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Organic Sulfur Compounds. VIII. The Formation of Sulfinate Esters by the Alkylation of Sulfinic Acid Salts

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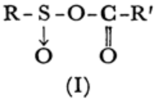
The alkylation of the sulfinic acid salts with triethyloxonium fluoroborate results in the formation of the ethyl sulfinates, not in the usual sulfone formation.

Sulfinic acid salts are known to react with many alkylating reagents to give the sulfones; indeed, this reaction is one of the established methods for the preparation of sulfones.¹⁾

Although the fact that the electronegativity of an oxygen atom is higher than that of sulfur suggests the localization of the negative charge mainly on the oxygen atoms in a sulfinate anion, every reported alkylation of the sulfinic acid salts has taken place on the sulfur atom, thus resulting in the formation of the sulfones; this mode of *S*-alkylation has been believed to be the general one for the sulfinate anion.



$$R-\underset{\underset{\displaystyle O}{\downarrow}}{S}-O-\underset{\underset{\displaystyle O}{\|}}{C}-R'$$

(I)

In the course of our study of the reaction of the sulfinic acid salt with carboxylic chloride, the formation of a sulfinic carboxylic anhydride (I) as an intermediate has been deduced.²⁾ This means an *O*-alkylation in the sulfinate anion. Since the above reaction is a very rapid one (completed in a few minutes even at −70°C) compared to the usual slow alkylation of the sulfinic acid salts to form the sulfones, it occurred to the author that a highly-reactive alkylating reagent may attack the sulfinate anion on oxygen atom to give a sulfinic ester.

Triethyloxonium fluoroborate is known to be a very efficient ethylating reagent.³⁾ When the reaction of sodium *p*-toluenesulfinate with this oxonium salt was attempted, the formation of ethyl *p*-toluenesulfinate in an almost quantitative yield was observed. The ethylation of a pyridinium *p*-nitrobenzenesulfinate with the same reagent also gave ethyl sulfinate. No sulfone formation was detected. Therefore, it may be concluded that,

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1) Houben-Weyl, "Methoden der Organischen Chemie," 4th ed., Vol. IX, Georg Thieme, Stuttgart (1955), p. 231.

2) Part III of this series: M. Kobayashi, This Bulletin, **39**, 967 (1966).

3) N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **86**, 2681 (1964).

with a highly-reactive alkylating reagent, the attack on the sulfinate anion proceeds in a kinetically controlled manner to give a relatively unstable sulfinate ester, while in the reaction with weak alkylating reagents a thermodynamically controlled attack gives more stable isomeric sulfones. A similar idea concerning the dual nature of the electrophilic attack on the ambident anions has been well established by Kornblum and his coworhers in the cases of active methylene compounds.⁴⁾

Experimental

Ethyl *p*-Toluenesulfinate.—Into a solution of 3.5 g. of triethyloxonium fluoroborate⁵⁾ in 20 ml. of methylene chloride, 3.0 g. of finely-powdered anhydrous sodium *p*-toluenesulfinate in several portions was vigorously stirred over a 5 minute period. The reaction proceeded quickly, with a slight evolution of heat. After 30 ml., the reaction mixture was repeatedly shaken with a large volume of water and the organic layer was dried over magnesium sulfate. The infrared spectrum of an aliquot of this solution indicated the formation of 2.92 g. of ethyl *p*-toluenesulfinate in 95% yield. The vacuum distillation of the remaining part of the solution gave the pure ethyl ester, b. p. 100°C/1 mmHg.

Ethyl *p*-Nitrobenzenesulfinate.—When 0.45 g. of dry pyridine in 20 ml. of methylene chloride was added to a suspension of 0.92 g. of *p*-nitrobenzenesulfinic acid in 50 ml. of the same solvent, a yellow solution was obtained. The addition of 2 g. (excess) of triethyloxonium fluoroborate in 20 ml. of methylene chloride to the above solution with the stirring over a 2 minute period resulted in the decolorization of the solution and the precipitation of white crystals. After 5 min., the reaction mixture was poured into a lot of water, and the methylene chloride layer was separated, dried, and evaporated. The pale yellow residue was recrystallized from petroleum ether to give 0.39 g. of ethyl *p*-nitrobenzenesulfinate, m. p. 48—50°C (lit.⁶⁾ 49—51°C) in 37% yield. Its identity was confirmed by its infrared spectrum.

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4) N. Kornblum, P. J. Berrigan and W. J. Le Noble, ibid., **82**, 1257 (1960); **85**, 1141 (1963); N. Kornblum, P. Pink and K. V. Yorka, ibid., **83**, 2780 (1961); N. Kornblum, R. Seltzer and P. Haberfield, ibid., **85**, 1148 (1963).

5) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939).

6) T. Dewing, W. H. Gray, B. C. Platt and D. Stephenson, *J. Chem. Soc.*, **1942**, 239.