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Oxosulfonium Salts. III. Methylation of Optically Active Sulfoxides.[1]

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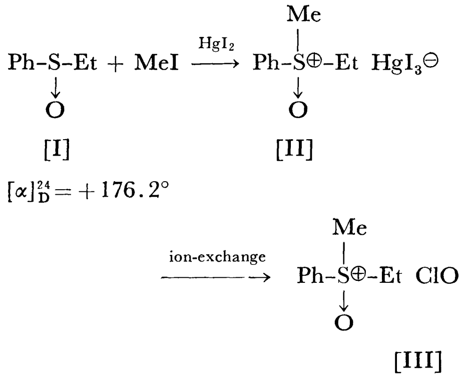
A report was previously given on the synthesis, optical resolution and determination of absolute configuration of ethylmethylphenyloxosulfonium perchlorate.[2] The oxosulfonium salt was prepared by methylation of racemic sulfoxide followed by optical resolution. Since optically active sulfoxides can be prepared by the reaction of the optically active menthyl sulfinates with the Grignard reagents, methylation of such sulfoxides seems to be an attractive route for the synthesis of optically active oxosulfonium ions. Methylation of optically active ethyl phenyl sulfoxide was therefore investigated.

R-(+)-Ethyl phenyl sulfoxide ($[\alpha]_D^{24}=+176.2°$) [I], prepared from (—)-menthyl benzenesulfinate, was refluxed in excess methyl iodide in the presence of mercury (II) iodide (1/3 mol per mol I) under a nitrogen atmosphere for 63 hr. When unchanged I and methyl iodide were removed by extraction with ether and the remaining crystals were recrystallized from methanol, ethylmethylphenyloxosulfonium mercuritriiodide [II] was obtained in 27.7% yield (based on the moles of HgI_2 used).

Since its specific rotation was very small, II was converted into perchlorate by use of an ion-exchange resin column; $[\alpha]_D^{22}=+9.8°$ (c=2.2, acetone); optical purity, 72%.[3]



$$\underset{\substack{\downarrow\\ \text{O}}}{\text{Ph-S-Et}} + \text{MeI} \xrightarrow{\text{HgI}_2} \text{Ph-}\underset{\substack{\downarrow\\ \text{O}}}{\overset{\substack{\text{Me}\\ |}}{\text{S}^{\oplus}}}\text{-Et HgI}_3^{\ominus}$$

[I] [II]

$[\alpha]_D^{24}=+176.2°$

$$\xrightarrow{\text{ion-exchange}} \text{Ph-}\underset{\substack{\downarrow\\ \text{O}}}{\overset{\substack{\text{Me}\\ |}}{\text{S}^{\oplus}}}\text{-Et ClO}_4^{\ominus}$$

[III]

The dextrorotatory III should have an *R*-configuration, since it was established that (+)-III obtained by optical resolution has this configuration.[2] This shows that alkylation of sulfoxides proceeds with retention of configuration.

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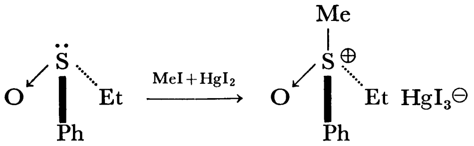
[1] Organic Sulfur Compounds, Part XLIV.

[2] M. Kobayashi, K. Kamiyama, H. Minato, Y. Oishi, Y. Takada, and Y. Hattori, *Chem. Commun.*, **1971**, 1577.

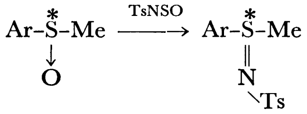
[3] Optically active II was found not to racemize under the reaction conditions. Therefore, the low optical purity observed is probably due to the racemization of the sulfoxide during the reaction (*cf.* the following work by Modena *et al.*).

[4] G. Modena, U. Quintly, and G. Scorrano, *J. Amer. Chem. Soc.*, **94**, 202 (1972); K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964).



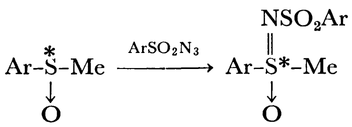
The reaction among, I, methyl iodide, and mercury(II) iodide is rather complex and the yield of II is often very small unless the reaction conditions are carefully controlled. Products other than II were ethylmethylphenylsulfonium salt, dimethyl ether, and iodine.

Conversion of optically active sulfoxides into sulfilimines was found to proceed with retention of configuration.⁵⁾



$$\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{Ar{-}\overset{*}{S}{-}Me}} \xrightarrow{\mathrm{TsNSO}} \underset{\underset{\mathrm{N}\diagdown\mathrm{Ts}}{\|}}{\mathrm{Ar{-}\overset{*}{S}{-}Me}}$$

Another example of reactions proceeding with retention of configuration is the formation of sulfoximines from sulfoxides.⁶⁾



$$\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{Ar{-}\overset{*}{S}{-}Me}} \xrightarrow{\mathrm{ArSO_2N_3}} \underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{NSO_2Ar}}{\|}}{\mathrm{Ar{-}S^{*}{-}Me}}}$$

The conversion of I into II is unique in that a sulfur–carbon bond is formed with retention of configuration without breaking any bond in the sulfoxides. Since optically active sulfoxides are readily available from (—)-menthyl sulfinates, this method is better for formation of optically active oxosulfonium ions in comparison with the optical resolution of racemic oxosulfonium ions.²⁾

Experimental

(+)-Ethyl Phenyl Sulfoxide [I]. Benzenesulfinic acid and (—)-menthol were condensed by dicyclohexylcarbodiimide in dichloromethane,⁷⁾ and the diastereomeric mixture of menthyl sulfinates formed was separated by recrystallization; one diastereomer crystallized more readily. The crystalline diastereomer was allowed to react with ethylmagnesium iodide, and (+)-I was obtained;⁸⁾ bp, 92—94 °C/2 mmHg; IR, 1050 cm^{-1} ($\nu_{\mathrm{S-O}}$); $[\alpha]_{\mathrm{D}}^{24}=+176.2°$ ($c=1.03$, acetone); optical purity, 94% (176.2/187.5×100).

Methylation of I. After a mixture of mercury(II) iodide (1.20 g, 2.64 mmol) and methyl iodide (5 ml) was stirred for 40 min under nitrogen, (+)-II (0.968 g, 6.27 mmol) was added, and the mixture was refluxed for 63 hr. Evaporation of methyl iodide under reduced pressure gave a brown oil, which was converted into crude crystals by washing out the remaining I with ether. They were recrystallized twice from methanol, and pure II was obtained; yield, 0.547 g (11.6%) (27.7% based on HgI_2); mp 69.5—70.5 °C; IR, 1210, 1240 cm^{-1}; NMR, δ, 1.55(3H, t), δ, 4.39 (3H, s), δ, 4.54 (2H, q), δ, 8.10 (5H, m).

Conversion of I to II. A small amount of an acetone-water (5 : 1) solution of I (0.520 g) was added to an anion-exchange column (Amberlite IRA 400) which had been adjusted to ClO_4^- type. Elution with acetone–water (1 : 1) and evaporation of the eluate (150 ml) gave an oil, which crystallized upon addition of ethanol. Recrystallization was repeated twice, and the pure II amounted to 0.150 g (80.7%); mp, 70.5—72.0 °C; $[\alpha]_{\mathrm{D}}^{22}=+9.8°$ ($c=2.2$, acetone); optical yield 72.1%; IR, 1240, 1210, 1100 cm^{-1}; Found: C, 40.77; H, 4.98. Calcd for $C_9H_{13}SO_5Cl$: C, 40.23; H, 4.88.

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5) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 2721 (1968).

6) M. A. Sabol, R. W. Davenport, and K. K. Andersen, *Tetrahedron Lett.*, **1968**, 2159.

7) Y. Miyaji, H. Minato, and M. Kobayashi, This Bulletin, **44**, 862 (1971).