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SELECTIVE OXIDATION OF *GEM*-DISULPHIDES TO MONOSULPHONE DERIVATIVES

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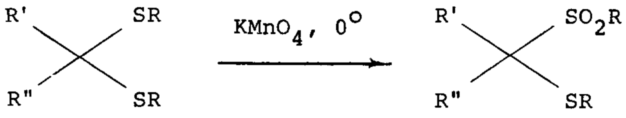
Backer[1] reported in 1946 that potassium permanganate in acetone solution oxidized dimethylthiomethane (1a) to the corresponding disulphoxide. However, careful reinvestigation of this procedure in our laboratory demonstrated that the product was methylsulphonylmethylthiomethane (2a). Although the spectral data[2] were consistent with the monosulphone structure, definitive proof was obtained through synthesis by an alternative route according to Böhme and Heller[3].

An adaptation of the permanganate procedure afforded the monosulphone 2a in 70% yield. This method was extended to a series of *gem*-disulphides, sufficiently varied to demonstrate the selectivity and scope of the reaction.



1 2

a : R'=R"=H, R=Me
b : R'=R"=H, R=CMe_3
c : R'=H, R=R"=Me
d : R=R'=R"=Me
e : R'=R"=$PhCH_2$, R=Me
f : R'=H, R"=*p*-ClC_6H_4, R=Me
g : R'=H, R"=$C_6H_4(CO)_2NC_2H_4$, R=Me

We have now found that the monosulphones 2a-g can be prepared directly from the corresponding *gem*-disulphides 1a-g[4] by oxidation with potassium permanganate in acetone at 0°. The reaction proceeded at rather slow rate and no detectable amounts (TLC) of sulphoxides were formed at any stage. The mechanism of the oxidation is unclear; under the same conditions 1,2-di(*tert*-butylthio)-ethane (3)[5] was over-oxidized to the disulphone 4 (95%, m.p. 230-1°)[6], suggesting the requirement of *gem*-grouping for selective conversion into monosulphones.

Table : *gem*-Sulphonyl-sulphides 2

Compd[a]	Yield[b]	Recrystn solvent	m.p. (°C)[c]	νSO_2 (cm^{-1})[d]		Prepn of 1
a	70%	ethanol	51-2	1289	1117	(1)
b	88%	CCl_4-hexane	116-7	1295	1113	(4a)
c	81%	ethanol	40-1	1290	1113	(4b)
d	80%	ethanol	60-1	1290	1107	(4c)
e	89%	CH_2Cl_2-hexane	115-6	1286	1127	(4d)
f	85%	CH_2Cl_2-hexane	131-2	1300	1130	(4d)
g	77%	$CHCl_3$-hexane	185-6	1302	1130	(4e)

a) Satisfactory analytical (±0.3% for C,H,N and S), and NMR (in $CDCl_3$) spectral data were obtained for all new compounds listed in Table. *b*) Yields are based on recrystallized products. *c*) M.ps. are uncorrected. *d*) IR spectra (in KBr).

General procedure : The oxidation is conveniently carried out by gradual addition of finely powdered potassium permanganate (0.06 moles) to a stirred solution of *gem*-disulphide (1, 0.02 moles) in acetone (100-150 ml) at -5°C. An additional amount of permanganate (0.04 moles) was added in several portions in the course of five days. When the reaction is complete (8-10 days at 0°), the precipitated manganese dioxide was filtered off, the solvent removed, and the residue purified by crystallization from an appropriate solvent.

From the mother liquors 6-10% of unchanged *gem*-disulphide 1 could be recovered.

In summary, the method is highly specific, it encompasses a variety of *gem*-disulphides, and excellent yields are obtainable under mild conditions[7].

REFERENCES AND NOTES

1. H.J. Backer, *Rec.trav.chim.* 65,53(1946) obtained the compound, m.p. 51-2°,in 24% yield. Failure of this product to react with MeI, or give an additional product with $HgCl_2$, has eliminated the alternative monosulphone structure.
2. We found no infrared bands ascribable to sulphoxides, while the NMR spectrum displayed three singlets at δ 3.88 (CH_2), 3.03 (SO_2Me), and 2.40 (SMe); the apparent discrepancy between this spectrum and those of both disulphoxides was overlooked by R.Louw and H.Nieuwenhuyse, *Chem.Comm.* 1968,1561.
3. H.Böhme and P.Heller, *Chem.Ber.* 86,785(1953) prepared 2a, m.p. 50-1°, in a poor yield, from chloromethyl methyl sulphone through several steps. This compound was identical in all respects with our oxidation product 2a.
4. a) H.J.Backer and P.Stedehouder, *Rec. trav. chim.* 52,437(1933). b) D.T.Gibson, *J. Chem. Soc.* 1931,2640. c) B.P.Fedorov and I.S.Savel'eva, *Izvest. Akad. Nauk SSSR, otdel Khim. Nauk* 1950,223. d) New compounds 1e, m.p. 48-9°(EtOH), and 1f, m.p. 40-1°(EtOH), were prepared in 70-80% yields by method of H.J. Boonstra,L.Brandsma,A.M.Wiegman and J.F.Arens, *Rec. trav. chim.* 78,252(1959). e) A.Deljac,Z.Štefanac and K.Balenović,*Tetrahedron* 22,Suppl.8,33(1966).
5. H.B.Henbest,J.A.W.Reid and C.J.M.Stirling, *J. Chem. Soc.* 1964,1220.
6. H.J.Backer,J.Strating and J.F.A.Hazenberg, *Rec. trav. chim.* 72,813(1953) have reported the same m.p. 230-1° for 1,2-di(*tert*-butylsulphonyl)-ethane.
7. *This research was assisted financially by the Croatian Research Foundation.*