

Organic Sulfur Compounds. V. Reactions of Arylsulfonic Acids with Alkyl and Aryl Chlorosulfites

By Asami YAMAMOTO* and Michio KOBAYASHI**

Department of Chemistry, Yokohama City University, Mitsuura-machi, Kanazawa-ku, Yokohama

(Received December 14, 1965)

Silver *p*-toluenesulfonate has been found to react with alkyl and aryl chlorosulfite to give *p*-toluenesulfonic esters. Mixed anhydrides of the sulfonic acid and monoalkyl or monoaryl sulfite were postulated as the intermediates. No rearrangement of the alkyl group was observed during the reaction. The reaction mechanism was studied by means of the ^{18}O tracer technique.

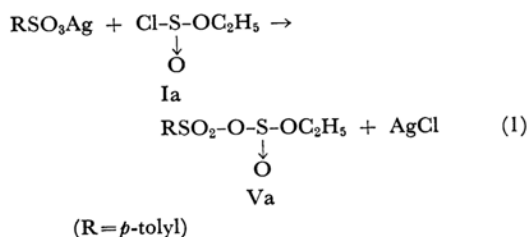
The reaction of arylsulfonic acid with alkyl chlorocarbonates was described in a previous paper.¹⁾ Studies of the reactions of *p*-toluenesulfonic acid with alkyl and aryl chlorosulfites will be reported in this paper.

Results and Discussion

The Reaction of Alkyl Chlorosulfites.—

Ethyl chlorosulfite (Ia) reacted with silver *p*-toluenesulfonate (II) in acetonitrile at room temperature to precipitate silver chloride quantitatively. Upon the warming of the filtrate, sulfur dioxide evolved and ethyl *p*-toluenesulfonate (IIIa) was obtained in a 30% yield. *p*-Toluenesulfonic anhydride (IV) and *p*-toluenesulfonic acid were by-products.

A mixed anhydride (Va) of the sulfonic acid and monoalkyl sulfite, namely, ethoxysulfinyl *p*-toluenesulfonate, may be postulated as a probable intermediate:

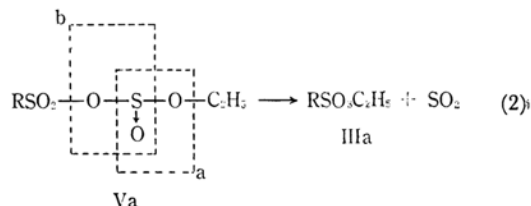


Although the formation of Va could not be verified, the presence of analogous mixed anhydrides in the case of isobutyl and phenyl derivatives was supported by infrared spectra, as will be described below.

There seem to be two reactions, one to lead to the formation of the alkyl sulfonate and another to produce the sulfonic anhydride. These two

reactions will be considered separately in the following discussion.

Alkyl Sulfonate Formation.—i) The Mode of the Cleavage of the Mixed Anhydride.—There are two possible modes of cleavage by which Va can give ethyl sulfonate IIIa, namely, alkyl-oxygen splitting (path a) and alkoxy-sulfonyl splitting (path b):



In a similar decomposition of the mixed anhydride of *p*-toluenesulfonic acid and monoalkyl carbonate¹⁾ alkyl-oxygen splitting has been established, while alkoxy-acyl splitting has been established as taking place in the cases of the mixed anhydride of *p*-toluenesulfonic acid and monoalkyl sulfite²⁾ and of the carbonic-carboxylic anhydride.³⁾ On the other hand, 75% alkoxy-acyl splitting and 25% alkyl-oxygen splitting were observed in the nitric-carbonic anhydride.⁴⁾

When the reaction of silver *p*-toluenesulfonate- ^{18}O and ethyl chlorosulfite was carried out, the resultant ethyl *p*-toluenesulfonate- ^{18}O was found to retain all three oxygen atoms originally present in silver sulfonate. Therefore, alkyl-oxygen cleavage (path a) is definitely established for the reaction 2.

ii) Mechanism.—Several mechanisms may be formulated for the reaction 2, every one of them consistent with the alkyl-oxygen splitting. At first, the mechanism shown below involving a free alkyl cation was considered to be the most plausible:

* Present address: Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo.

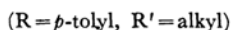
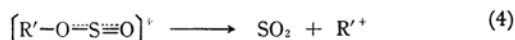
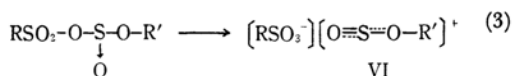
** To whom correspondence should be sent: Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo.

1) Part IV of this series. This Bulletin, 39, 1283 (1966).

2) Part I of this series. M. Kobayashi, M. Terao and A. Yamamoto, *ibid.*, 39, 802 (1966).

3) C. J. Michejda, D. S. Tarbell and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 84, 4113 (1962).

4) R. Boschan, *ibid.*, 81, 3341 (1959).

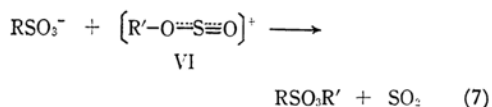
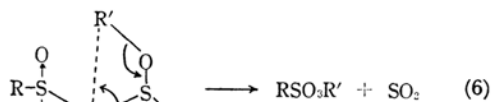


In hope of confirming this assumption, the reaction of II with isobutyl chlorosulfite (Ib) was investigated. If a free isobutyl cation was formed over the intermediate Vb (V: R' = isobutyl) as is shown in the reactions 3 and 4, its facile rearrangement to *s*-butyl and *t*-butyl carbonium ion would lead to the formation of *s*-butyl *p*-toluenesulfonate, as is found in the decomposition of carboisobutoxy *p*-toluenesulfonate.¹²

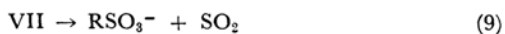
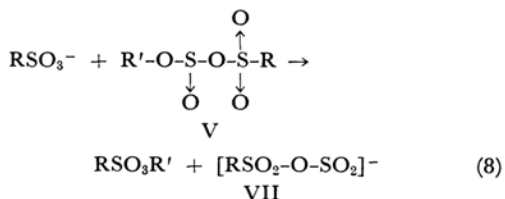
In repeated attempts, however, the isolation of *s*-butyl *p*-toluenesulfonate was always unsuccessful. In the ester fraction, isobutyl sulfite and isobutyl *p*-toluenesulfonate (IIb) were detected, in yields varying according to the reaction conditions.

Thus, a free alkyl cation mechanism (reactions 3, 4 and 5) can find no experimental support for the decomposition of alkoxysulfinyl arylsulfonate V. This contrasts clearly with the decomposition of the formally analogous sulfonic-carbonic anhydride.¹²

The following three mechanisms, involving no free alkyl cation formation, could be presumed:

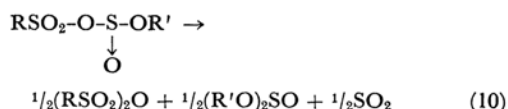


and finally:

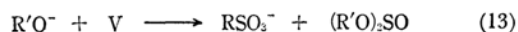
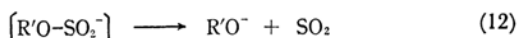
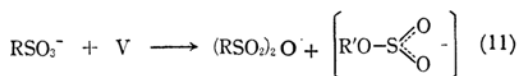
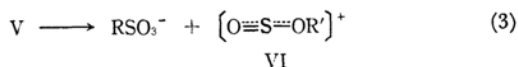


Of these three mechanisms, the second (reaction 7) and third (reaction sequence 8 and 9) belong to the S_N2 type, whereas the first one (reaction 6) is a S_Ni type four center cyclic mechanism. The study of the reaction of an optically active chlorosulfite with II would help to decide which mechanism should be chosen.

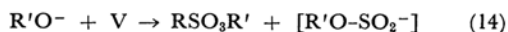
The mechanism of the Formation of the Sulfonic Anhydride.—The formation of IV and isobutyl sulfite suggests the occurrence of the disproportionation reaction (10) in the decomposition of the mixed anhydride V:



For the mechanism of this reaction, the following ionic chain reaction sequence seems to be plausible:

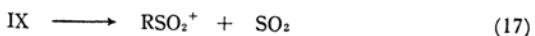
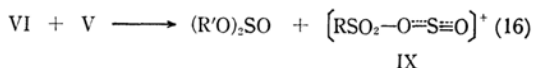
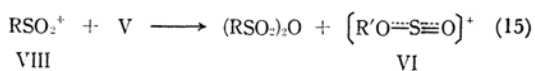


The attack on V by R'O⁻ anion might occur on the sulfone group, not on the sulfinyl group, as is shown below:



However, if this is the case, the resultant sulfonic ester should retain only two out of the three oxygen atoms of the sulfonic acid; this is contrary to the experimental evidence obtained with ¹⁸O, at least for alkyl chlorosulfite.

Another mechanism, which postulates the intermediate formation of a sulfonyl cation (VIII), could be formulated for the disproportionation reaction 10:



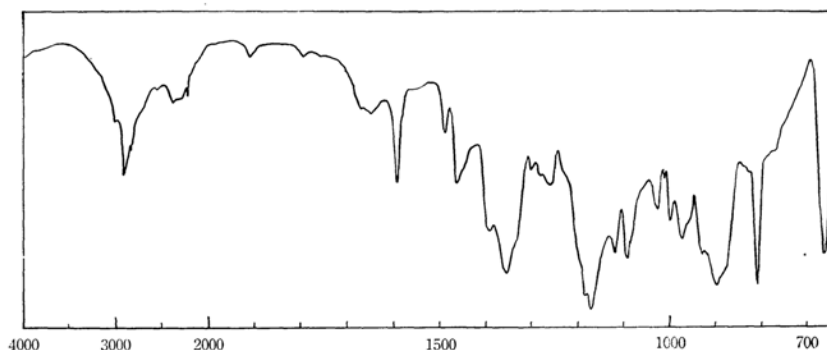
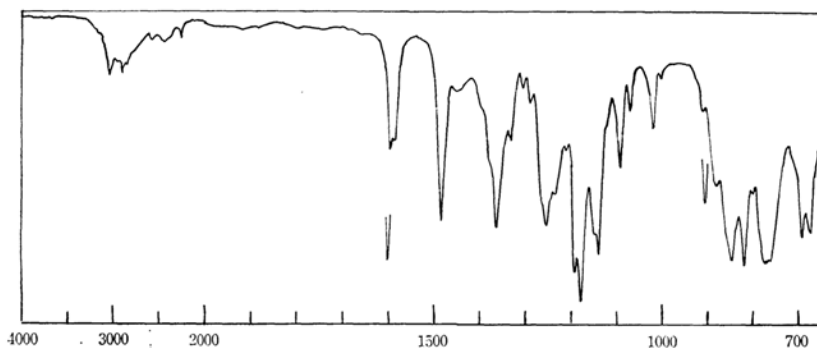
Although the sulfonyl cation VIII has been postulated in the Friedel-Crafts' sulfonylation⁵ and in the reaction of tosyl chloride with Lewis acids^{6,7}, its formation as a free molecular species seems rather doubtful.⁷

While the anionoid attack of R'O⁻ on V (reaction 13) is considered to occur on the sulfinyl group, as has been stated above, the other anionoid attack by RSO₃⁻ on V seems to occur only on the sulfone group (reaction 11). Probably the attack

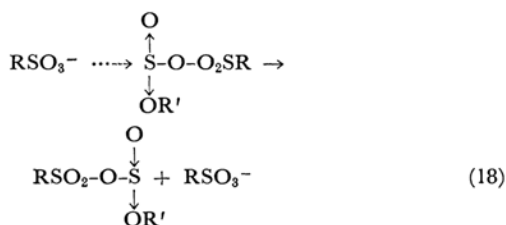
5) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 4042 (1958).

6) F. Klages and K. Hoheisel, *Chem. Ber.*, **96**, 2057 (1963).

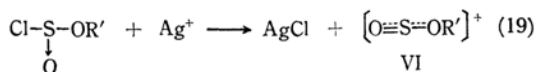
7) Studies on the sulfonylation will be described in the following paper.

Fig. 1. Infrared spectrum of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-O-S-OBu}^i$ (Vb) in CH_2Cl_2 .Fig. 2. Infrared spectrum of $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-O-S-OC}_6\text{H}_5$ (Vc) in acetonitrile.

by RSO_3^- could take place on sulfinyl sulfur too, but with the net result of a simple exchange of RSO_3^- (18):



A Question about the Existence of the Mixed Anhydride V.—For the formation of the alkyl sulfonate in the reaction of II with alkyl chlorosulfite, the following mechanism, which could take place without the formation of the intermediate V, can be postulated:



The reaction sequence 19 and 7 is analogous to the one, which has been proposed⁴⁾ and later denied on the basis of kinetic evidence for the formation

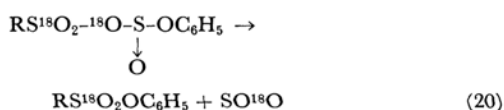
of the nitric ester from silver nitrate and alkyl chlorocarbonate.⁸⁾

In order to verify the formation of an intermediate Vb and to support our postulation against the above mechanism (19 and 7), the reaction between II and Ib was carried out at 0°C and the solvent was distilled off in a vacuum at 0°C. The infrared spectrum of the residue in methylene chloride (Fig. 1) was rather close to that of *s*-butyl *p*-toluenesulfonate, but upon the treatment of this solution with ice water, isobutyl sulfite and a small amount of isobutyl *p*-toluenesulfonate were obtained without any trace of *s*-butyl *p*-toluenesulfonate. This experiment was repeated three times. Since a similar spectrum was recorded in every case, this spectrum is now believed to be attributable to Vb. The evaporation of the methylene chloride solution in a vacuum resulted in an oily residue containing crystals of the sulfonic anhydride IV. The work-up of this residue gave isobutyl sulfite in a good yield and isobutyl *p*-toluenesulfonate as a minor product. These products were considered to have been produced from Vb during the evaporation and/or the subsequent work-up.

8) D. N. Kevill and G. H. Johnson, *J. Am. Chem. Soc.*, **87**, 928 (1965).

The Reaction of Phenyl Chlorosulfite.—As has been described above, the decomposition of the sulfonic-monoalkylsulfurous anhydride V and sulfonic-carbonic anhydride proceeds by alkyl-oxygen cleavage, while the decomposition of the carbonic-carboxylic anhydride and of the sulfonic-monoalkylsulfurous anhydride proceeds by alkoxy-acyl cleavage. These facts correspond to the other facts that the alkyl sulfonate was hydrolyzed by alkyl-oxygen splitting,⁹⁾ while alkyl sulfinate¹⁰⁾ and carboxylic ester¹¹⁾ were hydrolyzed by alkoxy-acyl splitting. Therefore, it seems that it would be interesting to examine the mode of the decomposition of phenoxy-sulfinyl *p*-toluenesulfonate Vc, since aryl sulfonate has been known to undergo aryloxy-sulfonyl splitting¹²⁾ upon hydrolysis.

The reaction of silver *p*-toluenesulfonate-¹⁸O with phenyl chlorosulfite was carried out in order to answer this question. Although the yield of the expected phenyl *p*-toluenesulfonate-¹⁸O was low, its ¹⁸O atom% was exactly 2/3 of that of the starting silver sulfonate. Consequently, phenoxy-acyl cleavage is operative in the decomposition of Vc; this again corresponds to the mode of the hydrolysis.



The infrared spectrum of an intermediate, believed to be Vc, was observed in acetonitrile (Fig. 2). After boiling for 9 hr., this solution was evaporated under reduced pressure. From the residue, *p*-toluenesulfonic acid and a lot of a resinous material were obtained, besides phenyl *p*-toluenesulfonate.

The mechanism of the decomposition of Vc has not yet been determined. Mechanism 14 could be applied to reaction 20, but the formation of the phenoxy anion would lead to the formation of diphenyl sulfite, at least as a by-product. Actually, however, none of this compound was detected. Instead, a large amount of a resinous material with an unknown structure was produced, as has been described above.

Experimental

Materials.—Ethyl chlorosulfite (Ia), b. p. 59°C/85 mmHg, was prepared from ethyl alcohol and thionyl chloride. Isobutyl chlorosulfite, b. p. 61°C/25 mmHg, was obtained in a similar way. Phenyl chlorosulfite, b. p. 105–107°C/10 mmHg, was synthesized from phenol and 4 mol. of thionyl chloride.¹³⁾ *p*-Toluene-

sulfonic acid-¹⁸O was the same sample as was used in a previous paper.¹⁾ The ¹⁸O atom% was 0.61%. The preparation of isobutyl- and *s*-butyl *p*-toluenesulfonates was also described in the same report.¹⁾

The Reaction of Silver *p*-Toluenesulfonate (II) and Ethyl Chlorosulfite (Ia).—To a solution of 13.5 g. of II in 50 ml. of acetonitrile, there was added, drop by drop, 7.0 g. of Ia in 10 ml. of acetonitrile; the precipitate of silver chloride appeared at once. The mixture was then left for 35 min., and silver chloride was filtered off. Its weight was 6.7 g. (97%). After the filtrate had been warmed on a water bath for several hours and left overnight, the solvent was distilled off in vacuo. The residue was dissolved in ether, washed with water, and evaporated to give 3.45 g. of IIIa, m. p. 32–34°C, in a 36% yield.

Reaction of Silver *p*-Toluenesulfonate-¹⁸O with Ia.—The reaction of 4.5 g. of Ia with 9.2 g. of silver *p*-toluenesulfonate-¹⁸O in 40 ml. of acetonitrile was carried out in a way similar to that described above. The solvent was expelled in a vacuum, the residue was dissolved in benzene, and silver chloride (4.5 g.; 100%) was filtered off. The filtrate was washed with a sodium carbonate solution, dried, and evaporated. The oily residue was then extracted with petroleum ether to give 4.2 g. of ethyl *p*-toluenesulfonate-¹⁸O, m. p. 32–33°C. Upon recrystallization, 3.0 g. (46%) of the pure ester was obtained. The ¹⁸O atom% of this sample was 0.62%. From the insoluble part in petroleum ether, 1.6 g. of *p*-toluenesulfonic anhydride-¹⁸O was obtained as colorless crystals, (m. p. 122–124°C; lit. 122–125°C) in a yield 30% of the theoretical yield.

The Reaction of II with Isobutyl Chlorosulfite Ib.—i) Reaction at 0°C.—A solution of 3.5 g. of Ib in a few milliliters of acetonitrile was added, drop by drop, to an ice-cooled solution of 7.0 g. of II in 30 ml. of the same solvent. After the reaction mixture has been cooled in ice water for a few hours, acetonitrile was distilled off in vacuo at 0°C to leave the colorless oil; it turned purple overnight. This oil was dissolved in methylene chloride, filtered, and evaporated in vacuo to give a mixture of crystals and oil. The crystals were separated by filtration and identified as IV. Oil was extracted with petroleum ether, and 0.5 g. of *p*-toluenesulfonic acid was obtained from the insoluble part. The soluble part was chromatographed over alumina with petroleum ether, (b. p. under 40°C) to afford 0.9 g. of diisobutyl sulfite (40% of the theoretical yield) from the early eluent and 0.3 g. of isobutyl *p*-toluenesulfonate (IIIb) (6%). Although every fraction in elution chromatography was examined by infrared spectroscopy, there was no indication of the presence of *s*-butyl *p*-toluenesulfonate.

ii) The Identification of the Intermediate.—The reaction was carried out with the same amounts of the reactants and in a manner similar to that described above. After the solvent had been removed in vacuo, the residue was taken up in methylene chloride and filtered. The infrared spectrum of the filtrate is shown in Fig. 1. This solution was poured into ice water; the organic layer was washed with 5% sodium carbonate and water successively, and dried over potassium carbonate, and then its infrared spectrum was measured again. Although the infrared spectrum in Fig. 1 was similar to that of *s*-butyl *p*-toluenesulfonate, the second infrared spectrum, taken after the hydrolysis with ice water,

9) Ader, Thesis, London, 1949, quoted in Ref. 12.

10) C. A. Bunton and B. N. Hend, *J. Chem. Soc.*, **1962**, 2562; **1963**, 627.

11) J. Hine, "Physical Organic Chemistry," second ed., McGraw-Hill, New York, N. Y. (1962), p. 275.

12) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, **1951**, 1872.

13) W. E. Bissinger and F. E. Kung, *J. Am. Chem. Soc.*, **70**, 2664 (1948).

showed only a very weak absorption of the sulfonic ester in the 1380 cm^{-1} region. The main product was identified as diisobutyl sulfite. In a separate experiment, a specimen of *s*-butyl *p*-toluenesulfonate was treated with a sodium carbonate solution and potassium carbonate, as described above; no appreciable decomposition was found to be effected by such purification procedure.

iii) The Hydrolysis of the Intermediate.—A reaction with the same amounts of the reactants as in i) was carried out, and then the reaction mixture was decomposed with ice water after 20 min. at 0°C . The organic matter was extracted with 200 ml. of methylene chloride, washed with water and 5% sodium carbonate, and dried over magnesium sulfate; the solvent was then removed in vacuo to give a colorless oil, which was shown by infrared spectrum to be pure diisobutyl sulfite. Upon distillation, 1.7 g. of sulfite was isolated at $100^\circ\text{C}/20\text{ mmHg}$ in a 78% yield. Since no *p*-toluenesulfonic anhydride was detected among the products, this sulfite was considered to be produced by the interaction of Vb with isobutyl alcohol, one of the products of the hydrolysis of Vb, not by the disproportionation reaction (11).

The Reaction of Phenyl Chlorosulfite (Ic) with II.—i) The Identification of an Intermediate.—A solution of 4.0 g. of Ic in a few milliliters of acetonitrile was added, drop by drop, to a solution of 6.0 g. of II in 30 ml. of the same solvent at room temperature; thereupon silver chloride began to precipitate immediately. The mixture was filtered through a fritted glass funnel, and the infrared spectrum of the filtrate was recorded (Fig. 2). This solution was then refluxed in an oil bath for 9 hr., and the solvent was removed in vacuo. The viscous residue was extracted repeatedly with carbon tetrachloride to leave a mixture of *p*-toluenesulfonic acid and a resinous matter. The extract was evaporated, and the residue (2.2 g.) was chromatographed over

alumina with benzene to give 1.1 g. of phenyl *p*-toluenesulfonate (identified by melting point and infrared), in 21% yield.

ii) Reaction at the Boiling Point.—To a solution of 2.2 g. of II in 10 ml. of acetonitrile, 1.5 g. of Ic in a few milliliters of the same solvent was added at room temperature. The reaction mixture was refluxed without the filtration of the precipitated silver chloride for 2 hr. The next day, then, the solution was filtered and the solvent was distilled off from the filtrate in a vacuum. The crystalline residue was dissolved in ether to remove some insoluble matter and again evaporated. There was a strong smell of sulfur dioxide. The residue was extracted with benzene, and the soluble part was chromatographed to afford 0.5 g. of phenyl *p*-toluenesulfonate (25%). From the insoluble part in benzene, 0.5 g. of *p*-toluenesulfonic acid was isolated (35%).

*The Reaction of Silver *p*-Toluenesulfonate- ^{18}O with Ic.*—A solution of 1.5 g. of Ic in a few milliliters of acetonitrile was added to a solution of 2.2 g. of silver sulfonate ^{18}O in 10 ml. of the same solvent over a 1.5 hr. period; then the mixture was refluxed for a few hours. Silver chloride was filtered off, and the solvent was removed from the filtrate by distillation. The residue was taken up in 70 ml. of benzene, washed with a sodium carbonate solution and water successively, and dried over magnesium sulfate. Upon elution chromatography over alumina with benzene, 0.2 g. of phenyl *p*-toluenesulfonate- ^{18}O was obtained. The ^{18}O atom% of this ester was 0.49%. (The calculated atom% based on 2/3 retention was 0.48%).

Thanks are due to Dr. Reiko Kiritani of the Radiation Center of Osaka Prefecture for the analysis of ^{18}O , and to Professor Shigeru Oae of Osaka City University for the donation of the heavy oxygen water.