

## **Thiosulphonium Ion Intermediate in the Oxidation of a Thiol with Dimethyl Sulphoxide**

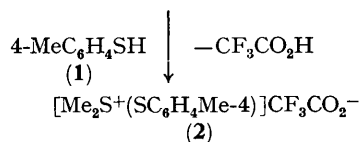
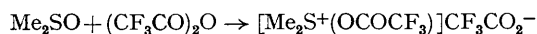
By RIKUHEI TANIKAGA,\* KAZUHIKO TANAKA, and ARITSUNE KAJI

*(Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606, Japan)*

*Summary* A thiosulphonium ion was isolated as intermediate in the oxidation of a thiol to a disulphide with dimethyl sulphoxide; the reactions of the ion are described.

THIOLS are oxidized to disulphides with sulphoxides,<sup>1</sup> and the oxidation has been suggested to proceed *via* an unstable thiol-sulphoxide adduct such as a thiosulphonium ion.<sup>2</sup> The isolation of the thiosulphonium ion is of interest in connection with the possibility of an attack of a sulphide sulphur atom on a sulphonium sulphur cation.<sup>3</sup>

Here we report the isolation of a thiosulphonium ion during the oxidation of 4-methylbenzenethiol (**1**) with Me<sub>2</sub>SO in the presence of (CF<sub>3</sub>CO)<sub>2</sub>O. In a typical procedure, solutions of (CF<sub>3</sub>CO)<sub>2</sub>O (3 equiv.) and (**1**) in dry CH<sub>2</sub>Cl<sub>2</sub> were successively added to a solution of Me<sub>2</sub>SO (3 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> at -80 °C. After evaporation of the solvent and Pummerer rearrangement<sup>4</sup> products *in vacuo* at room temperature, the residue was washed with dry hexane. The thiosulphonium ion (**2**) was obtained as a yellow liquid in 90% yield (Scheme) [ $\delta$ (CDCl<sub>3</sub>) 2.48 (3H, s, Me-C), 2.89 (6H, s, Me-S<sup>+</sup>), 7.40 (2H, d), and 7.60 (2H, d)].



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On keeping at room temperature for several hours, (**2**) partially decomposed into (4-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub> (**3**) and some

unidentified compounds. The ion (**2**) is sensitive to water and on contact is decomposed quantitatively into (**3**) and 4-MeC<sub>6</sub>H<sub>4</sub>SSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4.

Compound (**2**) was also prepared from 4-MeC<sub>6</sub>H<sub>4</sub>SCl, dimethyl sulphide, and silver trifluoroacetate in a manner similar to that described for the preparation of thiosulphonium perchlorate.<sup>5</sup>

Treatment of (**2**) with (**1**) instantly generated (**3**) in 98% yield. This means that (**2**) is an intermediate in the oxidation of (**1**) to (**3**). Treatment of (**2**) with 2-methylpropane-2-thiol afforded *t*-butyl tolyl disulphide in 87% yield, but no symmetrical disulphides were detected.

The ion (**2**) rapidly reacted with cyclohexene at room temperature to give 1-(4-tolylthio)-2-trifluoroacetoxy-cyclohexane [50% yield; b.p. 130 °C at 0.8 mmHg;  $\delta$ (CCl<sub>4</sub>) 1.2-2.2 (8H, m, CH<sub>2</sub>), 2.34 (3H, s, Me), 3.02 (1H, m, CH-S), 4.88 (1H, m, CH-O), 7.08 (2H, d), and 7.30 (2H, d);  $\nu_{\text{max}}$  1780 cm<sup>-1</sup> (C=O);  $m/e$  318 (M<sup>+</sup>)]. Treatment of (**2**), like thiosulphonium perchlorate,<sup>5</sup> with anisole afforded 4-methoxyphenyl tolyl sulphide [48% yield; b.p. 145 °C at 0.8 mmHg;  $\delta$ (CCl<sub>4</sub>) 2.29 (3H, s, Me), 3.75 (3H, s, Me-O), 6.80 (2H, d), 7.04 (4H, s), and 7.32 (2H, d)]. This suggests that the isolated intermediate (**2**) resembles thiosulphonium perchlorate.

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