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Organic Sulfur Compounds. IV. The Reactions of Arylsulfonic Acids with Alkyl Chlorocarbonates

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The reactions of *p*-toluenesulfonic acid salt with alkyl chlorocarbonates have been investigated and their mechanism discussed. The reactions were slow at low temperature, and the intermediates, sulfonic carbonic anhydrides, could be isolated. When heated, these mixed anhydrides decomposed to alkyl sulfonates and carbon dioxide. *p*-Toluenesulfonic acid-¹⁸O was prepared and its reaction with ethyl chlorocarbonate examined. All three oxygen atoms of the sulfonic acid were retained in the ethyl sulfonate formed. The reaction of isobutyl chlorocarbonate with silver *p*-toluenesulfonate gave a mixture of isobutyl- and *s*-butyl sulfonate. On the basis of these experiments, the mechanism involving the free alkyl cation has been proposed for the decomposition of the sulfonic-carbonic anhydrides.

Alkyl and aryl chlorocarbonates have been known to react with the carboxylic acid salts to form the carboxylic-carbonic anhydrides, which have drawn much attention recently.¹⁻⁶) The chlorocarbonates also give the nitric-carbonic anhydrides with silver nitrate; the decomposition of the anhydrides to nitric esters and carbon dioxide has been the subject of several recent publications.⁷⁻⁹ Although many other reactions of the chlorocarbonates have been reported,¹⁰ little is known about their reaction with sulfonic acid. In this paper, studies of the reaction of p-toluenesulfonic acid salt with alkyl chlorocarbonates will be described.

Results and Discussion

When ethyl chlorocarbonate (Ib) was added to a solution of silver p-toluenesulfonate (II) in acetonitrile at room temperature, the reaction proceeded very slowly with the precipitation of silver chloride. When this solution was warmed, a copious formation of carbon dioxide was observed and ethyl p-toluenesulfonate (IIIb) was isolated from the reaction mix-

- 2) T. B. Windholz, ibid., 23, 2044 (1958).
- 3) D. S. Tarbell and E. J. Longosz, ibid., 24, 774 (1959).
- 4) T. B. Windholz, ibid., 25, 1703 (1960).
- 5) E. J. Longosz and D. S. Tarbell, ibid., 26, 2161 (1961).
- 6) C. J. Michejda, D. S. Tarbell and W. H. Saunders, Jr., J. Am. Chem. Soc., 84, 4113 (1962).
 - 7) R. Boschan, ibid., 81, 3341 (1959).
 - 8) G. A. Mortimer, J. Org. Chem., 27, 1876 (1962).
- 9) D. N. Kevill and G. H. Johnson, J. Am. Chem. Soc., 87, 928 (1965).
- 10) M. Matzner, R. P. Kurkjy and R. J. Cotter, Chem. Revs., 64, 645 (1964).

ture in 35% yield.

At room temperature this reaction was very slow; it was only one-third completed after 17 days, as estimated by the yield of silver chloride precipitated. The reaction mixture was concentrated under reduced pressure, the residue was extracted with methylene chloride, and its infrared spectrum (Fig. 1) was measured to show the presence of a strong carbonyl band in the 1786 cm^{-1} region which could not be attributed to the unchanged ethyl chlorocarbonate. By the evaporation of the solvent in a vacuum, a colorless oil was obtained. The similarity of its infrared spectrum to that of the corresponding methyl ester (IVa) described below suggested that this oil was carboethoxy p-toluenesulfonate (IVb). When this oil was heated on a water-bath, carbon dioxide was evolved and the infrared spectrum of the residue showed no C=O absorption. By the elution chromatography, pure IIIb was isolated.

$$RSO_{3}Ag + CI-C-OR' \rightarrow \bigcup_{O}^{I} O$$

$$I$$

$$O$$

$$R-S-O-C-OR' + AgCl (1)$$

$$O$$

$$IV$$

$$O$$

$$R-S-O-C-OR' \rightarrow R-S-O-R' + CO_{2} (2)$$

$$O$$

$$IV$$

$$III$$

$$Ia, IIIa, IVa R' = methyl$$

$$Ib, IIIb, IVb R' = ethyl$$

$$Ic, IIIc, IVc R' = isobutyl$$

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¹⁾ D. S. Tarbell and N. A. Leister, J. Org. Chem., 23, 1149 (1958).



A similar treatment of methyl chlorocarbonate (Ia) with II in acetonitrile gave carbomethoxy p-toluenesulfonate (IVa) as colorless crystals in 10% yield. This compound has been prepared recently in a completely different way.¹¹ The infrared spectrum of our sample is shown in Fig. 2. Unexpectedly, this compound was rather stable in a pure state, but it decomposed to methyl p-toluenesulfonate (IIIa) when heated at 120—140°C for 5 hr. When warmed with water, it was hydrolyzed to form a clear solution of the sulfonic acid.

The reaction of silver nitrate with alkyl chlorocarbonate has been reported to be catalyzed by pyridine.⁸³ The reaction of Ib with II in the presence of pyridine was carried out in the hope of accelerating the rate of an otherwise very slow formation of the mixed anhydride (IVb), but it was found that in the presence of pyridine merely the decomposition of Ib occurred, while the sulfonic acid remained unchanged, indicating the absence of any catalytic effect of the tertiary base.

The same mixed anhydride (IVa) was expected to be formed by the reaction of p-toluenesulfonyl chloride with sodium methyl carbonate (V) as is shown below:

¹¹⁾ R. J. Crawford and R. Raap, J. Org. Chem., 28, 2419 (1963).

June, 1966]

Equimolecular amounts of tosyl chloride and V were treated in acetonitrile for one week, and the insoluble powder was filtered off. The solvent was removed by vacuum distillation and the residue was dissolved in methylene chloride. The infrared spectrum of this solution showed strong absorption bands at 1830 and 1790 cm⁻¹ which were attributed to dimethyl pyrocarbonate (VI). Upon evaporation, a mixture of methyl *p*-toluenesulfonate and this pyrocarbonate, but no mixed anhydride (IVa), was obtained. Probably, once formed, IVa reacted with the unchanged V to give VI according to the reaction 4:

$$\begin{array}{ccc} \operatorname{RSO}_2\text{-}O\text{-}C\text{-}OCH_3 + \operatorname{NaO}\text{-}C\text{-}OCH_3 \rightarrow \\ & & \parallel \\ O & O \\ IVa & V \\ \operatorname{RSO}_3\operatorname{Na} + \operatorname{CH}_3\operatorname{O}\text{-}C\text{-}O\text{-}C\text{-}OCH_3 & (4) \\ & & \parallel \\ O & O \\ VI \end{array}$$

The preparation of diethyl pyrocarbonate from 2 mol. of sodium ethyl carbonate and one mole of tosyl chloride, reported in a recent publication,¹²) may be based on the formation of IVb as an intermediate.

There are two possibilities in the decomposition of the sulfonic carboxylic anhydride (IV) to alkyl sulfonate, namely path a and path b, as is shown below:

$$\mathbb{R} \xrightarrow{\mathsf{O}}_{\mathsf{O}} \xrightarrow{\mathsf{O}}_{\mathsf{O}} \xrightarrow{\mathsf{O}}_{\mathsf{O}} \mathbb{R}' \xrightarrow{\mathsf{O}}_{\mathsf{O}} \mathbb{R}' \xrightarrow{\mathsf{O}}_{\mathsf{O}} \mathbb{R}' + \mathbb{C}_{2}$$
(5)

Path a is alkyl-oxygen splitting, while path b alkoxycarbonyl splitting. This problem has been solved by the isotope labeling. If the sulfonic acid containing the heavy oxygen is used, path a should give the sulfonic ester which retains all three oxygen atoms. On the other hand, path b would lead to the sulfonic ester, which should have 2 out of the 3 oxygen atoms which originally exist in the sulfonic acid.

p-Toluenesulfonic acid-¹⁸O was prepared from tosyl chloride and H_2 ¹⁸O. The reaction of its

silver salt with Ib gave ethyl *p*-toluenesulfonate-¹⁸O, which ¹⁸O atom% was the same as that of the ethyl ester prepared by the direct alkylation of the same silver salt with ethyl bromide.¹³ This finding definitely shows that the path a is the only way of cleavage.

However, there remained another question to solve concerning the mechanism of the decomposition of the mixed anhydride IV. The alkyl-oxygen splitting of IV could occur by either the intramollecular four-center cyclic mechanism (reaction 6) or the free alkyl carbonium ion mechanism (reaction 7):

$$\underset{O}{\text{RSO}_2\text{-}O\text{-}C\text{-}OR'} \rightarrow \text{RSO}_3^- + \text{CO}_2 + \text{R'}^+ \quad (7)$$

To solve this question, the reaction of isobutyl chlorocarbonate (Ic) and II was investigated. If the free alkyl cation, isobutyl carbonium ion in this case, was formed, the rearrangement to s-butyl and t-butyl carbonium ion would be expected, finally resulting in the formation of s-butyl p-toluenesulfonate. t-Butyl p-toluenesulfonate is unstable and is not expected to survive under the reaction conditions.

When an equimolecular amounts of Ic and II were treated at room temperature in acetonitrile, a slow reaction started, forming a compound which was believed to be carboisobutoxy p-toluenesulfonate (IVc). Its decomposition gave a mixture of isobutyl p-toluenesulfonate and s-butyl p-toluenesulfonate in a 0.8 : 1.0 mol. ratio, with a quantity of isobutene and free p-toluenesulfonic acid. Isobutene was considered to be derived from the t-butyl cation.

Therefore, the following mechanism is proposed to the decomposition of the mixed anhydride IVc:

$$RSO_{3}Ag + ClC-OBu-i \rightarrow \\ \bigcup_{O}^{\parallel} O$$

$$RSO_{2}-O-C-OBu-i + AgCl \qquad (8)$$

$$\bigcup_{O}^{\parallel} O$$

$$IVc$$

$$IVc \rightarrow [RSO_3^-][O \cong C \cong OBu_i]^+$$
 (9)

 $[O \cong C \cong OBu-i] \rightarrow CO_2 + i-Bu^+$ (10)

- $i-\mathrm{Bu}^+ \rightleftharpoons s-\mathrm{Bu}^+ \rightleftharpoons t-\mathrm{Bu}^+$ (11)
- $RSO_3^- + i Bu^+ \rightarrow RSO_3 Bu i$ (12)

$$RSO_3^- + s Bu^+ \rightarrow RSO_3 Bu - s \tag{13}$$

¹²⁾ L. Rosnati, Chem. Ber., 96, 3098 (1963).

¹³⁾ W. D. Emmons and A. F. Ferris, J. Am. Chem. Soc., 75, 2257 (1953).

1286

$$RSO_{3}^{-} + t - Bu^{+} \rightarrow RSO_{3}H + (CH_{3})_{2}C = CH_{2}$$
(14)

When the reaction temperature was raised, a reaction giving the sulfonic anhydride (VII) occurred, along with the decomposition to the alkyl sulfonate. The most probable reaction to form VII would be the disproportionation of the mixed anhydride IV (reaction 15), but no detailed discussion of this reaction will be given at the present stage since only a slight amount of diisobutyl carbonate was detected among the products.

Experimental

Materials. — Silver *p*-toluenesulfonate (II) was prepared from silver oxide and p-toluenesulfonic acid, recrystallized from distilled water, and dried in a vacuum. Methyl chlorocarbonate (Ia) and ethyl chlorocarbonate (Ib) were commercial products and purified by distillation. Isobutyl chlorocarbonate (Ic) was prepared from phosgen and isobutyl alcohol in chloroform, b. p. 126-128°C. vc=0 absorption band in 1780 cm^{-1} (neat). Isobutyl *p*-toluenesulfonate was prepared from tosyl chloride and isobutyl alcohol in the presence of pyridine, b. p. 161-165°C/3-4 mmHg. IR 1372 (antisymm. s-o), 1192, 1180 (symm. s-o), 982, 944, 818 cm⁻¹ (in CCl₄ or CH₂Cl₂). s-Butyl p-toluenesulfonate was prepared from s-butyl alcohol in a similar way and purified by rapid elution chromatography over silica gel with petroleum ether benzene mixture, since the repeated attempts to purify it by vacuum distillation resulted in a partial decomposition. IR 1370, 1192, 1180, 910, 819 cm⁻¹ (in CH₂Cl₂).

The Reaction of Silver p-Toluenesulfonate with Ethyl Chlorocarbonate.-Reaction at the Boiling Point.-To a solution of 11.5 g. of II in 40 ml. of warm acetonitrile 4.0 g. of Ib diluted with 3 ml. of the same solvent was added. The precipitation of silver chloride proceeded slowly, along with a slow evolution of carbon dioxide (50 ml. in one night; calculated volume, 870 ml.). This mixture was refluxed until the evolution of gas ceased. The total gas volume was 800 ml., and the weight of silver chloride was 5.1 g. (90% of the theoretical yield). Acetonitrile was expelled from the filtrate by vacuum distillation, and the residue was taken up in benzene to remove the unchanged II, washed with aqueous sodium carbonate, and dried over magnesium sulfate. The evaporation of the solvent from this solution and the recrystallization of the residue gave 2.0 g. of IIIb, m. p. 32-34°C, in a 30% yield of the theoretical.

Reaction at Room Temperature.—To a solution of 7.0 g. of II in 35 ml. of acetonitrile 2.7 g. of Ib in 10 ml. of acetonitrile was added drop by drop; the mixture was then left at room temperature for 17 days. The solvent and all other volatile materials were removed by vacuum distillation at room temperature, and the residue was dissolved in 50 ml. of methylene chloride and filtered. Its infrared spectrum is shown in Fig. 1. From the yield of silver chloride, 1.2 g., the reaction was estimated to have been 1/3 completed. The evaporation of this solution under reduced pressure gave a sirup which showed the same infrared spectrum as in Fig. 1, suggesting the presence of carboethoxy *p*-toluenesulfonate (IVb)¹⁴) contaminated with some ethyl *p*toluenesulfonate. When heated, this sirup formed carbon dioxide, and the residue gave pure IIIb by column chromatography over alumina with benzene.

The Reaction of II with Methyl Chlorocarbonate. -The reaction of II (7.0 g.) with Ia (2.3 g.) was carried out in a way similar to that described above for the ethyl ester. After 17 days at room temperature, silver chloride was filtered off and the volatile matter was. expelled from the filtrated by vacuum distillation at. room temperature. To the residue 50 ml. of methylene chloride was added and the infrared spectrum was. measured; we thus found a strong C=O band at 1790 cm^{-1} . From the yield of silver chloride, 1.2 g., and also from the intensity of the above C=O band, a 35% conversion was estimated. Upon the evaporation of the solvent in a vacuum and the recrystallization of the residue from a mixture of *n*-hexane: benzene (2:1), 0.65 g. of IVa was obtained as a colorless prism, m. p. 57-59°C (lit.11) 60-61°C). Heating at 120°C for 20 min. produced no change in the infrared spectrum of IVa, while heating at 120-140°C for 5 hr. resulted in a complete decomposition to methyl p-toluenesulfonate.

The Reaction of p-Toluenesulfonyl Chloride with Sodium Methyl Carbonate (V).-When 9 g. of tosyl chloride was mixed with 4.0 g. of V, prepared. by passing carbon dioxide into a solution of sodium methoxide in methanol and by the evaporation of the reaction mixture in a vacuum to complete dryness, an exothermic reaction started at once. The mixture was cooled immediately, diluted with 30 ml. of acetonitrile, and kept at room temperature for one week. The insoluble powder was filtered off, and the solvent: was removed in vacuo. The residue was dissolved in methylene chloride and its infrared spectrum examined; this spectrum exhibited strong absorptions att 1830 and 1790 cm⁻¹, corresponding to those of methyl³ pyrocarbonate. The work-up of this solution gave: methyl p-toluenesulfonate too, but no IVa.

The Preparation of Silver p-Toluenesulfonate-¹⁸O.—A mixture of 20 g. of tosyl chloride and 5 ml. of H₂¹⁸O (18O: 1.5 atom%) was heated in a water bath for 2 days; the contents of the flask were thereby solidified. Another few milliliters of H218O and 10 ml. of anhydrous dioxane were added to this solid, and the homogeneous mixture was heated for sevaral hours. The volatile matter was expelled by vacuum evaporation, and distilled water was added to the residue. The water was then distilled off in vacuo to ensure the removal of the hydrogen chloride formed. Finally the residue was dissolved in 100 ml. of distilled water and warmed with 13 g. of silver oxide. This solution was filtered while hot, and the filtrate was cooled in ice water to deposit the desired salt. The concentration of the mother liquid gave a second croup. Recrystallized silver salt was dried in a vacuum, powdered and dried again in vacuo.

June, 1966]

The Preparation of Ethyl p-Toluenesulfonate-⁴⁸O.—To a solution of 5.0 g. of silver p-toluenesulfonate-⁴⁸O in 20 ml. of warm acetonitrile, 4.0 g. of ethyl bromide was added; the reaction mixture was then refluxed for one hour and cooled. After another hour at room temperature, the mixture was filtered and the solvent was distilled off from the filtrate. The crystalline residue was recrystallized from petroleum ether to give 2.4 g. of ethyl p-toluenesulfonate-¹⁶O. The ¹⁸O .atom% of this ester was 0.61%.

The Reaction of Silver p-Toluenesulfonate-18O with Ib.—A solution of 5.5 g. of Ib (1.4 mol. equivalent) in 5 ml. of acetonitrile was added to a solution of 10.0 g. of silver salt-18O in 40 ml. of acetonitrile at 95°C. The precipitation of silver chloride started at once. The total volume of the evolved gas was 950 ml.; it thus exceeded the calculated volume, 860 ml. The infrared spectrum of the filtrate indicated the presence of some diethyl carbonate ($\nu_{C=0}$, 1740 cm⁻¹). Acetonitrile was removed from the filtrate by vacuum distillation, and the residue was taken up in methylene chloride to free it from unchanged silver sulfonate. The evaporation of this solution, the repeated extraction of the residue with petrolum ether, and finally filtration chromatography through alumina gave 0.4 g. of ethyl p-toluenesulfonate-18O, m. p. 31°C. The ¹⁸O atom% of this ester was 0.62%.

The Reaction of II with Isobutyl Chlorocarbonate.---i) Reaction at Room Temperature.---To a solution of 7.0 g. of II in 30 ml. of acetonitrile, 3.4 g. of Ic in 10 ml. of the same solvent was added. No change was observed. The mixture was then kept at room temperature for 8 days, and the precipitated silver chloride (1.0 g., 1/3 of the calculated) was filtered off. Acetonitrile was removed in a vacuum, and the residue was dissolved in methylene chloride and filtered from the runchanged II. The solvent was distilled off in vacuo, and the residue was warmed with a mixture of benzene petroleum ether (1:2). Upon cooling, some colorless crystals separated; they were identified as p-toluenesulfonic acid. The filtrate and the insoluble matter in the solvent mixture were combined, diluted with ether, washed with a sodium carbonate solution and water, and dried over magnesium sulfate. Upon the evaporation of the solvent in vacuo, a colorless sirup was obtained which exhibited a strong C=O absorption in the infrared spectrum (Fig. 3), suggesting the presence of carboisobutoxy p-toluenesulfonate (IVc), probably contaminated with some butyl p-toluenesulfonate. All attempts to isolate the mixed an hydride (IVc) in the crystalline form were unsuccessful. After one week at room temperature, the sirup was dissolved in ether, treated with an excess of pphenylenediamine to decompose the unchanged IVc to N-carboisobutoxy p-phenylenediamine and the sulfonic acid, washed with diluted sulfuric acid, filtered through decolorizing carbon, and finally evaporated. The oil thus obtained in a small yield was a mixture of isobutyl and s-butyl p-toluenesulfonate, plus a slight amount of diisobutyl carbonate. The ratio of isobutyl sulfonate to s-butyl sulfonate was estimated by infrared spectroscopy to be 0.79: 1.00. The low yield of butyl p-toluenesulfonates was attributed to the too mild

decomposition conditions (one week at room temperature).

ii) Reaction at Boiling Point.-A solution of 7.0 g. of II and 3.7 g. of Ic in 40 ml. of acetonitrile was refluxed until the evolution of gas (total 565 ml., nearly 1 mol.) ceased. The presence of isobutene in gas was confirmed by converting it into dibromide (identified by boiling point and infrared spectrum). Acetonitrile was removed under reduced pressure, and the residue was taken up in methylene chloride, filtered, washed with dilute sodium carbonate solution, and dried over magnesium sulfate. Upon the evaporation of the solvent, a mixture of p-toluenesulfonic anhydride (VII) and its free acid was crystallized. The infrared spectrum of the filtrate indicated that the yield of butyl p-toluenesulfonates was very low, if there was any at all. An attempt to isolate them from the filtrate by column chromatography was unsuccessful.

iii) Reaction at a Moderate Temperature.—A solution of 7.0 g. of II and 3.4 g. of Ic in 30 ml. of acetonitrile was warmed at 40-60°C for several hours; a gaseous mixture of carbon dioxide and isobutene (identified as dibromide) evolved. Treatment similar to that in i) gave an oil which again exhibited a strong C=O band at 1788 cm⁻¹. Excess aniline was added to this oil to form a semisolid mixture, which left the white crystals undissolved upon the addition of diluted nitric acid. The recrystallization of these crystals from petroleum ether gave carboisobutoxyaniline, m. p. 82-84°C; melting point upon admixture with authentic specimen, 82-83°C. The acidic aqueous filtrate gave only a trace of silver chloride with a silver nitrate solution. Therefore, the presence of the C=O absorption band and the formation of urethan could not be attributed to the presence of the unchanged Ic in the oil. The concentration of the petroleum ether mother filtrate from urethan and treatment with active carbon gave a mixture of isobutyl and s-butyl p-toluenesulfonate. The mole ratio of iso : sec. was estimated by infrared spectroscopy to be 0.86:1.00. By elution chromatography over silica gel with petroleum etherbenzene, these two esters could be separated (the isobutyl ester was eluted first), from each other, and the formation of s-butyl ester was confirmed. From the yield of carboisobutoxyaniline and butyl sulfonates, about half of the mixed anhydride IVc was considered to have decomposed to butyl sulfonates.

The Preparation of Carboisobutoxyaniline.— When an excess of aniline was added to 0.3 g. of Ic, the reaction occurred immediately, giving a solid mass. The addition of diluted nitric acid to this mass left undissolved crystals; they were recrystallized from 10 ml. of petroleum ether to give the desired product, m. p. $85-86^{\circ}C$ (lit. 80 or $86^{\circ}C$). Its high yield indicated the absence of any appreciable s-butyl chlorocarbonate as an impurity in the sample used for the present study.

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