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Organic Sulfur Compounds. I. Reactions of Arylsulfinic Acids with Alkyl Chlorosulfites

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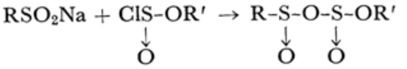
The salts of arylsulfinic acids were found to react with alkyl chlorosulfite to form alkyl sulfinates. *p*-Toluenesulfinic acid-^{18}O was synthesized and treated with ethyl chlorosulfite to give ethyl *p*-toluenesulfinate-^{18}O, which retained half of the oxygen atoms existing in the original sulfinic aicd. A mechanism for this novel reaction was proposed.

The formation of carboxylic esters from the salts of carboxylic acids and chlorosulfites has previously been known.[1,2] The possibility of an analogous preparation of the sulfinic esters from the salt of sulfinic acids and chlorosulfites has now been investigated; the results will be described in this paper.

Ethyl chlorosulfite was added to the suspension of sodium *p*-toluenesulfinate in acetonitrile; this reaction mixture then warmed at 60°C for 2 hr. to form *p*-toluenesulfinate, as expected, in a 59% yield. When this reaction was carried out without a solvent, sulfur dioxide evolved vigorously and ethyl sulfinate was obtained in a 42% yield. Sodium *p*-bromobenzenesulfinate gave the ethyl ester in a 34% yield by a similar treatment.

A solution of *p*-toluenesulfinic acid in pyridine reacted rapidly with ethyl chlorosulfite to give ethyl *p*-toluenesulfinate in a 21% yield. Since alkyl chlorosulfites are known to decompose very rapidly to alkyl chlorides and sulfur dioxide in the presence of pyridine, the above result suggests that the rate of the reaction of the sulfinate anion with alkyl chlorosulfite is also very high.

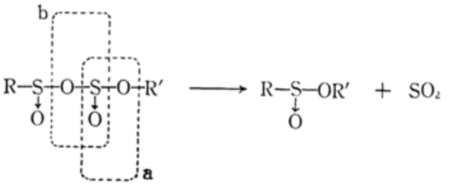
The formation of the mixed anhydride of sulfinic acid and monoalkyl sulfite (I) is suggested by these reactions, although the actual isolation of the intermediate was not possible.



$$\mathrm{RSO_2Na} + \mathrm{Cl}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{OR'} \rightarrow \mathrm{R}\text{-}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{O}\text{-}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{OR'} \qquad (1)$$

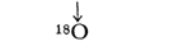
(I)

There are two possibilities for the decomposition of the mixed anhydride (I), namely, the alkyl-oxygen cleavage (path a) and alkoxy-sulfur cleavage (path b):

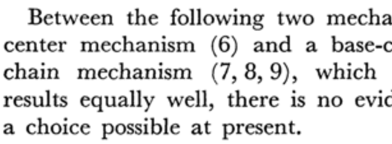


$$\mathrm{R}\text{—}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{—}\mathrm{O}\text{—}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{—}\mathrm{O}\text{—}\mathrm{R'} \longrightarrow \mathrm{R}\text{—}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{—}\mathrm{OR'} + \mathrm{SO_2} \qquad (2)$$

When sodium *p*-toluenesulfinate-^{18}O, which had been prepared from *p*-toluenesulfinyl chloride and ^{18}O water, was treated with ethyl chlorosulfite, the resultant ethyl *p*-toluenesulfinate-^{18}O was found to contain about a half of the heavy oxygen atoms originally incorporated in the starting sulfinic acid. Therefore, the alkoxy-sulfur splitting (path b) may be chosen.

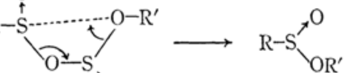


$$\mathrm{CH_3C_6H_4}\text{-}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{Cl} + \mathrm{H_2{}^{18}O} \rightarrow \mathrm{CH_3C_6H_4S^{18}O_2H} \qquad (3)$$



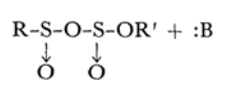
$$\mathrm{CH_3C_6H_4S^{18}O_2Na} + \mathrm{Cl}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{OC_2H_5} \rightarrow \mathrm{CH_3C_6H_4}\text{-}\underset{\overset{\downarrow}{^{18}\mathrm{O}}}{\mathrm{S}}\text{-}^{18}\mathrm{O}\text{-}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{OC_2H_5} \qquad (4)$$

(Ia)

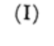


$$\mathrm{Ia} \rightarrow \mathrm{CH_3C_6H_4}\underset{\overset{\downarrow}{^{18}\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{OC_2H_5} + \mathrm{SO^{18}O} \qquad (5)$$

Between the following two mechanisms, a four-center mechanism (6) and a base-catalyzed ionic chain mechanism (7, 8, 9), which fit the above results equally well, there is no evidence to make a choice possible at present.



(6)



$$\mathrm{R}\text{-}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{O}\text{-}\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{S}}\text{-}\mathrm{OR'} + :\mathrm{B}$$

(I)

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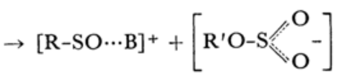
[1] P. Carré and D. Libermann, *Bull. soc. chim. France*, [4], **53**, 1050 (1933).

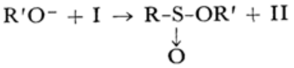
[2] M. S. Newman and W. S. Fones, *J. Am. Chem. Soc.*, **69**, 1046 (1947).



$$\rightarrow [\text{R-SO}\cdots\text{B}]^{+} + \left[\text{R'O-S}\begin{smallmatrix}\nearrow \text{O} \\ \searrow \text{O}\end{smallmatrix}\ -\right] \qquad (7)$$

(II)

$$\text{II} \rightarrow \text{R'O}^{-} + \text{SO}_2 \qquad (8)$$



$$\text{R'O}^{-} + \text{I} \rightarrow \text{R-}\underset{\overset{\downarrow}{\text{O}}}{\text{S}}\text{-OR'} + \text{II} \qquad (9)$$

(:B indicates the base catalyst)

Experimental

Ethyl *p*-Toluenesulfinate.—*Reaction in Acetonitrile.*—Sodium *p*-toluenesulfinate dihydrate[3] was dehydrated by heating it at 130°C for a few hours in a vacuum to anhydrous salt. To a suspension of 5.8 g. of the fine powder of this salt in 20 ml. of acetonitrile there was added 4.5 g. of ethyl chlorosulfite (b. p. 45°C/55 mmHg) drop by drop. The reaction mixture was warmed at 60°C for 2 hr. and kept overnight. Extraction with ether and distillation in a vacuum gave ethyl *p*-toluenesulfinate (b. p. 115°C/5 mmHg) (3.6 g.) in a 59% yield of the theoretical.

Reaction without a Solvent.—When ethyl chlorosulfite was added to the fine powder of sodium *p*-toluenesulfinate at room temperature, sulfur dioxide evolved quickly (about 70% of the theoretical yield). The reaction mixture became jelly-like after being heated at 60°C for 2 hr. A work up similar to that above gave 2.8 g. of ethyl *p*-toluenesulfinate from 5.8 g. of the sodium salt in a 42% yield of the theoretical.

Ethyl *p*-Bromobenzenesulfinate.—To 8.0 g. of the finely-powdered sodium *p*-bromobenzenesulfinate there was added 6.0 g. of ethyl chlorosulfite. When the first exothermic reaction accompanying the evolution of 350 ml. (45%) of sulfur dioxide subsided, the reaction mixture was extracted with petroleum ether. Vacuum distillation gave ethyl *p*-bromobenzenesulfinate (2.8 g.) (b. p. 132°C/2 mmHg) in a yield 34% of the theoretical yield.

Ethyl *p*-Toluenesulfinate.—*Reaction in Pyridine.*—Four grams of *p*-toluenesulfinic acid was dried in a vacuum overnight and dissolved in 20 ml. of anhydrous pyridine. When 3.5 g. of ethyl chlorosulfite was added to this solution drop by drop, the reaction proceeded with the evolution of heat. After it had stood overnight, the mixture was diluted with water, acidified, and extracted with petroleum ether. The yield of ethyl *p*-toluenesulfinate was 1.0 g., 21% of the theoretical.

_p_-Toluenesulfinyl Chloride.—Prepared from 15 g. of *p*-toluenesulfinic acid and 20 g. of thionyl chloride. The yield was 13.3 g (116°C/5 mmHg).

Sodium *p*-Toluenesulfinate-^{18}O.—To 13.3 g. of *p*-toluenesulfinyl chloride there was added 1.8 g. of $H_2{}^{18}O$ (^{18}O: 1.5 atom %) with cooling in an ice bath. The reaction started immediately, and white crystals of sulfinic acid were deposited. These crystals were vigorously stirred into an ice-cooled solution of sodium hydroxide (7 g.) in 30 ml. of water. The mixture was warmed to ensure a complete dissolution and then cooled in an ice bath in order to precipitate the sodium sulfinate. The salt filtrated was recrystallized once from the distilled water to give 9.0 g. of sodium *p*-toluenesulfinate-^{18}O dihydrate. The concentration of the mother liquid gave 6 g. of the second crop. The dehydration of the first crop in a vacuum afforded 7.5 g. of the anhydrous salt. It was confirmed in a separate experiment that no exchange of oxygen atoms occurred between sulfinic acid and water in neutral or basic conditions. The ^{18}O content of the anhydrous salt was 0.69, 0.70 atom %.

Ethyl *p*-Toluenesulfinate-[sulfinyl-^{18}O].—In 25 ml. of acetonitrile, 5.8 g. of sodium *p*-toluenesulfinate-^{18}O was treated with 4.5 g. of ethyl chlorosulfite. The mixture was then warmed at 60°C for one hour and left at room temperature for 2 days. A precipitated powder was filtered off, and the filtrate was evaporated under reduced pressure. The residue was extracted with petroleum ether, and the extract was washed with water and dried over magnesium sulfate. Vacuum distillation gave 2.4 g. of ethyl *p*-toluenesulfinate-^{18}O in a yield 41% of the theoretical. The ^{18}O atom % of this ester was 0.41%. The calculated ^{18}O atom %, based on the retention of half of the oxygen atoms, was 0.46%.

The infrared spectra of all the products in the above experiments were superimposable with those of an authentic specimen.

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[3] "Organic Syntheses," Coll. Vol. 1, 492 (1941).