The second dibasic acid appears to be a product (IX) of five-membered ring closure, and on Dieckmann cyclization of the ester, followed by hydrolysis and decarboxylation gives what is probably a benzazulene derivative X.

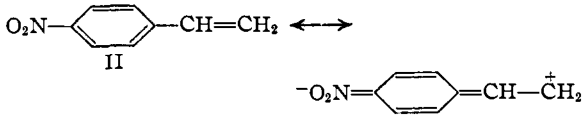
MADISON, WISCONSIN RECEIVED NOVEMBER 5, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reaction of Certain Substituted Styrenes with Dioxane Sulfotrioxide[1]

BY WILLIAM E. TRUCE AND PAUL F. GUNBERG[2]

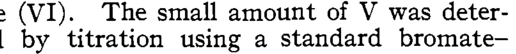
The reaction of dioxane sulfotrioxide (I) with *p*-nitrostyrene (II) and *m*-nitrostyrene (III) has been investigated to determine whether the latter isomer, lacking resonance interaction between the nitro group and the olefinic group, would react more rapidly than II in which resonance of the type IIa should inhibit reaction with an electrophilic reagent at the ω-carbon atom.



II

IIa

Some support for this prediction was furnished by the reactions of 2- and 4-vinylpyridines (where resonance would be expected to impose an electron deficiency on the terminal carbon atoms) with nucleophilic reagents, whereas 3-vinylpyridine failed to react under the same conditions.[3]

The reaction of I and II, surprisingly rapid at 1–7°, led to the isolation of a product (as a barium salt) considered to be the sulfate ester of 2-(*p*-nitrophenyl)-2-hydroxyethane-1-sulfonic acid (IV), *i. e.*, . Barium and nitrogen analyses were consistent with this structure. Since the barium sulfonate(s) gave a very weak reaction with permanganate, the presence of a small amount of barium 2-(*p*-nitrophenyl)-ethene-1-sulfonate (V), was considered. Another component was assumed to be barium 2-(*p*-nitrophenyl)-2-hydroxyethane-1-sulfonate (VI). The small amount of V was determined by titration using a standard bromate–bromide solution.[4] From the barium analyses of the mixed sulfonates the relative amounts of IV and VI were then calculated. On this basis, IV was calculated to be formed in 83–88% yields.

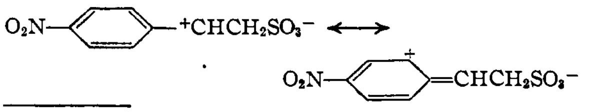
Product IV was converted to the following crystalline derivatives: the corresponding S-benzylthiuronium salt, 2-(*p*-nitrophenyl)-ethene-1-sulfonyl chloride (VII), and 2-(*p*-nitrophenyl)-ethene-1-sulfonamide (VIII). Both VII and VIII are described in the literature, having been prepared via the nitration of 2-phenylethene-1-sulfonyl chloride.[5] Further proof of the structure of VIII was obtained by reducing it to 2-(*p*-aminophenyl)-ethene-1-sulfonamide as described in the literature,[5] and then deaminating it by diazotization in the presence of hypophosphorus acid to 2-phenylethene-1-sulfonamide.[6]

Comparable results were obtained in the sulfonation of III. The sulfate ester of 2-(*m*-nitrophenyl)-2-hydroxyethane-1-sulfonic acid was formed in 69–71.5% yields. Analogous derivatives were prepared and the method of proving the structure was the same as above.

Because of the intermediate effect of a chlorophenyl group, between that of the phenyl and nitrophenyl groups, on the side-chain reactions of certain benzene derivatives,[7] the reaction of I with *m*-chlorostyrene was also investigated. In this case the principal product was 2-(*m*-chlorophenyl)-2-hydroxyethane-1-sulfonic acid. On the basis of analytical data, it was estimated that the corresponding sulfate ester was obtained (as the barium salt) in only 7–15% yields. A water-insoluble crystalline product was also obtained. This was considered to be a sultone analogous to that obtained by the sulfonation of styrene.[4] From the mixed barium sulfonates, 2-(*m*-chlorophenyl)-ethene-1-sulfonyl chloride and the corresponding sulfonamide were prepared.

Although the reaction of I with styrene has been investigated thoroughly,[4] we repeated the sulfonation in an effort to find some evidence for the formation of a sulfate bond. Our findings were essentially the same as described in the literature. The presence of the sulfate ester of 2-phenyl-2-hydroxy-1-ethanesulfonic acid was not detected by the methods used.

Discussion.—In the reaction of I with an α-olefin, the electrophilic agent always attacks the terminal olefinic carbon atom.[8] In the case of styrenes, resonance stabilization of the resulting intermediates would be expected, *e. g.*



---

[1] Presented before the Division of Organic Chemistry at the 116th Meeting of the American Chemical Society, Atlantic City, September, 1949.

[2] General Laboratories, United States Rubber Co., Passaic, New Jersey.

[3] Doering and Weil, THIS JOURNAL, 69, 2461 (1947).

[4] Bordwell and Rondestvedt, *ibid.*, 70, 2429 (1948).

[5] Bordwell, Colbert and Alan, *ibid.*, 68, 1778 (1946).

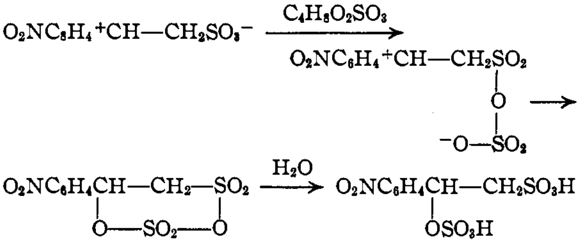
[6] Bordwell, Suter, Holbert and Rondestvedt, *ibid.*, 68, 139 (1946), and refs. cited therein.

[7] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 188.

[8] Bordwell, Suter and Webber, THIS JOURNAL, 67, 827 (1945).

If the attack were to occur on the α-carbon atom, the resulting intermediate would lack any such resonance stabilization. Furthermore, although it may be considered that the nitro group in *p*-nitrostyrene causes a displacement of electrons toward the nitrophenyl group, electrophilic attack occurs readily on the terminal carbon atom because, as a result of such resonance stabilization of the intermediate, the over-all energy requirement is probably not appreciably changed.

The subsequent course of the reaction is apparently influenced by the nature of the group attached to the α-carbon atom. The sequence of steps for the principal reaction with the nitrostyrenes may be



$$O_2NC_6H_4{}^+CH{-}CH_2SO_3^- \xrightarrow{C_4H_8O_2SO_3} O_2NC_6H_4{}^+CH{-}CH_2SO_2{-}O{-}SO_2{-}O^- \longrightarrow$$

$$O_2NC_6H_4\underset{|}{CH}{-}CH_2{-}\underset{|}{SO_2}\;(\text{ring via } O{-}SO_2{-}O) \xrightarrow{H_2O} O_2NC_6H_4\underset{OSO_3H}{\underset{|}{CH}}{-}CH_2SO_3H$$

Direct attack by the electrophilic sulfonating complex on the α-carbon atom of the intermediate (carbonium ion) would be unlikely. It might be considered that the hydroxysulfonic acid could form by some other mechanism, and that on pouring the reaction mixture into water, free sulfuric acid would be formed from unreacted sulfur trioxide, which would then react with the hydroxyl group to form the sulfate bond. However, it has been shown that the hydroxyl group in 2-hydroxy-2-phenylethane-1-sulfonic acid strongly resists esterification.[9] Furthermore, on treating II with an equimolar quantity of I, a large amount of the olefin was recovered unchanged, indicating that practically all of the sulfonating agent had reacted before hydrolysis.

Experimental

Sulfonation of *p*-Nitrostyrene.—*p*-Nitrostyrene was prepared by the dehydrobromination of *p*-nitro-β-bromoethylbenzene as described in the literature.[10] The product obtained on crystallization from petroleum ether at 0° melted at 20–21°.

Anal. Calcd. for $C_8H_7O_2N$: N, 9.40. Found: N, 9.45.

A slurry of dioxane sulfotrioxide was prepared by adding 20.3 g. (0.230 mole) of dioxane to a cold solution of 18.4 g. (0.230 mole) of sulfur trioxide in 150 ml. of ethylene chloride. To this cold slurry, under anhydrous conditions, was added dropwise 35.2 g. (0.236 mole) of *p*-nitrostyrene dissolved in 50 ml. of ethylene chloride. After addition was complete, stirring was continued for three hours at 0° after which the reaction mixture was allowed to warm up to room temperature. The mixture was then poured into 500 ml. of cold water and the layers separated. From the ethylene chloride layer there was obtained 16.1 g. (0.108 mole) of unreacted *p*-nitrostyrene. The aqueous layer was treated with barium hydroxide and any excess base was precipitated with carbon dioxide. The mixture was boiled with a total of one liter of water and then filtered while hot to remove barium sulfate. The amount of barium sulfonates occluded in the crude barium sulfate precipitate was determined by ignition. It was calculated that only 10% of the sulfur trioxide had been recovered as barium sulfate. Three crops of mixed barium sulfonate crystals, totaling 52.3 g., were obtained on evaporation of the filtrate. Crop 1 was considered on the basis of analysis to be the barium salt of the sulfate ester of 2-(*p*-nitrophenyl)-2-hydroxyethane-1-sulfonic acid.

Anal. Calcd. for $C_8H_7O_9NS_2Ba$: Ba, 29.7; N, 3.03. Found: Ba, 29.4; N, 2.95.

This material did not react with cold, dilute, aqueous potassium permanganate. The S-*p*-chlorobenzylthiuronium salt was prepared and after several recrystallizations from water melted at 181.5–183°.

Anal. Calcd. for $C_{24}H_{27}O_9N_5S_4Cl_2$: C, 39.6; H, 3.71; N, 9.61. Found: C, 39.7; H, 4.0; N, 9.69.

The composition of the mixed sulfonates was then determined by titration of the 2-(*p*-nitrophenyl)-ethene-1-sulfonate with a standard bromate–bromide solution.[4] This was carried out by adding an excess of the reagent, converting free bromine to iodine with a 10% aqueous solution of potassium iodide and back-titrating the iodine with a standard sodium thiosulfate solution. Carbon tetrachloride was added and the end-point determined by disappearance of the violet color from the organic layer. The relative amounts of the sulfate–sulfonic acid and the hydroxysulfonic acid were then calculated on the basis of the barium analyses. The following yields of products were calculated; sulfate–sulfonic acid, 83%; hydroxysulfonic acid, 5%; unsaturated sulfonic acid, 3%.

A second sulfonation of *p*-nitrostyrene was carried out using two moles of dioxane sulfotrioxide per mole of olefin. Less than 1% of the olefin failed to react. The products were worked up as described in the previous experiment. It was calculated that the sulfate–sulfonic acid was formed in 88% yield and the other two components each in 6% yield.

2-(*p*-Nitrophenyl)-ethene-1-sulfonyl Chloride.—A sample of the mixed barium sulfonates was converted to the corresponding sodium salts by metathesis. The latter was heated under anhydrous conditions on a steam-bath for six hours with an equimolar quantity of phosphorus pentachloride. After removal of phosphorus oxychloride under vacuum, the residue was washed with cold water and then recrystallized from a mixture of chloroform and carbon tetrachloride. From 39.0 g. (0.084 mole) of the mixed barium sulfonates, there was obtained 12.6 g. (0.051 mole) of the sulfonyl chloride corresponding to a yield of 61%. The product melted at 169–171°. When mixed with an authentic sample[11] there was no depression in the melting point.

Anal. Calcd. for $C_8H_6O_4NSCl$: N, 5.66. Found: N, 5.70.

Deamination of 2-(*p*-Aminophenyl)-ethene-1-sulfonamide.—Into a tube equipped with a stirrer and immersed in an ice-bath were placed 0.68 g. (0.00344 mole) of the amine, 6.81 g. of 50% hypophosphorous acid and 9.1 ml. of distilled water. To this was added a solution of 0.257 g. (0.0035 mole) of sodium nitrite in 9.1 ml. of distilled water at such a rate as to keep the temperature of the solution below 5°. The reaction mixture was stored at 0° for four hours and then filtered. Upon crystallization from water there was obtained 0.22 g. (0.0012 mole) of crude 2-phenylethene-1-sulfonamide corresponding to a 35% yield. Further recrystallization gave a light yellow solid, m. p. 140–141°, which gave no depression in melting point when mixed with an authentic sample of 2-phenylethene-1-sulfonamide.[6]

Sulfonation of *m*-Nitrostyrene.—*m*-Nitrostyrene was prepared by the decarboxylation of *m*-nitrocinnamic acid.[12] The product was purified by distillation at reduced pressure, b. p. 76–77° (1.0 mm.), $n^{20}D$ 1.5836.

---

[9] Kharasch, Schenk and Mayo, This Journal, 61, 3092 (1939).

[10] Strassburg, Gregg and Walling, *ibid.*, 69, 2141 (1947).

[11] Kindly supplied by Dr. F. G. Bordwell, Northwestern Univerisity.

[12] Wiley and Smith, This Journal, 70, 2296 (1948).

Fourteen and one-half grams (0.0975 mole) of *m*-nitrostyrene dissolved in 50 ml. of ethylene chloride was added gradually to the cold sulfonating reagent composed of 7.8 g. (0.0975 mole) of sulfur trioxide, 8.6 g. (0.0975 mole) of dioxane and 150 ml. of ethylene chloride. The same procedure was followed as with *p*-nitrostyrene. From the ethylene chloride layer there was recovered 6.4 g. (0.043 mole) of *m*-nitrostyrene which was 44% of the original olefin used. Five per cent. of the sulfur trioxide was recovered as barium sulfate. Barium analyses of 28.4%, 28.0% and 27.3% for the three crops of barium sulfonates (total 22.2 g.) indicated that somewhat less of the sulfate structure was formed than in the sulfonation of *p*-nitrostyrene. Upon analysis (as described for *p*-nitrostyrene) of the barium sulfonate mixtures, it was calculated that the products were formed in the following yields: sulfate ester of 2-(*m*-nitrophenyl)-2-hydroxyethane-1-sulfonic acid, 71.5%; 2-(*m*-nitrophenyl)-2-hydroxyethane-1-sulfonic acid, 21%; and 2-(*m*-nitrophenyl)-ethene-1-sulfonic acid, 4%. The S-benzylthiuronium salt of the sulfate–sulfonic acid was prepared and upon repeated recrystallization from water melted at 112–113°.

Anal. Calcd. for $C_{24}H_{29}O_9N_5S_4$: N, 10.61. Found: N, 10.65.

When two moles of dioxane sulfotrioxide were used per mole of *m*-nitrostyrene, less than 1% of the olefin failed to react, whereas 15% of the original sulfur trioxide was recovered as barium sulfate. After titration with a bromate–bromide solution, the composition of the mixed sulfonates was calculated to be as follows: sulfate–sulfonic acid, 69%; hydroxysulfonic acid, 27%; and the unsaturated sulfonic acid, 4%.

2-(*m*-Nitrophenyl)-ethene-1-sulfonyl Chloride.—The same procedure was used as was described for the para isomer. A sample of the mixed barium sulfonates was converted to the sulfonyl chloride in 34% yield. It crystallized readily from carbon tetrachloride and melted at 116.5–117.5°.

Anal. Calcd. for $C_8H_6O_4NSCl$: N, 5.66. Found: N, 5.64.

2-(*m*-Nitrophenyl)-ethene-1-sulfonamide was readily obtained by treating the corresponding sulfonyl chloride with liquid ammonia. The product, recrystallized from water, was obtained in 87% yield. It melted at 147–148°.

Anal. Calcd. for $C_8H_8O_4N_2S$: N, 12.28. Found: N, 12.15.

2-(*m*-Aminophenyl)-ethene-1-sulfonamide.—Using the procedure described for the para isomer,[6] the amine was obtained in 41% yield. On recrystallization from water it melted at 177–178°.

Anal. Calcd. for $C_8H_{10}O_2N_2S$: N, 14.13. Found: N, 14.21.

The same deamination procedure was used as previously described for the para isomer. The product, 2-phenylethene-1-sulfonamide, was obtained in 40% yield. After recrystallization from water, it melted at 141–142°. This material when mixed with an authentic sample gave no depression in the melting point.

Sulfonation of *m*-Chlorostyrene.—*m*-Chlorostyrene was prepared by the dehydration of *m*-chlorophenylmethylcarbinol as described by Brooks.[13] The product was purified by distillation at reduced pressure, b. p. 42–43° (3.3 mm.), n^{20}_D 1.5620.

To a slurry of the sulfonating agent containing 17.2 g. (0.215 mole) of sulfur trioxide, 18.9 g. (0.215 mole) of dioxane, 150 ml. of ethylene chloride and cooled to 0°, was gradually added 29.8 g. (0.215 mole) of *m*-chlorostyrene dissolved in 50 ml. of ethylene chloride. On pouring the reaction mixture into 500 ml. of water, an emulsion formed. The layers were separated only after adding a large excess of ethylene chloride. The water-insoluble component was tentatively identified as 2,4-di-(*m*-chlorophenyl)-1,4-butanesultone. This material was formed in 19% yield. It melted at 169–170° on recrystallization from 95% ethyl alcohol. Qualitative analysis showed the presence of sulfur and chlorine.

Anal. Calcd. for $C_{16}H_{14}O_3Cl_2S$: C, 53.8; H, 3.93. Found: C, 54.1; H, 4.20.

The aqueous fraction was neutralized with 32.0 g. (0.1015 mole) of barium hydroxide and the precipitated barium sulfate was removed by filtration. All the olefin reacted, but 5% of the original sulfur trioxide was recovered as barium sulfate. Three crops of barium sulfonates were obtained (total 50.6 g.) giving barium analyses of 22.8, 25.8 and 27.9%. Their compositions, determined as previously described, were sulfate ester of 2-(*m*-chlorophenyl)-2-hydroxyethane-1-sulfonic acid, 7%; 2-(*m*-chlorophenyl)-2-hydroxyethane-1-sulfonic acid, 54%; and 2-(*m*-chlorophenyl)-ethene-1-sulfonic acid, 13%.

A second sulfonation was carried out using two moles of dioxane sulfotrioxide per mole of *m*-chlorostyrene. Again the olefin reacted completely but there was no sultone formation. All the products were water-soluble. From the amount of barium sulfate recovered it was calculated that 32% of the sulfur trioxide did not react. From analysis of the mixed barium sulfonates the products of reaction were calculated to be formed in the following yields: the sulfate ester of 2-(*m*-chlorophenyl)-2-hydroxyethane-1-sulfonic acid, 15%; 2-(*m*-chlorophenyl)-2-hydroxyethane-1-sulfonic acid, 67%; 2-(*m*-chlorophenyl)-ethene-1-sulfonic acid, 18%.

2-(*m*-Chlorophenyl)-ethene-1-sulfonyl Chloride.—From 20.0 g. of the mixed barium sulfonates, there was obtained 5.2 g. of the sulfonyl chloride corresponding to a yield of 30%. The product recrystallized readily from carbon tetrachloride as pale yellow needles which melted at 94–95°.

Anal. Calcd. for $C_8H_6O_2SCl_2$: C, 40.5; H, 2.53. Found: C, 40.6; H, 2.41.

2-(*m*-Chlorophenyl)-ethene-1-sulfonamide was obtained in 86% yield on treating the sulfonyl chloride with liquid ammonia. It recrystallized readily from water and melted sharply at 142–143°.

Anal. Calcd. for $C_8H_8O_2NSCl$: N, 6.44. Found: N, 6.46.

Acknowledgment.—Our thanks are due to the Purdue Research Foundation and the Atomic Energy Commission for financial support in this work.

Summary

1. Sulfonation of *p*-nitrostyrene gave an 83–88% yield of the sulfate ester of 2-(*p*-nitrophenyl)-2-hydroxyethane-1-sulfonic acid. *m*-Nitrostyrene gave a similar product but in somewhat smaller yield, 69–71%. Under the same conditions, *m*-chlorostyrene gave only 7–15% of the sulfate–sulfonic acid. In the sulfonation of styrene there was no evidence for formation of the sulfate bond.

2. A mechanism for this reaction is discussed. There appears to be some correlation between the amount of sulfate formation and the inductive character of the substituted phenyl group.

LAFAYETTE, INDIANA RECEIVED JULY 16, 1949

---

[13] Brooks, This Journal, **66**, 1296 (1944).