide series is reported; chemical, spectral, and X-ray evidence indicated the stereoelectronic discrimination between two modes of approach of electrophile in the conversion to* meso-*2,2-bis(methylsulphinyl)-1,3-diphenylpropane (2).*

The reaction of thioacetals with two equivalents of peroxy acids generally affords epimeric *gem*-disulphoxides, the ratio of epimers being subject to kinetic and/or equilibrium control.[1] We wish to report the first example of stereospecific oxidation in this series. 2,2-Bis(methylthio)-1,3-diphenylpropane (1) was smoothly oxidized to the corresponding *meso*-disulphoxide 2 with *m*-chloroperbenzoic acid ($CHCl_3$, -15°). After the usual work-up[1] yields of 2 were almost quantitative;[2] m. p. 115°; νmax (KBr) 1040, 1028 cm^{-1}. The study of conformational properties in solution by NMR[3,4] indicated a *trans-gauche* orientation of sulphoxide oxygens and of diastereotopic[5] phenyl groups: ^{1}H NMR ($CDCl_3$), δ 7.42, 7.25 (mc, 10H, *si* and *re*Ph), 3.56 (s, 2H, *si*CH_2), 3.13 (s, 2H, *re*CH_2), 2.40 (s, 6H, SOMe);[6] ^{13}C NMR ($CDCl_3$), δ 133.5-127.5 (Ph), 73.3 (s), 35.4 (t, *re*CH_2), 34.4 (q, SOMe), 28.9 (t, *si*CH_2). In boiling toluene 2 undergoes a stereospecific elimination of sulphenic acid to give (±)-*Z*-olefin 3 (90%);[2] m. p. 105-6°; νmax (KBr) 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 7.33, 7.24 (mc, 10H, Ph), 6.64 (t, 1H, =CH-, ^{4}J 3), 3.94 (ddd, 2H, CH_2, ^{2}J 16), 2.53 (s, 3H, SOMe);[6] ^{13}C NMR ($CDCl_3$), δ 146.6 (s, *C2*), 138.1-126.8 (Ph), 135.4 (d, *C1*), 38.5 (q, SOMe), 31.8 (t, CH_2).

The constitutionally isomeric monosulphone 4[7] displayed an unexpected coalescence of the methyl proton signals: ^{1}H NMR ($CDCl_3$), δ 7.32 (m, 10H, Ph), 3.26 (dd, 4H, CH_2 ^{2}J 14, $\Delta\nu$ 22), 2.44 (s, 6H, SO_2Me + SMe).[6] Anisotropic shielding influences associated with *trans-gauche* orientation of phenyl groups are consistent with the preferred conformation of 4. On addition of $Pr(FOD)_3$ the signal was resolved into two singlets of equal intensities. ^{13}C NMR ($CDCl_3$), δ 134.0-127.6 (Ph), 74.4 (s, *C2*), 39.2 (q, SO_2Me), 38.4 (t, CH_2), 13.3 (q, SMe).

The conformations of 2 and 4 resemble that of the parent *gem*-disulphide 1. The fitting of *gauche-gauche* methyl groups into the *trans-gauche* *gem*-dibenzyl locks two diastereomorphic conformations 1a and 1b. In either case the attack of oxygen on the sulphur atoms takes place from the least hindered side (Scheme).



SCHEME. Only one of two enantiomorphic conformations is depicted, and hindered lone-pairs are shaded; i, m-$ClC_6H_4CO_2H$; ii, $KMnO_4$; iii, excess of i ; iv, 110°/toluene.

The crystallographic data reveal that the dibenzyl lock actually owes its efficiency to the *syn*-axial interaction of *trans*-*gauche* phenyl groups with the sulphoxide lone-pairs in 2.

Crystal data: crystals of 2, $C_{17}H_{20}O_2S_2$, are orthorhombic, space group $P2_12_12_1$, with a=14.137, b=13.518, c=8.480 Å, V=1620.6 Å^3, D_m=1.31 gcm^{-3}, D_c=1.313 gcm^{-3}, Z=4, λ=1.5481 Å. Intensity data were measured on a Philips PW-1100 automatic four-circle diffractometer using Cu-$K\alpha$ radiation with a graphite monochromator. The structure was solved by direct methods using MULTAN 76.[8] In all, 1699 unique, non-zero reflections were used in analysis; full-matrix least-squares refinement gave the final R=0.037 (R_w=0.048). Positional and thermal parameters defining the crystal structure are given in the Table. An ORTEP plot of the molecule 2 is shown in the Figure. Important conformational features: C(1)-S(1)...S(2)-C(10), ∡ *gauche-gauche*, 70.1°; O(1)-S(1)...S(2)-C(10), ∡ *syn*, 1.6°; ∡ *re*Ph/*si*Ph planes, 88.9°. Non-bonded interactions: short intramolecular contacts O(1)...H(102), 2.48(5), and C(12)...H(122), 2,55(4) Å; intermolecular short distance O(2)...H(11), 2.41(4) Å.

TABLE. Atomic Co-ordinates.

Atom	x	y	z	U	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.29118(5)	0.77020(4)	0.67314(8)		469(7)	305(6)	463(7)	29(3)	32(3)	-54(3)
S(2)	0.29859(5)	0.54713(4)	0.59951(8)		406(7)	286(6)	511(7)	-16(2)	-48(3)	22(3)
C(1)	0.2990(2)	0.7130(2)	0.8646(4)		466(15)	601(18)	440(15)	18(15)	80(12)	-57(14)
C(2)	0.3359(2)	0.6729(2)	0.5375(3)		355(13)	293(13)	377(14)	-3(10)	-24(11)	-7(10)
O(1)	0.1877(2)	0.7810(2)	0.6445(3)		510(13)	579(14)	689(16)	188(11)	15(11)	-51(12)
O(2)	0.3367(2)	0.4793(1)	0.4754(3)		617(14)	327(11)	770(16)	35(9)	31(13)	-160(11)
C(3)	0.2971(2)	0.6968(2)	0.3712(3)		509(15)	320(13)	428(15)	-33(12)	-85(12)	10(11)
C(4)	0.3272(2)	0.7962(2)	0.3035(3)		474(15)	366(13)	357(13)	-17(11)	-82(11)	9(11)
C(5)	0.4113(2)	0.8080(2)	0.2215(4)		638(19)	497(17)	471(17)	92(14)	134(15)	34(14)
C(6)	0.4351(3)	0.8997(3)	0.1562(4)		672(21)	634(20)	562(20)	-36(17)	140(17)	132(18)
C(7)	0.3733(3)	0.9780(2)	0.1690(5)		661(21)	474(17)	663(21)	-90(15)	-38(18)	173(17)
C(8)	0.2901(2)	0.9664(2)	0.2488(5)		522(17)	409(15)	888(25)	-8(14)	-69(18)	157(17)
C(9)	0.2666(2)	0.8763(2)	0.3159(4)		378(14)	399(15)	679(19)	-12(11)	-81(14)	102(15)
C(10)	0.1738(2)	0.5531(2)	0.5687(5)		431(15)	492(17)	700(22)	-94(13)	-19(15)	69(16)
C(11)	0.4455(2)	0.6721(2)	0.5355(3)		350(14)	462(15)	410(15)	-20(11)	15(12)	14(12)
C(12)	0.4971(2)	0.6607(2)	0.6901(3)		274(12)	404(14)	453(14)	3(10)	2(11)	0(12)
C(13)	0.5324(2)	0.7434(2)	0.7660(4)		338(13)	447(15)	632(20)	-20(11)	-41(13)	-45(14)
C(14)	0.5768(2)	0.7354(3)	0.9115(5)		403(15)	678(20)	641(21)	-9(14)	-83(15)	-195(18)
C(15)	0.5856(2)	0.6445(3)	0.9817(4)		414(16)	932(26)	533(19)	25(17)	-100(14)	-5(19)
C(16)	0.5538(2)	0.5613(3)	0.9070(4)		431(15)	678(20)	650(20)	-6(14)	-86(15)	197(18)
C(17)	0.5101(2)	0.5684(2)	0.7592(4)		364(12)	428(14)	576(16)	9(11)	-68(12)	18(13)
H(5)	0.449(3)	0.760(3)	0.203(6)	74(12)						
H(6)	0.493(3)	0.906(3)	0.099(5)	61(10)						
H(7)	0.384(3)	1.044(3)	0.129(6)	86(14)						
H(8)	0.240(3)	1.030(2)	0.280(5)	79(14)						
H(9)	0.208(3)	0.866(3)	0.371(5)	64(12)						
H(13)	0.525(3)	0.815(3)	0.699(5)	64(11)						
H(14)	0.596(3)	0.784(3)	0.953(6)	76(13)						
H(15)	0.614(3)	0.638(4)	1.077(7)	100(15)						
H(16)	0.567(3)	0.502(3)	0.955(5)	65(11)						
H(17)	0.496(2)	0.512(3)	0.720(4)	46(9)						
H(31)	0.227(2)	0.691(2)	0.370(4)	38(7)						
H(32)	0.317(2)	0.644(2)	0.302(4)	41(8)						
H(111)	0.466(3)	0.725(3)	0.500(5)	54(10)						
H(112)	0.470(3)	0.626(2)	0.461(5)	59(10)						
H(11)	0.254(3)	0.657(2)	0.874(5)	61(11)						
H(12)	0.363(2)	0.685(3)	0.886(4)	56(10)						
H(13)	0.299(4)	0.764(4)	0.931(8)	122(21)						
H(101)	0.155(3)	0.554(3)	0.445(5)	72(12)						
H(102)	0.149(3)	0.603(4)	0.619(7)	93(16)						
H(103)	0.147(3)	0.497(3)	0.629(6)	75(13)						

Positional and thermal parameters (C, O, and S $\times 10^4$, H $\times 10^3$) with estimated standard deviations in parentheses.

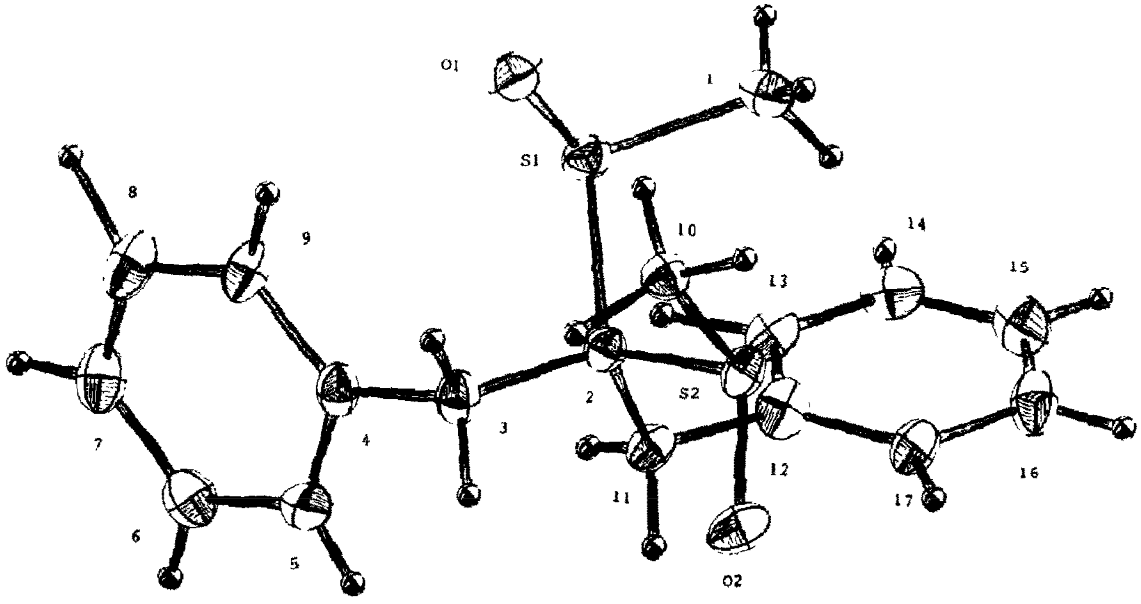


FIGURE. Computer-drawn model of 2.

Obviously, the particular stereochemical course of the conversion to 2 cannot be directed by steric effects, but must have an electronic origin.[9] The stereospecific *trans-gauche* approach of attacking oxygen atoms may be rationalized by considering the transition state. An interaction with the developing negative charge on the acid oxygen and/or repulsive secondary orbital interactions[10] between the phenyl ring and incoming oxygen would be expected to exert a strongly destabilizing influence in both the *trans-trans* and the *gauche-gauche* mode of attack on 1b (Scheme).

Stabilities of 1, 2, and 4 toward the oxidation beyond the dioxide level are consistent with such an interpretation. The crowded disulphone 5 can be prepared in 40-60% yields using a six-fold excess of *m*-chloroperbenzoic acid in chloroform, followed by careful evaporation of solvent and prolonged reaction in the solid state (5-7 days); m. p. 148-9°; ν_{max}(KBr) 1307, 1293, 1141, 1127 cm^{-1}; ^{1}H NMR(CDCl$_3$), δ 7.33(mc,10H,Ph), 3.58(s,4H,CH$_2$), 2.97(s,6H,SO$_2$Me).[6]

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REFERENCES AND NOTES

1. C. Y. Meyers, L. L. Ho, A. Ohno, and N. Kagami, *Tetrahedron Letters* 729 (1974) and references cited therein.
2. All new compounds gave appropriate elemental analyses, and yields are based on recrystallized products (chloroform-hexane). M. ps. are uncorrected. The IR spectra were recorded on a Perkin-Elmer 257 spectrometer. NMR spectra were obtained with a Varian T-60 and a Varian XL-100 spectrometer.
3. M. Poje, O. Nota, and K. Balenović, *Tetrahedron*, in press.
4. J. B. Stothers, *"Carbon-13 NMR Spectroscopy"*, Academic Press, New York, 1972; N. K. Wilson and J. B. Stothers, *Topics Stereochem.* 8, 1 (1974).
5. The descriptors *re* and *si* was used to specify the topic relationships in the propseudochiral molecule 2: V. Prelog and G. Helmchen, *Helv. Chim. Acta* 55, 2581 (1972).
6. It is worthy of note that analogous *gem*-disulphoxides usually give rise to signals near δ 2.8 (SOMe), monosulphones near 3.1 (SO$_2$Me) and 2.4 (SMe), and disulphones near 3.3 (SO$_2$Me). The shielding effect ($\sigma \simeq 0.7$) associated with the *syn* Me/Ph orientation is persistent across the S-oxide series 2, 4, and 5. A similar shielding influence is also evident from an upfield shift of methyl resonance in 1 (δ 1.8).
7. M. Poje and K. Balenović, *Tetrahedron Letters* 1231 (1978).
8. J. P. Declercq, S. E. Hull, G. Germain, L. Lessinger, P. Main, and M. M. Woolfson, *MULTAN 76: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, Universities York and Louvain, 1976.
9. Under the same conditions 3,3-bis(methylthio)-pentane gave epimeric disulphoxides in a 1:1 ratio, as estimated by NMR(CDCl$_3$), δ 2.88 and 2.81 (*meso+d,l* SOMe).
10. K. Okada and T. Mukai, *J. Am. Chem. Soc.* 100, 6509 (1978) and references cited therein.

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