Optical Resolution and Absolute Configuration of Oxosulphonium Ions

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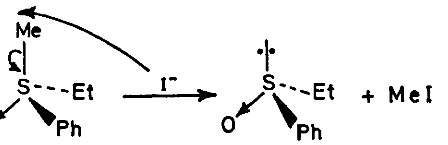
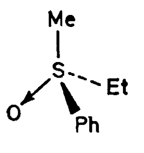
Summary Optically active ethylmethylphenyloxosulphonium salts have been prepared and their absolute configuration has been determined.

OPTICALLY active compounds containing pyramidal sulphur atoms are known, *e.g.*, sulphoxides, sulphinate esters, and sulphonium ions. However, no optically active tetrahedral sulphur compounds have been reported except benzyl *p*-tolyl $[^{16}O^{18}O]$sulphone[1] and phenyl toluene-*p*-sulphonate [sulphonyl $^{16}O^{18}O$].[2] We here report the optical resolution and absolute configuration of ethylmethylphenyloxosulphonium ion, which, without reliance on isotopes, is the first example of optically active tetrahedral sulphur compounds.

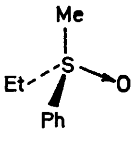


(+)*R* (+)*R*



[α]$_D$ +14·5°

(A)

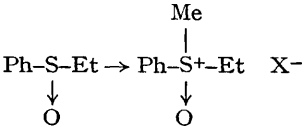


[α]$_D$ −14·3°

(B)

A mixture of the sulphoxide (I), MeI, and HgI$_2$ was heated under reflux for 60 h under nitrogen. Unchanged (I) and MeI were removed with ether; the crude crystals were recrystallized from methanol to give the mercuritriiodide (IIa) (18%), m.p. 94—95°; δ 1·54 (t, 3H), 4·37 (s, 3H), 4·58 (q, 2H), and 8·10 (m, 5H) p.p.m.; ν_{max} 1240 and 1210 cm^{-1}. Various side reactions occurred including formation of dimethyl ether; the best result was obtained with a molar ratio of HgI$_2$ to (I) of 1 : 3 and a large excess of MeI.

When (IIa) was mixed with silver (+)-camphor-10-sulphonate in acetonitrile at room temperature, AgI and HgI$_2$ precipitated, and the hygroscopic sulphonate (IIb) was obtained (81%): $[\alpha]^{34}_{D}$ = + 25·6° (*c* 8·32, EtOH); ν_{max} 1730, 1210, 1190, and 1170 cm^{-1}.



$$\underset{\underset{O}{\downarrow}}{\text{Ph–S–Et}} \rightarrow \underset{\underset{O}{\downarrow}}{\text{Ph–}\overset{\overset{\text{Me}}{|}}{\text{S}^{+}}\text{–Et}} \quad X^-$$

(I) (IIa): X = HgI$_3$
(IIb); X = (+)-C$_{10}$H$_{15}$O-10-SO$_3$
(IIc); X = ClO$_4$

Repeated fractional recrystallization of (IIb) (18·6 g) from acetone gave crystals of (+)-(+)-(IIb) (3·1 g, 33%) m.p. 142—143·5°; $[\alpha]^{33}_{D}$+39·7° (*c* 2·90, EtOH) and (−)-(+)-(IIb) (1·07 g, 12%) m.p. 120—121°; $[\alpha]^{32}_{D}$ +11·6° (*c* 4·66, EtOH). A solution of (+)-(+)-(IIb) or (−)-(+)-(IIb) in acetone–water (1 : 1) was then passed through an anion-exchange resin column which had been treated with NaClO$_4$. On recrystallization from ethanol, white crystals of (+)-(IIc) (1·52 g) m.p. 79·0–79·5°; $[\alpha]^{32}_{D}$ +14·5°, (*c* 5·52, acetone) ν_{max} 1240, 1210, and 1100br cm^{-1}, and (−)-(IIc) (0·63 g), m.p. 79·0—79·5°; $[\alpha]^{30}_{D}$ −14·3°, (*c* 4·61, acetone) were obtained. The absolute configurations (+)- and (−)-(IIc) were determined by conversion into sulphoxides.

A mixture of (+)-(IIc) and NaI (mol. ratio 1:2) was heated under reflux in acetone for 1 h, and water was added to the mixture. The sulphoxide was extracted with ether and then passed through a Florisil column. The ethyl phenyl sulphoxide obtained was found to be dextrorotatory $\{[\alpha]_D^{26}$ +185·6°, (*c* 0·71, acetone)$\}$. Mislow and his coworkers have established that (+)-alkyl aryl sulphoxides possess the *R*-configuration,[3] so the (+)-sulphoxide obtained above must also possess the *R*-configuration. Since demethylation of the ethylmethylphenyloxosulphonium ion proceeds by S_N2 attack of iodide ion on the methyl group, not the sulphur atom, the stereochemistry of the sulphur atom must be retained during this demethylation. Consequently, the (+)-ethylmethylphenyloxosulphonium ion must also have the *R*-configuration.

Similarly, laevorotatory ethyl phenyl sulphoxide ($[\alpha]_D^{35}$ −173·4°) was formed from (−)-(IIc); chromatographic purification could not be carried out owing to lack of material. These findings establish assignments (A) and (B) for absolute configuration of the oxosulphonium ions.

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[2] M. A. Sabol and K. K. Andersen, *J. Amer. Chem. Soc.*, 1969, **91**, 3603.

[3] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1965, **87**, 1958.