BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 967—970 (1966)

Organic Sulfur Compounds. III. The Reactions of Toluenesulfinic Acid with Acyl Chlorides

By Michio KOBAYASHI

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

(Received September 21, 1965)

Sodium *p*-toluenesulfinate reacts with acetyl chloride to form acetic anhydride, *p*-toluenesulfinyl chloride, thiolsulfonate, and sodium *p*-toluenesulfonate. A reaction with benzoyl chloride gives benzoic anhydride in a good yield. A mixed anhydride of sulfinic acid and carboxylic acid is postulated as an intermediate, one which survives for a few hours at −60°C. The reaction mechanism is discussed.

The literature contains three reports on the reactions between arylsulfinic acid and carboxylic chloride. The reaction of sodium *p*-toluenesulfinate (I) and benzoyl chloride has been claimed[1] to form a ketosulfone, $C_6H_5COSO_2C_6H_4CH_3$, but this was questioned in a later paper.[2] The reaction of the same salt as a dihydrate with benzoyl chloride was reported in the second paper to give benzoic acid in a quantitative yield and *p*-tolyl *p*-toluenethiolsulfonate (IVa) in 20 mol.%,[2] but the exact material balance was not examined, nor was the reaction mechanism considered. On the other hand, the reaction of the anhydrous salt (I) and benzoyl chloride in xylene or in ether gave sodium *p*-toluenesulfonate, IVa, and an oil, which reacted with aniline to form benzanilide. A reaction mechanism involving a mixed anhydride of sulfinic acid and carboxylic acid was suggested.[3]

In this paper, studies of the mechanism of the reaction of *p*-toluenesulfinic acid with acetyl chloride and benzoyl chloride will be described.

---

[1] E. P. Kohler and M. B. MacDonald, *Am. Chem. J.*, **22**, 219 (1899).

[2] H. T. Hookway, *J. Am. Chem. Soc.*, **71**, 3240 (1949).

[3] L. Panizzi and R. A. Nicolaus, *Gazz. chim. ital.*, **80**, 431 (1950).

Results and Discussion

The reaction of anhydrous sodium *p*-toluenesulfinate (I) with an equimolar amount of benzoyl chloride (II) was carried out at room temperature, and the reaction mixture was extracted with carbon tetrachloride. Infrared analysis revealed the formation of about 50 mol.%, namely 100% of the theoretical yield, of benzoic anhydride (III), and thiolsulfonate (IVa) in a 20 mol.% yield. The insoluble products in carbon tetrachloride contained sodium *p*-toluenesulfonate (25 mol.%). Therefore, the fate of the 100% portion of the benzoyl group and that of the 65% portion of $CH_3C_6H_4S$ group were clarified. The formation of benzoic anhydride was confirmed by the preparation of benzanilide in a yield 84% of the theoretical. The amount of the unchanged sulfinic acid was very small.

When the reaction mixture of I and acetyl chloride (V) was treated with anhydrous methanol, methyl *p*-toluenesulfinate was obtained in a low yield.

In another experiment, I was treated with acetyl chloride, and the reaction mixture was distilled in a vacuum to give acetic anhydride in a yield 68% of the theoretical. The residue gave 15.8 mol.% of the thiolsulfonate (IVa) and 14.2 mol.% of *p*-toluenesulfonate as *S*-benzylthiuronium salt (VI). The fact that sulfonic acid existed in the original residue as sodium salt was confirmed by the infrared spectrum in KBr disk, where a byproduct, sodium chloride, did not interfere at all.

There remained at least one-fourth of the sulfur atoms, which fate had still not been explained. Since sulfonic acid was formed as sodium salt, it was clear that not all the chlorine atom could exist as sodium chloride in equimolar reaction conditions. This suggests that some of the sulfur compounds might be formed as chloride, such as sulfonyl chloride or sulfinyl chloride.

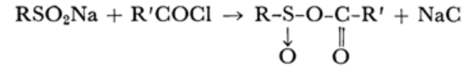
The reaction mixture of I and V was subjected to vacuum distillation as in the foregoing experiment. After the acetic anhydride had been collected, the distillation was continued and an orange-yellow high-boiling distillate was obtained. By its infrared spectrum and by the rapid reaction with water to give *p*-toluenesulfinic acid, this liquid was identified as *p*-toluenesulfinyl chloride, VII. The yield was 18.3 mol.% From the residue, 22.2 mol.% of *p*-toluenesulfonic acid was again isolated as VI.

On the basis of the above results, it was concluded that almost 100% of the acyl group was converted into the acyl anhydride, and that about 1/4 of the sulfur was recovered as sulfonic acid salt, another 1/4 as sulfinyl chloride, and 1/2 as thiolsulfonate. This means that the overall reaction can be expressed by the following formula 1:

$$\begin{aligned}&\mathrm{RSO_2Na + R'COCl} \rightarrow \\ &\quad {}^1/_2\mathrm{(R'CO)_2O} + {}^1/_4\ \mathrm{RSO_2SR} \\ &\quad + {}^1/_4\ \mathrm{RSO_3Na} + {}^1/_4\ \mathrm{RSOCl} \\ &\quad + {}^3/_4\ \mathrm{NaCl} \qquad (1)\end{aligned}$$

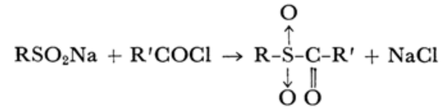
The formation of methyl *p*-toluenesulfinate in the reaction of methanol with the reaction mixture between I and V is explained by the interaction of methanol with the VII produced in reaction 1.

As the first step of the reaction of sulfinic acid salt with carboxylic chloride, either of the following two reactions could take place:



$$\mathrm{RSO_2Na + R'COCl} \rightarrow \mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}O\text{-}\underset{\substack{\|\\ O}}{C}\text{-}R' + NaCl} \qquad (2)$$

(VIII)



$$\mathrm{RSO_2Na + R'COCl} \rightarrow \mathrm{R\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}\underset{\substack{\|\\ O}}{C}\text{-}R' + NaCl} \qquad (3)$$

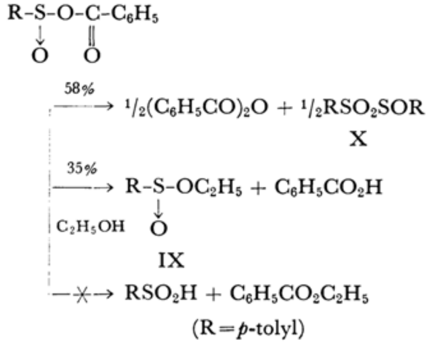
Although the usual alkyltion of sulfinate anion results in the formation of a *S*-alkyl derivative, not of a *O*-alkyl compound, the formation of carboxylic sulfurous anhydride[4] indicates the possibility of the formation of the VIII type. This class of compound, a mixed anhydride of sulfinic acid and carboxylic acid has been suggested[3] as described above, but never been isolated, and not expected to be stable compound.

The following experiments were carried out to determine whether the transitory formation of VIII in the reaction between sulfinate and acyl chloride could be verified.

A solution of free sulfinic acid and II in ether was cooled at −66°C and treated with triethylamine. An aliquot of the reaction mixture was then filtered, and its infrared spectrum was measured at once, in order to determine if any carbonyl band was present which could be attributed to VIII. Surprisingly, there was already strong absorption of benzoic anhydride; its yield was estimated to be almost theoretical. This must mean that the reaction is completed at −66°C or within several minutes at room temperature, the time interval needed to filter the solution and to inject the filtrate into the infrared cell. Anhydrous ethanol was added to the main portion of the above reaction mixture kept at −66°C. The usual work-up of this mixture gave benzoic anhydride in 29 mol.% yield, not in the 50 mol.% estimated above, and ethyl *p*-toluenesulfinate (IX) in a 35 mol.% yield, with a slight amount of ethyl benzoate. Therefore, the intermediate VIII may be considered to survive at a low temperature such as −66°C for some time, and to be converted into sulfinic ester by reaction 5, which proceeds along with the disproportionation 4:

---

4) Part 2 of this series.



$$\mathrm{\underset{\substack{\downarrow\\ O}}{R\text{-}S}\text{-}O\text{-}\underset{\substack{\|\\ O}}{C}\text{-}C_6H_5} \xrightarrow{58\%} {}^{1}/_{2}\mathrm{(C_6H_5CO)_2O} + {}^{1}/_{2}\underset{\mathrm{X}}{\mathrm{RSO_2SOR}} \tag{4}$$

$$\xrightarrow[\mathrm{C_2H_5OH}]{35\%} \underset{\mathrm{IX}}{\mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}OC_2H_5}} + \mathrm{C_6H_5CO_2H} \tag{5}$$

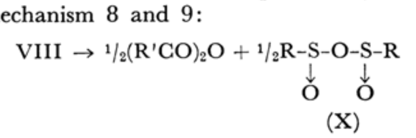
$$\not\longrightarrow \mathrm{RSO_2H + C_6H_5CO_2C_2H_5} \tag{6}$$

$$(\mathrm{R}=p\text{-tolyl})$$

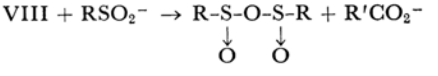
Ethyl sulfinate IX could be formed by the reaction of sulfinyl chloride (VII), which might be formed in a reaction analogous to reaction 1, with ethanol, but in such a case the yield would not exceed 25 mol.%. The preferential attack of ethanol on VIII on the sulfur atom (reaction 5), rather than on the carbonyl group of VIII (reaction 6), may be explained by the attraction of the nucleophilic reagent to the positive center of the sulfinyl sulfur.

The fact that the sulfinyl anion rapidly reacted with benzoyl chloride, even at −66°C, suggested the possibility of preparing IX by reacting I with II in the presence of ethanol; here the sulfinyl anion would react with II ahead of ethanol to form VIII, and then this VIII would react with ethanol according to the reaction 5 prior to the decomposition by the disproportionation 4. Indeed, I suspended in absolute ethanol reacted with II at 0°C to give the mixture, which consisted of IX in a 74 mol.% yield, III in a yield 19% of the theoretical, and ethyl benzoate in a 6 mol.% yield. These results showed that the rate of the reaction 5 was slightly higher than that of the disproportionation 4. It should be noticed that no thiolsulfonate (IVa) was detected in this experiment, although III was formed in yields as high as 10 mol.%. This indicated that thiolsulfonate was not the primary product of the disproportionation 4.

The variety of the products formed in the overall reaction 1 implies the complicated nature of this reaction. After the first step 2, the disproportionation 7 of VIII could proceed by the following mechanism 8 and 9:



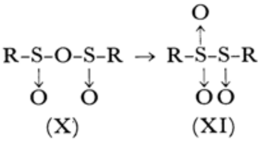
$$\mathrm{VIII} \rightarrow {}^{1}/_{2}\mathrm{(R'CO)_2O} + {}^{1}/_{2}\underset{\mathrm{(X)}}{\mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}O\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}R}} \tag{7}$$



$$\mathrm{VIII + RSO_2^-} \rightarrow \mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}O\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}R + R'CO_2^-} \tag{8}$$

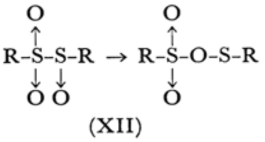
$$\mathrm{R'CO_2^- + VIII \rightarrow (R'CO)_2O + RSO_2^-} \tag{9}$$

The sulfinic anhydride (X) has been considered to be very unstable, and it is expected to be isomerized to the sulfinyl sulfone XI, which has been prepared from the sulfinic acid by the dehydration with acetic anhydride.5-7)



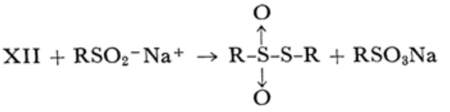
$$\underset{\mathrm{(X)}}{\mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}O\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}R}} \rightarrow \underset{\mathrm{(XI)}}{\mathrm{R\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\,\downarrow\\ O\,O}}{S}}\text{-}S\text{-}R}} \tag{10}$$

XI would further rearrange to a mixed sulfenic sulfonic anhydride XII8):



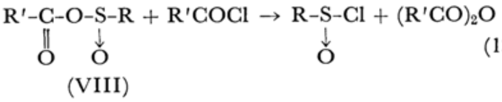
$$\mathrm{R\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\,\downarrow\\ O\,O}}{S}}\text{-}S\text{-}R} \rightarrow \underset{\mathrm{(XII)}}{\mathrm{R\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}O\text{-}S\text{-}R}} \tag{11}$$

The formation of the thiolsulfonate IV could be explained by the reaction 12, which is similar to the proposed reaction for the formation of IV in the disproportionation of the sulfinic acid under acidic conditions.8)

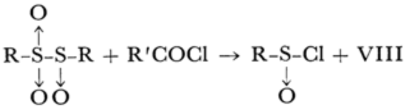


$$\mathrm{XII + RSO_2^-Na^+} \rightarrow \mathrm{R\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}S\text{-}R + RSO_3Na} \tag{12}$$

The formation of the sulfinyl chloride would then be the result of one of the following two reactions, of which the former is our choice:

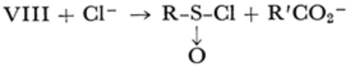


$$\underset{\mathrm{(VIII)}}{\mathrm{R'\text{-}\underset{\substack{\|\\ O}}{C}\text{-}O\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}R}} + \mathrm{R'COCl} \rightarrow \mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}Cl + (R'CO)_2O} \tag{13}$$



$$\mathrm{R\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\,\downarrow\\ O\,O}}{S}}\text{-}S\text{-}R + R'COCl} \rightarrow \mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}Cl + VIII} \tag{14}$$

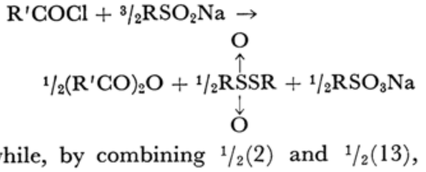
Therefore, the following reaction sequences would lead to the net reaction 13:



$$\mathrm{VIII + Cl^-} \rightarrow \mathrm{R\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}Cl + R'CO_2^-} \tag{15}$$

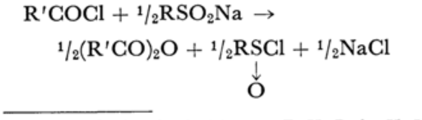
$$\mathrm{R'CO_2^- + RCOCl \rightarrow (R'CO)_2O + Cl^-} \tag{16}$$

By combining (2), (7), $^{1}/_{2}$(11) and $^{1}/_{2}$(12), the following formula 17 was obtained:



$$\mathrm{R'COCl} + {}^{3}/_{2}\mathrm{RSO_2Na} \rightarrow {}^{1}/_{2}\mathrm{(R'CO)_2O} + {}^{1}/_{2}\mathrm{R\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}SR} + {}^{1}/_{2}\mathrm{RSO_3Na} \tag{17}$$

while, by combining $^{1}/_{2}$(2) and $^{1}/_{2}$(13), Formula (18) was given:



$$\mathrm{R'COCl} + {}^{1}/_{2}\mathrm{RSO_2Na} \rightarrow {}^{1}/_{2}\mathrm{(R'CO)_2O} + {}^{1}/_{2}\mathrm{R\underset{\substack{\downarrow\\ O}}{S}Cl} + {}^{1}/_{2}\mathrm{NaCl} \tag{18}$$

---

5) H. Bredereck, A. Wagner, E. H. Beck, H. Herlinger and K. G. Kottenhahn, *Angew. Chem.*, **70**, 268 (1958).

6) F. Knoevenagel and L. Polack, *Ber.*, **41**, 3323 (1908).

7) H. Bredereck, A. Wagner, H. Beck and R. J. Klein, *Chem. Ber.*, **93**, 2736 (1960).

8) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

Finally, we get the overall reaction formula 1 by adding 17 to 18 and by dividing by 2.

Experimental

The Reaction of Sodium *p*-Toluenesulfinate and Benzoyl Chloride without a Solvent.—To 7.0 g. of II there was added 9.0 g. (equimolecular) of a fine powder of I (dried in a vacuum at 140°C for a few hours) with cooling; exothermic reaction then started. After 30 min., 80 ml. of carbon tetrachloride was added to the jelly-like reaction mixture, and the insoluble white powder was filtered off. An aliquot of the filtrate was taken, diluted to 10 times of its volume, and its infrared specturm was measured. The formation of 50 mol.% of III, and 19.8 mol.% of IVa was observed, and trace of the II was unchanged. Into the main portion of the filtrate 6 g. of aniline were then stirred in order to precipitate the white crystals of benzanilide, 4.2 g. (84% of the theoretical yield), which was identified by its infrared spectrum. The filtrate of benzanilide was evaporated, and the residue was recrystallized from petroleum ether to give 2.3 g. of IVa (16.6 mol.%). The mother liquid was chromatographed through an alumina column, and 0.2 g. (4 mol.%) of *p, p'*-ditolyl disulfide was obtained as colorless crystals from the first eluant. A part of the white powder, insoluble in carbon tetrachloride, was examined by means of the infrared spectrum in a KBr disk and so found to contain *p*-toluenesulfonic acid as sodium salt, not as a free form. The main part of the salt residue was taken up in water, where a negligible amount remained undissolved. The addition of *S*-benzylthiuronium chloride gave 4.0 g. (25 mol.%) of the precipitate of *S*-benzylthiuronium *p*-toluenesulfonate (VI). To a part of the aqueous solution there was then added a ferric chloride solution, where the characteristic red color of ferric sulfinate was observed but no precipitate[9] was separated after one night.

The Reaction of *p*-Toluenesulfinic Acid with Benzoyl Chloride in Ether.—*p*-Toluenesulfinic acid was liberated from its sodium salt and dried in a vacuum. A solution of 3.0 g. of this acid in 70 ml. of anhydrous ether was then cooled in a dry ice - ethanol bath at −66°C. Three grams of the freshly-distilled II were dissolved in 20 ml. of ether, added to the above solution, and cooled; most part of the sulfinic acid was crystallized out. A solution of 2.0 g. of triethylamine in 20 ml. of ether was then added to the above suspension drop by drop over a 20 min. period. When the white precipitate filled the solution, one milliliter of the reaction mixture was taken out by suction, filtered through a fritted-glass funnel, and its infrared spectrum measured at once. The strong C=O absorption bands of benzoic anhydride were observed at 1790 and 1728 cm^{-1}; from their intensities, the yield of III was estimated to be 49.5 mol.%. To the main portion of the reaction mixture, kept at −66°C, 10 ml. of anhydrous ethanol was added in small portions. The mixture was cooled for 2 hr. at this temperature, allowed to warm to room temperature, and left overnight. The precipitate was filtered off and identified as triethylamine hydrochloride. The filtrate was washed by water, aqueous sodium carbonate and water successively, and dried over magnesium sulfate. On the evaporation of the filtrate, 3.2 g. of a colorless oil was obtained as a residue. Infrared analysis showed that this oil contained 1.3 g. of III (29 mol.%) and 1.3 g. of IX (35 mol.%). Actually, on vacuum distillation, 0.8 g. of IX (b. p. 115—117°C/4 mmHg) and 1.1 g. of III (b. p. 170°C/4 mmHg) were isolated. Ethyl benzoate was detected by infrared analysis, but its yield was too low to allow its isolation.

The Reaction of *p*-Toluenesulfinate with Benzoyl Chloride in Ethanol.—A suspension of 9.0 g. of I in 100 ml. of anhydrous ethanol was boiled once and cooled in ice water, whereby most of the I was separated as a fine powder. Into this ice-cooled suspension, 7.0 g. of II was stirred, and the reaction mixture was kept for 2 hr. in an ice bath. A lot of water was added to the mixture, and the heavy oil precipitated was extracted with 40 ml. of carbon tetrachloride. The infrared analysis of this extract showed the presence of 73.8 mol.% of IX, 9.6 mol.% of III and 6.1 mol.% of ethyl benzoate, with no thiolsulfonate IVa.

The Reaction of Sodium *p*-Toluenesulfinate with Acetyl Chloride (V).—i) To 9.0 g. of I 13.0 g. of freshly-distilled V were added with cooling. Heat was evolved, and a gel-like mixture resulted. After one hour, the whole mixture was vacuum-distilled to give 1.7 g. of a low boiling liquid, which was identified as acetic anhydride. Ether (40 ml.) was added to the residue, and an insoluble powder (3.4 g.) was filtered off. Ether was expelled from the extract, and 3.7 g. of the residue was treated with petroleum ether to give 1.7 g. of IVa. A white powder, insoluble in ether, was taken up in water and the insoluble matter was removed by filtration. The latter was also identified as IVa, the total yield of which reached 2.2 g. (63% of the theoretical). The yield of *p*-toluenesulfonic acid in the aqueous solution was determined as VI to be 14.2 mol.% (56.8% of the theoretical). A part of this aqueous solution again showed a red color with a ferric chloride solution, but it gave no precipitate of ferric sulfinate.

ii) To 5.3 g. of I 3.0 g. of V were added; then, after the initial exothermic reaction was over, 1 ml. of anhydrous methanol was added to the jelly-like mixture, whereby heat was evolved again. The mixture was diluted with water and extracted with petroleum ether to give 0.3 g. of methyl *p*-toluenesulfinate (6%).

iii) The reaction mixture of 9.0 g. of I and 5.0 g. of V was vacuum-distilled as in i). Three milliliter of a low boiling fraction was collected; it was found to contain 1.6 g. (63% of the theoretical) of acetic anhydride on redistillation. After it, a trace of a green-colored liquid came out, and finally 1.6 g. of an orange-yellow liquid at 100—110°C/3 mmHg (mostly at 110°C) was obtained. This oil formed colorless crystals of *p*-toluenesulfinic acid upon coming in contact with water. The infrared specturm of this liquid also confirmed it to be *p*-toluenesulfinyl chloride. The yield was 18 mol.% (73% of the theoretical yield, based upon formula 1). When the residue in the vacuum distillation was treated with water, the yield of *p*-toluenesulfonic acid was estimated to be 22.2 mol.% (89% of the theoretical yield) by precipitation as VI (3.63 g.).

---

[9] J. Mitchel, I. M. Kolthoff, E. S. Proskauer and A. Weissberger, "Organic Analysis," Vol. I, Interscience Publisher, Inc., New York, N. Y. (1953), p. 378.