Tetrahedron Letters No. 6, pp. 20-22, 1960. Pergamon Press Ltd.
Printed in Great Britain.

OXIDATION OF ORGANIC SULPHIDES WITH OPTICALLY ACTIVE PEROXY ACIDS. ASYMMETRIC SYNTHESIS OF SULPHOXIDES

K. Balenović, N. Bregant, and D. Francetić

Chemical Laboratory, Faculty of Science, University of
Zagreb, Strossmayerov trg 14, Zagreb, Yugoslavia

(Received 20 January 1960; in revised form 15 February 1960)

THE resolution of m-carboxyphenylmethylsulphoxide (I, R=H) has confirmed the fact that sulphoxides may exist in optically active forms[1], and indicates the tetrahedral structure of these compounds.

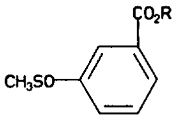
We have found at present that methyl m-methylthiobenzoate (II) oxidised with percamphoric acid showing $[\alpha]_D$ +52°[2] in ether at 0° gave m-carbomethoxyphenylmethylsulphoxide (I, $R=CH_3$) in a 74% yield with the

---

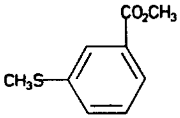
[1] P.W.B. Harrison, J. Kenyon, and H. Phillips, J. Chem. Soc. 2079 (1926).

[2] N.A. Milas and A. McAlevy, J. Amer. Chem. Soc. **55**, 349 (1933).

b.p. 80-90°/0.02 mm. (bath temp.) and $[\alpha]_D$ +2.2° ± 0.2° (c, 2.88 in methanol) (Found: C, 54.88; H, 5.29. $C_9H_{10}O_3S$ requires: C, 54.53; H, 5.09).



I



II

Hydrolysis of compound I ($R=CH_3$) in an equimolar amount of diluted aqueous sodium hydroxide afforded m-carboxyphenylmethylsulphoxide (I, R=H) in a 80% yield, m.p. 168°, and showing $[\alpha]_D$ +1.4° (in methanol). Fractional crystallisation from chloroform - petroleum ether gave the same compound with the m.p. 170° and $[\alpha]_D$ +5.3° ± 0.2° (c, 1.960 in methanol) (Found: C, 51.78; H, 4.38. Calc. for $C_8H_8O_3S$: C, 52.16; H, 4.38).

Analogous oxidation of methyl m-ethylthiobenzoate gave m-carbomethoxyphenylethylsulphoxide with the m.p. 100-105°/0.01 mm. and $[\alpha]_D$ +2.5° ± 0.2° (c, 2.225 in methanol) (Found: C, 56.74; H, 5.85. $C_{10}H_{12}O_3S$ requires: C, 56.58; H, 5.69).

Hydrolysis of the above compound afforded m-carboxyphenylethylsulphoxide[3], showing the m.p. 104° and $[\alpha]_D$ $+1.4^\circ \pm 0.2^\circ$ (c, 3.410 in methanol) (Found: C, 54.38; H, 5.25. Calc. for $C_9H_{10}O_3S$: C, 54.54; H, 5.09).

In all these oxidations with percamphoric acid the water - soluble sulphoxide was easily separated from the ether - soluble camphoric acid. In separate runs it was found that our sulphoxide was completely free of either camphoric or percamphoric acid.

The significance of these results for the determination of the absolute configuration of sulphoxides will be given in due course.

---

[3] J. Holloway, J. Kenyon, and H. Phillips, J. Chem. Soc. 3000 (1928).