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Organic Sulfur Compounds. VI. The Reactions of Arylsulfinic Acids with Alkyl Chlorocarbonates

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The reactions of the arylsulfinic acid salts with alkyl chlorocarbonates in various alcohols as solvents gave the alkyl sulfinates, in which the alkoxyl groups originated from the solvent alcohols, not from the chlorocarbonates. Sodium *p*-toluenesulfinate-^{18}O and ethyl chlorocarbonate in a large excess of methanol gave methyl *p*-toluenesulfinate-^{18}O, which was shown to contain about half of the ^{18}O atoms of the starting salt. The mixed anhydride of sulfinic acid and monoalkyl carbonate is postulated as an intermediate, the alcoholysis of which would give the sulfinate ester. Reactions have been studied also in the nonhydroxylic solvents.

The formation of sulfinic esters by the reaction of sodium sulfinates with alkyl chlorocarbonates in alcohols has long been known.[1,2] In solvents other than alcohol, the reaction was reported to

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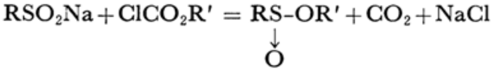
[1] R. Otto and A. Rössing, *Ber.*, **18**, 2493 (1885).

[2] R. Otto, ibid., **26**, 308 (1893).

be low and to stop in an early stage.[1] The reaction proceeded also without any solvent, but the yield and the purity of the resultant sulfinate ester were low.[3]



$$\mathrm{RSO_2Na + ClCO_2R' = R\underset{\substack{\downarrow\\ O}}{S}\text{-}OR' + CO_2 + NaCl} \quad (1)$$

In this paper, studies of the reactions of sodium arylsulfinates with alkyl chlorocarbonates in various solvents will be described.

Results

Sodium *p*-toluenesulfinate (I) reacted with ethyl chlorocarbonate (II) without solvent at room temperature very slowly. The reaction was accompanied by the evolution of carbon dioxide in a 40—60 mol. % yield, but the yield of ethyl *p*-toluenesulfinate (III) was only 10—18%, with the by-production of sulfinyl sulfone (IV) in a low yield. When dioxane was the solvent, hardly any sulfinate ester formation was observed and thiolsulfonate (V) was the chief product. Warming the reaction mixture at 70°C did not improve the result, although carbon dioxide evolution could reach a peak of 30 mol. % under some conditions.

In acetonitrile, the yields of the sulfinic ester depended on the reaction period; it was nearly 0% in 1—15 hr., 22% in 2 days. 13% in 5 days, and 39% in 8 days (with carbon dioxide in 35%) at room temperature. In pyridine, which dissolved sodium sulfinate partly, the reaction was rapid and the yield of the sulfinic ester was increased to 30% of the theoretical yield. When ethyl chlorocarbonate was added to a solution of free *p*-toluenesulfinic acid in anhydrous pyridine, carbon dioxide evolved immediately and ethyl sulfinate was obtained in a 42% yield. In a similar way, ethyl *p*-nitrobenzenesulfinate was prepared in a 43% yield.

Reactions between sodium sulfinate and chlorocarbonates in a large excess of alcohols were very rapid, and the yields of the sulfinic esters were usually satisfactory. For instance, the reaction of I with ethyl chlorocarbonate in ethanol gave ethyl *p*-toluenesulfinate in yields 36—62% of the theoretical yield. In a large excess of methanol, the reaction between ethyl chlorocarbonate and sodium *p*-toluenesulfinate was also very rapid, but in this case the ester formed was methyl *p*-toluenesulfinate, not the ethyl ester. The yield was 69—73%.

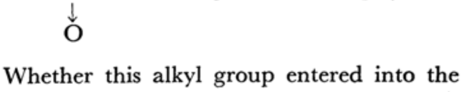
When I was treated with ethyl chlorocarbonate in *n*-butyl alcohol, *n*-butyl *p*-toluenesulfinate was obtained in 57 mol. %. The use of isopropyl alcohol as the solvent gave isopropyl *p*-toluenesulfinate in 20 mol. %. No sulfinic ester, neither ethyl nor *t*-butyl, was formed in *t*-butyl alcohol. Allyl alcohol gave allyl *p*-toluenesulfinate in a 55% yield. In carbitol, the reaction proceeded rapidly at room temperature, but no ethyl sulfinate formation was observed and carbitol sulfinate decomposed during the vacuum distillation.

From the above results, the reaction of sulfinate salts with ethyl chlorocarbonate in the primary or secondary alcohols was shown to form, not ethyl sulfinate, but alkyl sulfinates containing the alkyl group of the solvent alcohols.

These alkyl sulfinates might be the result of the ester exchange between ethyl sulfinate, a possible primary product, and the solvent alcohols. However, the reaction of sodium *p*-toluenesulfinate and ethyl chlorocarbonate in a mixture of ethyl *p*-toluenesulfinate of a 1/2 mol. equivalent of the sodium salt and a large excess of methanol gave a sulfinate ester mixture, which contained the same amount of ethyl *p*-toluenesulfinate as in the beginning and methyl *p*-toluenesulfinate in 42 mol. %. Under similar conditions without added ethyl sulfinate, the yield of methyl sulfinate from methyl chlorocarbonate and I in methanol was 42% of the theoretical yield. Therefore, it can be concluded that almost no ester exchange occurred under these reaction conditions, and the various alkyl sulfinates mentioned above may safely be regarded as the primary reaction products.

To confirm this point, the reaction of sodium *p*-toluenesulfinate with ethyl chlorocarbonate in dioxane containing 1 mol. of methanol was carried out; the sulfinate ester mixture, consisting of 82 mol. % of the methyl ester and 18 mol. % of the ethyl ester was thus found to be formed in 60% combined yield. On the other hand, the reaction of sodium *p*-toluenesulfinate and methyl chlorocarbonate in a mixture of 1 mol. of ethanol and a large volume of dioxane gave a mixture of methyl sulfinate and ethyl sulfinate in nearly the same molar ratio. In order to compare the relative reactivities of methanol and ethanol, the reaction of ethyl chlorocarbonate with I in a large excess of an equimolecular mixture of methanol and ethanol was carried out, resulting in the formation of a mixture of methyl- and ethyl-sulfinate in a 2 : 1 molar ratio.

These findings clearly indicate that the alkyl group of the alcohol used as a solvent entered into the resultant sulfinate ester, as is shown below:



$$\begin{aligned}&\mathrm{RSO_2Na + ClCO_2C_2H_5 + R'OH =}\\ &\mathrm{R\underset{\substack{\downarrow\\ O}}{S}\text{-}OR' + CO_2 + NaCl + C_2H_5OH}\end{aligned} \quad (2)$$

Whether this alkyl group entered into the ester in company with the oxygen atom should be clarified by the isotope labeling method. Sodium *p*-toluenesulfinate-^{18}O was prepared by the reaction of $H_2{}^{18}O$ with *p*-toluenesulfinyl chloride or by the hydrolysis of ethyl *p*-toluenesulfinate with sodium hydroxide in $H_2{}^{18}O$.

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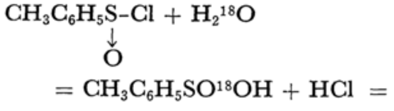
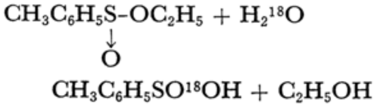
3) A. J. H. Houssa and H. Phillips, *J. Chem. Soc.*, **1929**, 2510.



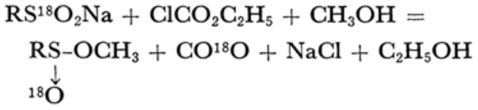
$$CH_3C_6H_5\underset{\overset{\downarrow}{O}}{S}-Cl + H_2{}^{18}O = CH_3C_6H_5SO^{18}OH + HCl = \qquad (3)$$



$$CH_3C_6H_5\underset{\overset{\downarrow}{O}}{S}-OC_2H_5 + H_2{}^{18}O \quad CH_3C_6H_5SO^{18}OH + C_2H_5OH \qquad (4)$$

Bunton and his collaborator[4] established that the hydrolysis of alkyl sulfinate proceeded with an alkoxy-sulfinyl splitting; this was indicated by the absence of heavy oxygen atom in the alcohol formed in the reaction 4. We have confirmed this point by detecting the presence of ^{18}O in nearly the calculated amount in the sulfinic acid formed.

The reaction of sodium *p*-toluenesulfinate-^{18}O containing 0.65 atom % of ^{18}O with ethyl chlorocarbonate in a large excess of methanol gave methyl *p*-toluenesulfinate-^{18}O, the ^{18}O atom % of which was found to be 0.41%. This finding clearly indicated that the methoxyl group of the sulfinate ester came from methanol used as a solvent. (The calculated ^{18}O atom % based on the reaction shown below is 0.427%.)



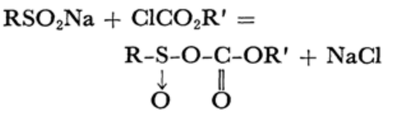
$$RS^{18}O_2Na + ClCO_2C_2H_5 + CH_3OH = \underset{\overset{\downarrow}{^{18}O}}{RS}-OCH_3 + CO^{18}O + NaCl + C_2H_5OH \qquad (5)$$

This alkoxy-acyl binding in the sulfinate ester formation corresponds well to the alkoxy-acyl splitting in the hydrolysis mentioned above.

Discussion

From the experimental results, the differences between the reaction in the alcoholic solvents and that in the non-hydroxylic solvents are clearly indicated. In primary or secondary alcohols, the reaction is fast, the yields of the sulfinate esters are high, and the alkoxy group of the solvent is introduced into the ester. On the other hand, the reaction is slow, the yield of the ester is very low, sometimes almost zero, and the sulfinate ester produced contains an alkyl radical of chlorocarbonates in a non-hydroxylic solvent other than pyridine. Pyridine is exceptional; in it the reaction proceeds rapidly and the ester yields are high.

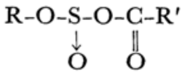
Since no ester formation was observed when the sodium sulfinate was treated with alcohols, there should be some intermediates which react with alcohols to give the sulfinate esters. Sulfinic carbonic anhydride VI, which has been suggested[3] in the reaction without alcohol, is considered to be the most probable such intermediate:



$$RSO_2Na + ClCO_2R' = \underset{\overset{\downarrow}{O}}{R-S}-O-\underset{\overset{\|}{O}}{C}-OR' + NaCl \qquad (6)$$

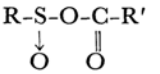
VI

Among similar mixed anhydrides, several carboxylic sulfurous anhydrides VII have been known,[5] and the probable existence of the sulfinic carboxylic anhydrides VIII has been pointed out.[6]



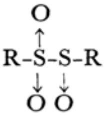
$$R-O-\underset{\overset{\downarrow}{O}}{S}-O-\underset{\overset{\|}{O}}{C}-R'$$

VII



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

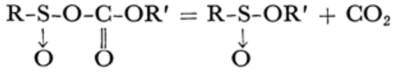
VIII



$$R-\underset{\overset{\downarrow}{O}}{\overset{\overset{O}{\uparrow}}{S}}-\underset{\overset{\downarrow}{O}}{S}-R$$

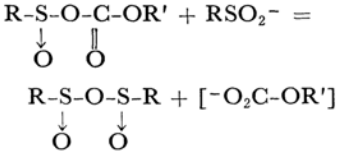
IV

The decomposition of VI would give the sulfinic ester thus:



$$R-\underset{\overset{\downarrow}{O}}{S}-O-\underset{\overset{\|}{O}}{C}-OR' = R-\underset{\overset{\downarrow}{O}}{S}-OR' + CO_2 \qquad (7)$$

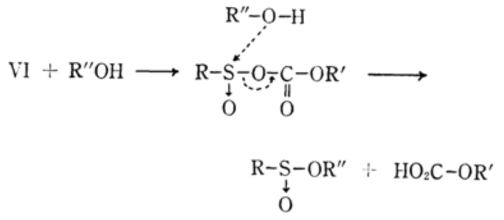
This decomposition seems to be base-catalyzed, since in pyridine the formation of carbon dioxide is very rapid. In other non-hydroxylic solvents, the reaction 7 is slow compared to such side reactions as 8, where the primary product, sulfinic anhydride (X), takes well-known, complicated courses to give the sulfinyl sulfone or thiolsulfonate[6]:



$$R-\underset{\overset{\downarrow}{O}}{S}-O-\underset{\overset{\|}{O}}{C}-OR' + RSO_2^- = R-\underset{\overset{\downarrow}{O}}{S}-O-\underset{\overset{\downarrow}{O}}{S}-R + [^-O_2C-OR'] \qquad (8)$$

X

In the hydroxylic solvents, the intermediate VI suffers attack by the solvent molecules, ahead of the decomposition 7, as follows:



$$VI + R''OH \longrightarrow R-\underset{\overset{\downarrow}{O}}{S}-O-\underset{\overset{\|}{O}}{C}-OR' \longrightarrow R-\underset{\overset{\downarrow}{O}}{S}-OR'' + HO_2C-OR' \qquad (9)$$

$$[HO_2C-OR'] \rightarrow CO_2 + R'OH \qquad (10)$$

This alcoholysis may also be base-catalyzed. The alcohol liberated in the reaction 10 could participate in the alcoholysis too; this evidently explains why the ester mixture is always afforded in the reaction in dioxane containing an equimolecular amount of alcohol. If the reactivity of two alcohols, one added and one liberated, are equal, an ester mixture containing 75 mol. % of the ester of the added alcohol and 25 mol. % of that of the liberated alcohol may be expected. Actually, methanol has a greater reactivity than ethanol, as is

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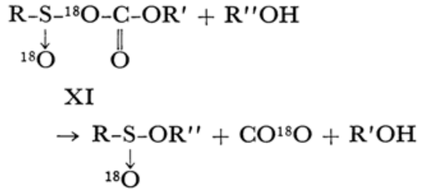
[4] C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, **1962**, 2562.

[5] Part II of this series. M. Kobayashi and A. Yamamoto, This Bulletin, **39**, 961 (1966).

[6] Part III of this series. M. Kobayashi, ibid., **39**, 967 (1966).

indicated by the competitive alcoholysis; this causes the formation of an ester mixture richer in methyl ester than had been calculated.

In the reaction of sodium *p*-toluenesulfinate-^{18}O, the labeled, mixed anhydride (XI) is alcoholized to give the alkyl sulfinate-[sulfinyl ^{18}O], which should retain half of the heavy oxygen atom in the original sodium sulfinate:



$$\mathrm{R{-}\underset{\substack{\downarrow\\ {}^{18}O}}{S}{-}{}^{18}O{-}\underset{\substack{\| \\ O}}{C}{-}OR'} + \mathrm{R''OH}$$

XI

$$\rightarrow \mathrm{R{-}\underset{\substack{\downarrow\\ {}^{18}O}}{S}{-}OR''} + \mathrm{CO^{18}O} + \mathrm{R'OH} \qquad (11)$$

Experimental

Materials.—Dioxane was purified as usual⁷⁾ and dried over sodium. Acetonitrile was refluxed over phosphorus pentoxide until a colorless product was obtained and then rectified. The alcohols were dehydrated by distillation from lithium hydride.

The Reaction of Sodium *p*-Toluenesulfinate (I) with Ethyl Chlorocarbonate (II). Without a Solvent.—To 4.0 g. of finely-powdered, anhydrous sodium salt (I) 2.4 g. of II was added at room temperature. About 330 ml. of carbon dioxide (60 mol. %) evolved slowly over 3 hr. The reaction mixture was then extracted with petroleum ether, and the extract concentrated and vacuum distilled to give 0.66 g. of ethyl *p*-toluenesulfinate (III) in a 18% yield. Most of the insoluble white powder in petroleum ether was soluble in water, but 0.2 g. of *p*-tolylsulfinyl *p*-tolylsulfone (IV: R=*p*-tolyl) remained. This was identified by melting point and mixture melting point determinations (87—90°C).

The General Procedure of the Reactions in Solvents Other Than Alcohols or Pyridine.—An equimolecular amount of II was stirred into a suspension of I; then the mixture was kept for an appropriate reaction period, from a few hours to several days, at room temperature. Water and petroleum ether were added to the resulting jelly, and the organic layer was separated, dried over magnesium sulfate, and subjected to vacuum distillation to give III. It was identified by its infrared spectrum and b. p. (102—106°C/5 mmHg, 98—102°C/3 mmHg).

Reaction in Pyridine.—A suspension of 4.0 g. of I in 30 ml. of pyridine was boiled once to effect the partial solution and then cooled to room temperature. To this mixture 3.2 g. of II was added, drop by drop, during which process the evolution of slight heat and 450 ml. of carbon dioxide was observed. After dilution with water, the product was extracted with petroleum ether, washed with dilute hydrochloric acid and water, dried, and distilled in vacuo to give 1.3 g. of III (30%).

Reactions in Alcohols.—i) In 30 ml. of methanol 5.0 g. of I was shaken to effect the partial solution. When 3.1 g. of II was added, drop by drop, to this solution, cooled with ice water, carbon dioxide formed immediately. After a few hours the reaction mixture was then diluted with water and extracted with petroleum ether. Vacuum distillation gave 3.3 g. of methyl *p*-toluenesulfinate at 90°C/3 mmHg in 69% yield.

ii) To a suspension of 17.5 g. of I in 100 ml. of ethanol 10.8 g. of II was added. Treatment similar to that above gave 6.7 g. of III at 98—102°C/3 mmHg in 36% yield.

iii) A suspension of 5.0 g. of I in 30 ml. of *n*-butanol was treated with 3.0 g. of III as described in i). After 15 hr. at room temperature, 4.3 g. of *n*-butyl *p*-toluenesulfinate was isolated; b. p. 118—120°C/3 mmHg in 57% yield.

iv) From 5.0 g. of I in 30 ml. of allyl alcohol and 3.0 g. of II, 3.0 g. of allyl *p*-toluenesulfinate, b. p. 98—102°C/3 mmHg, was obtained in 55% yield after one day's reaction.

v) A suspension of 5.0 g. of I in a mixture of 0.9 g. of methanol and 30 ml. of dioxane was treated with 3.0 g. of II at room temperature. After 10 min., the reaction started, accompanied by the evolution of carbon dioxide. The yield of the sulfinate ester mixture was 2.8 g. after 40 hr. Using the 970 cm^{-1} absorption band for methyl *p*-toluenesulfinate and the 884 cm^{-1} band for the ethyl ester, the composition of this ester mixture was estimated as 82 mol.% the methyl ester and 18 mol.% the ethyl ester by infrared spectrum, the total yield being 60% of the theoretical.

vi) When 2.8 g. of methyl chlorocarbonate was added to 5.0 g. of I in a mixture of 1.8 ml. of ethanol and 30 ml. of dioxane, 200 ml. of carbon dioxide (30%) evolved in 5 min. The reaction mixture afforded the sulfinate ester mixture, the composition of which was found by its infrared spectrum to be 48 mol.% the methyl ester and 52 mol.% the ethyl ester in a total yield 30% of the theoretical.

vii) The reaction of 5.0 g. of I and 3.0 g. of II in a mixture of 2.0 g. of III and 30 ml. of methanol gave 4.0 g. of the sulfinate ester mixture, b. p. 92—104°C/3 mmHg. Its infrared spectrum revealed the presence of 2.1 g. of III and 1.9 g. of methyl sulfinate (43% of the theoretical yield) in this mixture.

viii) Reaction in an equimolecular mixture of methanol and ethanol: To 7.0 g. of I in a mixture of 16 g. of methanol and 23 g. of ethanol, 4.5 g. of II was added with cooling in ice water. After one hour, the reaction mixtue was diluted with an excess of water and extracted with 60 ml. of carbon tetrachloride. The extract was found by infrared spectroscopy to contain 2.25 g. of methyl *p*-toluenesulfinate and 1.25 g. of III. The relative reactivity of methanol and ethanol for this reaction was calculated to be 2 : 1 from this competitive reaction.

Reaction in Pyridine.—i) When 2.5 g. of II was added, drop by drop, to a solution of 3.0 g. of *p*-toluenesulfinic acid in 20 ml. of anhydrous pyridine, the reaction occurred immediately, with the evolution of carbon dioxide and with the precipitation of pyridine hydrochloride. From the reaction mixture, 1.5 g. of III was obtained in 42% yield.

ii) When 2.0 g. of *p*-nitrobenzenesulfinic acid (10.7 mmol.) was added to 15 ml. of pyridine, a red suspension was obtained. The addition of 5.5 g. (50.7 mmol.) of II to this suspension over 40 min. caused the formation of 320 ml. (13.3 mml.) of carbon dioxide. The pale brown reaction mixture was then

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7) A. Weissberger and E. S. Proskauer, "Organic Solvents," 2nd Ed. (1955).

diluted with water and extracted by petroleum ether; the extract was washed with diluted hydrochloric acid and water, dried over magnesium sulfate, and evaporated. The recrystallization of the residue from petroleum ether gave 1.0 g. of ethyl *p*-nitrobenzenesulfinate, m. p. 48.5—50.5°C, in 34% yield.

Sodium *p*-Toluenesulfinate-^{18}O.—i) To 11.5 g. of *p*-toluenesulfinyl chloride[8] 2.5 g. of $H_2{}^{18}O$ ($^{18}O=$ 1.5 atom %) was slowly added with ice cooling. After 2 hr., the white reaction product mass was neutralized with 5 g. of sodium hydroxide in a few milliliters of light water; the crystals thus formed were recrystallized from distilled water to give 7.6 g. of sodium *p*-toluenesulfinate dihydrate, which was dehydrated in vacuo. The ^{18}O atom % of this salt was 0.86%. (The calculated value is 0.86%.)

ii) A mixture of 6.7 g. of III and 1.44 g. of sodium hydroxide in 6.00 ml. of $H_2{}^{18}O$ (1.5 atom % ^{18}O) was stirred with a magnetic stirrer for 2 hr., and cooled in an ice bath; the resultant crystals were filtered through a fritted-glass funnel to give 7.0 g. of the labeled dihydrate of I, which was then dehydrated in vacuo at 110°C for one hour. The ^{18}O atom % of this anhydrous salt was 0.65%, lower than the calculated value, 0.71%.

Ethyl *p*-Toluenesulfinate - [sulfinyl ^{18}O]. — A suspension of 5.0 g. of the labeled sodium sulfinate prepared as above ii) in 30 ml. of methanol was treated with 3.0 g. of II; after 3 hr., the reaction mixture was extracted by petroleum ether. The vacuum distillation of the extract after drying over magnesium sulfate gave 3.5 g. of methyl *p*-toluenesulfinate-[sulfinyl ^{18}O] in 74% yield. The ^{18}O atom % of this specimen was 0.41%. (The caluclated value, based on the reaction 5, was 0.43%).

Thanks are due to Dr. Teijiro Kitao and Miss Reiko Kiritani of the Radiation Center of Osaka Prefecture for their analyses of ^{18}O, and also to Professor Shigeru Oae of Osaka City University for his donation of the heavy oxygen water.

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[8] "Organic Syntheses," Vol. 34, 93 (1954).