Oxidation of Sulphoxides in Preference to that of Sulphides

By H. B. HENBEST* and S. A. KHAN
(*Department of Chemistry, The Queen's University of Belfast, Belfast* BT9 5AG)

SULPHOXIDES can often be obtained in good yields starting from sulphides, because the rates of further oxidation (to sulphones) are slower than those of the initial addition of oxygen to the corresponding sulphides. For example, diaryl sulphides are oxidised several hundred times more quickly than related diaryl sulphoxides when peracetic acid is used as oxidant.[1] Similarly, a 96% yield of dibenzyl sulphoxide is obtained[2] from the reaction between dibenzyl sulphide and sodium metaperiodate in aqueous methanol, the sulphoxide being relatively stable towards this oxidant (96—99% recovered under the same conditions; present work).

However, sulphoxides are often more reactive than sulphides towards the transition-metal oxidants, permanganate ion,[3] or osmium tetroxide, *cf.* the effectiveness of rhodium and iridium species as catalysts for the preferential aerial oxidation of sulphoxides.[4] Under conditions (sodium permanganate in aqueous dioxan at 20° for 5 min.) from which dibenzyl sulphide (97%) is recovered unchanged, dibenzyl sulphoxide is converted into the sulphone (95—100%). Closely similar results are obtained using diphenyl sulphide and sulphoxide, either separately or competitively. The stoicheiometry of the oxidation is expressed by the equation

$$3R_2SO + 2NaMnO_4 \rightarrow 3R_2SO_2 + Na_2O + 2MnO_2.$$

These results refer to unbuffered (alkaline) or buffered (using $MgSO_4$) reaction conditions. Oxidation is less selective in the presence of dilute acid (H_2SO_4): dibenzyl sulphide, for example, is converted into sulphoxide and sulphone, and there is a greater tendency for the solvent (dioxan) to be oxidized.

Whereas 1,4-dithian oxide, $S[CH_2{\cdot}CH_2]_2SO$, gives a mixture of *cis*- and *trans*-disulphoxides on treatment with hydrogen peroxide in acetic acid,[5] oxidation with permanganate gives a 63% yield of the thia-sulphone, $S[CH_2{\cdot}CH_2]_2SO_2$, made previously by a different route.[5]

In agreement with the statement[6] that sulphides "appear to be essentially inert to osmium tetroxide under ordinary conditions", diphenyl sulphide and dibenzyl sulphides are recovered in 99 and 96% yields respectively after being treated with the tetroxide (1 mol.) in boiling ether for 48 hr. However, thiacyclohexane, $S[CH_2]_5$, is converted into the related sulphone, $O_2S[CH_2]_5$, (58%) on treatment with osmium tetroxide (1 mol.) in cyclopentane at $-15°$ for 2 hr. and 20° for 1 hr., the result indicating that the sulphoxide → sulphone stage may be faster than the sulphide → sulphoxide stage. This was confirmed for the reactions of the compounds with phenyl or benzyl groups as substituents. For example, treatment of a mixture of diphenyl sulphide (1 mol.) and diphenyl sulphoxide (1 mol.) with osmium tetroxide (1 mol.) in boiling ether for 48 hr. gives sulphone (96%) and unchanged sulphide (99%). Experiments starting with an excess of sulphoxide show that sulphone is formed according to the equation:

$$R_2SO + OsO_4 \longrightarrow R_2SO_2 \ (+ \ OsO_3)$$

The black insoluble material that separates during these reactions is presumably osmium trioxide or a related substance.

(*Received, May 21st,* 1968; *Com.* 648.)

---

[1] J. Böeseken and E. Arrias, *Rec. Trav. chim.*, 1935, **54**, 711.
[2] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, 1962, **27**, 282.
[3] F. D. Chatterway and E. G. Kellett, *J. Chem. Soc.*, 1930, 1352 (one example described).
[4] J. Trocha-Grimshaw and H. B. Henbest, preceding Communication.
[5] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1928, 86.
[6] C. Djerassi and R. R. Engle, *J. Amer. Chem. Soc.*, 1953, **75**, 3838.