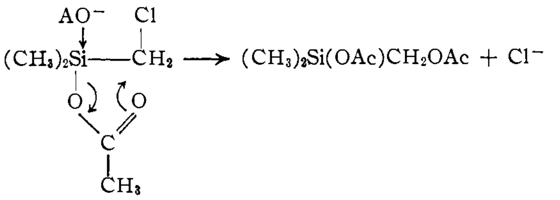
Acetoxysilanes are almost certainly intermediates in this rearrangement.[13] The acetoxysilane could then react intramolecularly with acetic acid or acetate ion to displace chloride ion



Acknowledgment.—We wish to thank Dr. J. R. Ladd for the preparation of the chloro compounds.

SCHENECTADY, N. Y.

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[13] Decamethyltetrasiloxane rearranges when heated with glacial acetic acid. The rearrangement proceeds much more rapidly in a 1 M solution of potassium acetate in acetic acid, presumably due to cleavage of silicon–oxygen bonds by acetate ion

$$\mathrm{AcO^{\ominus} + -SiOSi \rightleftarrows -SiOAc + -SiO^{\ominus}}$$

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Sulfonation of Olefins. III. Nature and Reactions of the Intermediate from Styrene

BY F. G. BORDWELL, MARVIN L. PETERSON[1] AND CHRISTIAN S. RONDESTVEDT, JR.[2]

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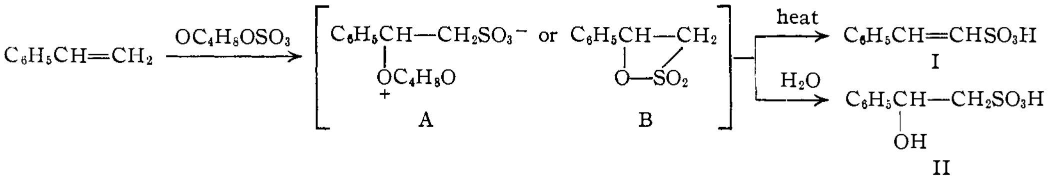
An unstable intermediate β-sultone (B) has been isolated by addition of pentane to the sulfonation solution prepared from styrene and an equimolar quantity of dioxane–sulfur trioxide complex in ethylene chloride. The reactions of the sulfonation solution with water, methanol, ethanethiol, aniline and pyridine have been formulated in terms of B as an intermediate. The product from the reaction of B with pyridine was a dipolar ion $C_6H_5CH(^+NC_5H_5)CH_2SO_3^-$ (VI). The pyridine group in VI was not displaced by reactions with thiourea or iodide ion, but was eliminated to give $C_6H_5CH{=}CHSO_3^-$ by the action of hydroxide ion. A dimer of B was obtained in small amounts when the sulfonation was run at a temperature of 40° instead of 0°; this dimer underwent reactions similar to those of B.

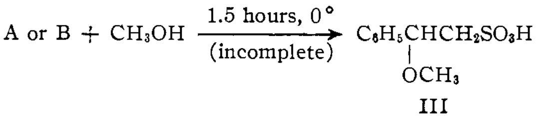
In the last paper in this series[3] the nature of the products from the reaction of styrene with the dioxane–sulfur trioxide addition complex[4] at 0° was shown to depend on the treatment of the resulting sulfonation solution. For example, heating the sulfonation solution prior to addition of water gave 2-phenylethenesulfonic acid (I) as the principal product, whereas direct hydrolysis gave chiefly 2-hydroxy-2-phenylethanesulfonic acid (II). These and other reactions of the sulfonation solution were rationalized[3] in terms of the presence of a dioxane-solvated-carbonium sulfonate (A). The results could also be explained on the basis of a β-sultone intermediate (B), but this was looked on with less favor.[5]



The rate of formation of the intermediate (A or B) has now been approximated by determining the amount of sulfate ion formed on hydrolysis after varied time intervals in a reaction of a 0.3 M solution of the dioxane–sulfur trioxide reagent with styrene in ethylene chloride at 0°. Under these conditions the reaction was 60% complete within one minute.

According to the representation formerly given,[3] A or B should be susceptible to attack by nucleophilic reagents other than water. This view has now been confirmed by observing similar reactions with methanol, aniline, ethanethiol and pyridine.

Reaction of the sulfonation solution with excess methanol for 1.5 hours at 0° gave, *on pouring into water*, approximately 30% of I, 25% of II and 45% of 2-methoxy-2-phenylethanesulfonic acid (III). The structure of III was established by synthesis of the sodium salt from 2-methoxy-2-phenyl-1-iodoethane and sodium sulfite, identity being established by comparison of the S-(*p*-chlorobenzyl)-thiuronium salts. The structure was further substantiated by hydrolysis of the pyridine salt of III to a salt of II in the presence of hot dilute acid. The 26% of II obtained in the original experiment was not derived, however, by hydrolysis of III, since no hydrolysis occurred in a model experiment using the pyridine salt of III under comparable conditions (at 20°). Instead, II must be formed from a portion of the sulfonation intermediate which did not react with methanol in the 1.5-hour period. In support of this conclusion, a sulfonation solution, which had stood with excess methanol at 0° for 15 days failed to yield II on addition of water.



$$\text{A or B} + CH_3OH \xrightarrow[\text{(incomplete)}]{\text{1.5 hours, 0°}} C_6H_5\underset{\substack{|\\ OCH_3}}{C}HCH_2SO_3H$$

III

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[1] Procter and Gamble Predoctoral Fellow, 1948–1951.

[2] National Research Council Predoctoral Fellow, 1946–1947.

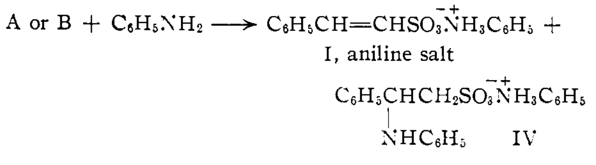
[3] F. G. Bordwell and C. S. Rondestvedt, Jr., THIS JOURNAL, **70**, 2429 (1948).

[4] C. M. Suter, P. B. Evans and J. M. Kiefer, *ibid.*, **60**, 538 (1938).

[5] See also, F. G. Bordwell, C. M. Suter and A. J. Webber, *ibid.*, **67**, 827 (1945). The part of the argument against a β-sultam in this instance which was based on the reported stability of a β-sultone is invalid, since the compound referred to was later shown to have a different structure, see W. Autenrieth and P. Rudolph, *Ber.*, **34**, 3467 (1901).

$$\underset{\text{III (pyridine salt)}}{[C_6H_5CH(OCH_3)CH_2SO_3^-]C_5H_5\overset{+}{N}H} \xrightarrow[\text{(very slow at 20°)}]{H_3O^+,\ \text{heat}} \underset{\text{II}}{C_6H_5CH(OH)CH_2SO_3^-H_3O^+}$$

Allowing a sulfonation solution to stand in the cold with excess aniline gave 30% of anilinium 2-phenyl-1-ethenesulfonate (aniline salt of I), 43% of anilinium 2-anilino-2-phenylethanesulfonate (IV) (an analog of II), 13% of anilinium sulfate, 2% of 2,4-diphenyl-1,4-butanesulfone,[3] and 6% of 2,4-diphenyl-4-anilino-1-butanesulfonic acid (V). The structure assigned to the aniline salt IV was supported by bromination to a tribromo derivative

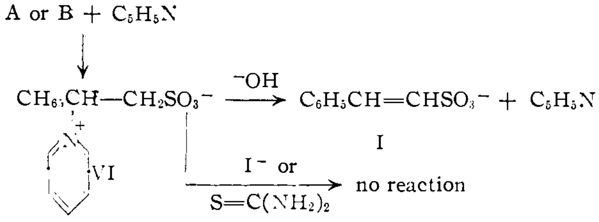


$$\text{A or B} + C_6H_5NH_2 \longrightarrow \underset{\text{I, aniline salt}}{C_6H_5CH{=}CHSO_3^-\overset{+}{N}H_3C_6H_5} + \underset{\text{IV}}{C_6H_5\underset{NHC_6H_5}{\underset{|}{C}}HCH_2SO_3^-\overset{+}{N}H_3C_6H_5}$$

and by acid-catalyzed cleavage to I. The structure of V was assigned on the basis of its preparation from 2,4-diphenyl-1,4-butanesultone[6] and aniline.

From a reaction of the sulfonation solution with ethanethiol, 42% of the reactants were recovered in the form of a salt, which is probably S-(*p*-chlorobenzyl)-thiuronium 2-ethylthio-2-phenylethanesulfonate.

The reaction of the sulfonation solution with pyridine is unique in that a dipolar ion (VI), 2-phenyl-2-(1-proto-1-pyridyl)-1-ethanesulfonate,[7] was formed. The structure of VI is supported by its physical properties, and by a quantitative elimination reaction initiated by base to give I and pyridine.

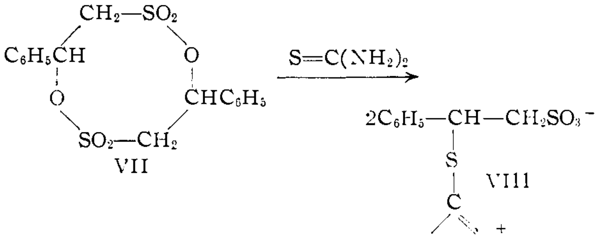


The failure of VI to react with iodide ion or thiourea in aqueous solution emphasizes the difficulty of cleavage of carbon–nitrogen bonds in displacement reactions, since this would appear to be a particularly favorable instance. It is of interest to contrast this with the facile cleavage of the carbon–nitrogen bond in the elimination reaction with hydroxide ion.

Attempts to prepare VI from styrene and the pyridine–sulfur trioxide complex were unsuccessful. No reaction occurred at room temperature, and at 84° the reaction was very slow, a 26% yield of I being obtained after 16 hours.

In our earlier representations of the course of the sulfonation,[3,5] formulation of the intermediate present in the sulfonation solution as a dioxane-solvated-carbonium ion (A) has been preferred to representation as a β-sultone (B). Prejudice against the β-sultone structure for the intermediate was built up by the isolation on one occasion of a small quantity of a compound which hydrolyzed to II, giving a neutral equivalent agreeing with structure B, *but at a rate much slower* than that observed for the sulfonation solution containing the intermediate. Unfortunately this sample[8] decomposed before its complete identity could be established, and all attempts to produce this substance during the next few years failed. We finally found that the compound was formed in sulfonations where the temperature was allowed to rise to 30–50° during addition of the styrene to the sulfonating agent (usually the temperature is maintained at 0°).

This compound (VII)[8] did not produce any acid when suspended in water, and the mixture allowed to stand at 0° for three days. Hydrolysis by heating in aqueous acetone gave over 90% of II. Methanol gave 70% of III, aniline gave 86% of IV, and pyridine gave 72% of I plus 17% of VI. Reaction with thiourea gave 86% of the thiuronium salt VIII. Thus, VII behaves qualitatively in a manner similar to the solution containing the sulfonation intermediate, but there are some differences in products, and the rate of hydrolysis is very much slower. Molecular weight determinations made by observing the freezing point lowering of benzene and nitrobenzene gave values agreeing with those for a *dimer of B*. The eight-membered formula VII appears reasonable. The reaction of VII with thiourea is given for illustration.



Subsequently it was found that addition of cold pentane to the sulfonation solution prepared in the usual manner caused the bulk of the material to precipitate in the form of an unstable low melting solid. This solid exhibited the same reactions as those of the solution of sulfonation intermediate, giving I and II rapidly on hydrolysis, and I and III on methanolysis. The major portion of the dioxane used in the sulfonation (1:1:1 mole ratio of styrene to sulfur trioxide to dioxane) was found in the ethylene chloride–pentane filtrate rather than with the solid, suggesting structure B rather than A for this intermediate.

Purification of the solid was difficult. It showed evidence of decomposition (discoloration and liquefaction) within a few minutes, when standing in air at room temperature. The major product of this

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(6) See F. G. Bordwell, F. B. Colton and M. Knell, THIS JOURNAL, **76**, 3950 (1954), regarding the structure of this compound.

(7) This nomenclature has been suggested by Dr. F. Y. Wiselogle to fill the need for a suitable prefix to designate a substituent which bears a positive charge. "Proto" signifies the addition of a proton: C_5H_5-N^+H is then protopyridine and $C_5H_5N^+$– is the 1-proto-1-pyridyl group. According to this nomenclature a dipolar ion, such as sulfanilic acid, can be given the systematic name, *p*-protoaminobenzenesulfonate, rather than *p*-aminobenzenesulfonic acid, which misrepresents the structure.

(8) First prepared by Mr. Barre Alan in 1945.

decomposition was I. Previous evidence[3] indicates considerable stability of the intermediate in solution, and the present investigation has shown that formation of I occurs slowly in solution at 0°, increasing from 8 to 18% in 19 hours, and to 60% in 17 days; see Table I. Some success in purification of the intermediate was finally achieved by a low temperature crystallization from methylene chloride and pentane carried out in a dry-box. The sample thus obtained gave a neutral equivalent and molecular weight agreeing with that calculated for B.

The evidence now seems clear-cut in favor of a β-sultone intermediate in the styrene sulfonation, and, by inference, in sulfonations of other olefins of this type. If the olefin has a β-branch intramolecular elimination to give an α,β-unsaturated sulfonic acid may be an alternative to formation of a β-sultone.[3] An equilibrium of A and B with selective precipitation of B by pentane seems unlikely, since A would be expected to be less soluble than B in non-polar solvents. Facile conversion of B to A would not be surprising, however, and there is some evidence that this may occur.[9] It is also possible that formation of A may precede that of B in the sulfonation process.

The facile reactions of B with water, methanol, ethanethiol, aniline and pyridine are readily understandable in view of the known reactivity of alkyl *p*-toluenesulfonates and of β-lactones.[10] Cleavage of the carbon–oxygen bond by nucleophilic displacements or hydrolysis should be rapid since the compound is a four-membered ring benzyl-type alkyl sulfonate. It is not surprising, then, that an attempt to measure the rate of hydrolysis of the β-sultone B conductometrically in a manner comparable to that used for a number of tertiary sultones[11] was unsuccessful. The hydrolysis of the β-sultone under these conditions was complete before the first reading could be taken (about 30 seconds).

Experimental[12]

Approximate Rate of Sulfonation of Styrene.—To the sulfonating agent at 0° in an ice-bath prepared from 7.97 g. (0.0966 mole) of sulfur trioxide, 9.0 g. (0.102 mole) of dioxane and 375 g. of ethylene chloride, a solution of 10.4 g. (0.100 mole) of styrene in 33 g. of ethylene chloride at 0° was added in one portion with rapid stirring. At the times indicated in Table I 25-ml. (31.1 g.) samples containing 0.00721 mole of the original sulfur trioxide were pipetted from the reaction mixture and added to an equal amount of water. The aqueous solution was analyzed for sulfuric acid, 2-phenylethenesulfonic acid (I) and 2-hydroxy-2-phenylethanesulfonic acid (II) by the method previously described.[3] The ethylene chloride layers were evaporated with an air jet; the residual weight of crude 2,4-diphenyl-1,4-butanesultone was found to be 8–12%.

Reaction of the Sulfonation Solution with Methanol.—The sulfonation solution was prepared from 209.2 g. of ethylene chloride, 50.3 g. (0.630 mole) of sulfur trioxide, 56.4 g. (0.640 mole) of dioxane and 65.4 g. (0.630 mole) of styrene. After this solution had stood for one-half hour in the ice–salt-bath, 200 g. of cold methanol was added and the solution allowed to stand at 0° for 1.5 hours.

TABLE I

VARIATION OF THE PRODUCTS FROM THE SULFONATION OF STYRENE AT 0° WITH TIME

Reacn. time, min.	Equiv. of acids	Sulfate weight	Sulfate %	Unsatd. sulfonate, ml. 0.2 *N* BrO_3^-	I, %	II, %
1	0.00934	0.664	39.4	..	..	29
2	.00793	.408	24.4	6.4	8.6	53
4	.00760	.292	17.3	..	..	55
7	.00734	...	..	6.5	8.7	65
13	.00713	.247	14.7	6.5	8.7	60
20	.00740	.241	14.3	6.0	8.3	66
30	.00740	.247	14.7	6.1	8.5	65
60	.00726	.231	13.7	6.1	8.5	65
137	.00737	.221	13.1	7.6	10.6	66
250	.00705	.198	11.8	8.9	12.3	62
1150	.00658	.183	10.8	13.3	18.4	51
17 days	.....	...	..	43.8	60.5	..

From this solution a portion of 115 g. (equivalent to 0.125 mole of the original sulfur trioxide) was added to 200 ml. of ice-water. After standing for several hours, the aqueous solution was neutralized with aqueous sodium hydroxide and evaporated to dryness under reduced pressure. Bromide–bromate titration[3] of the dry salts indicated the presence of 27% of sodium 2-phenylethenesulfonate (I).

To a sample of 0.5 g. of the dry sodium salts in 10 ml. of water a hot aqueous solution of S-(*p*-chlorobenzyl)-thiuronium chloride was added until no further precipitation occurred. The crude derivative, m.p. 185–195°, was recrystallized to give the derivative of I, m.p. 199–201°. The filtrate remaining from the first precipitation was treated with additional thiuronium chloride to give a further crystalline precipitate, m.p. 160–170°, which melted at 174–175° after four recrystallizations from water and did not depress the m.p. of a synthetic sample of S-(*p*-chlorobenzyl)-thiuronium 2-methoxy-2-phenylethanesulfonate, m.p. 176–176.5° (see below).

A portion of 4.0 g. of the sodium salts was dissolved in 15 ml. of water, and then ethanol was added to form 100 ml. of an 85% alcoholic solution. When this solution was cooled in an ice-bath, 0.7 g. of a white solid precipitated which was saturated to bromine water. The derivative of 2-hydroxy-2-phenylethanesulfonic acid (II), m.p. and mixed m.p. 178–180°, was obtained in low yield by adding S-(*p*-chlorobenzyl)-thiuronium chloride solution to an aqueous solution of this salt. Four crops of sodium salt crystals were obtained from the alcoholic filtrate which were 88%, 35%, 24% and 15% unsaturated. From the last sample (0.5 g.) S-(*p*-chlorobenzyl)-thiuronium derivatives of I and III were obtained. Assuming that the separation of II was quantitative, using the unsaturation titer value for I, and estimating the amount of III by difference, the relative amounts of I, II and III are 29%, 26% and 45%, respectively.

S-(*p*-Chlorobenzyl)-thiuronium 2-Methoxy-2-phenylethanesulfonate.—A 6.5-g. (0.025 mole) sample of 2-methoxy-2-phenyl-1-iodoethane, prepared by the method of Tiffeneau,[13] was dissolved in 50 ml. of ethanol, 3.5 g. (0.028 mole) of sodium sulfite in 150 ml. of water was added, and the heterogeneous mixture refluxed for 15 hours. The solvent was removed under reduced pressure, and the salts extracted with 250 ml. of hot alcohol (sodium sulfite is insoluble). Evaporation of the alcohol left 8.0 g. of salts from which an S-(*p*-chlorobenzyl)-thiuronium derivative was prepared in aqueous solution. After one crystallization from water, the compound melted at 176–176.5°.

Anal. Calcd. for $C_{17}H_{21}O_4N_2S_2Cl$: C, 48.97; H, 5.08. Found: C, 48.74; H, 4.95.

Pyridinium 2-Methoxy-2-phenyl-1-ethanesulfonate.—Anhydrous pyridine (11.89 g., 0.149 mole) was added to a sulfonation solution, which had been standing with methanol for 3 hours at 0°. After standing at 0° for 3 days, the solvent was evaporated under reduced pressure leaving the colorless crystalline pyridinium salt of III, contaminated with 9% of the pyridine salt of I (as shown by conversion to the barium salt and titration), and small amounts of 2,4-

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[9] F. G. Bordwell and M. L. Peterson, THIS JOURNAL, **76**, 3952 (1954).

[10] See T. L. Gresham, *et al.*, *ibid.*, **74**, 1323 (1952), and references cited therein concerning the reactions of β-propiolactone.

[11] Unpublished results of R. D. Chapman.

[12] Melting points are uncorrected. Microanalyses were by Misses Margaret Ledyard and Patricia Craig.

[13] M. Tiffeneau, *Compt. rend.*, **145**, 812 (1907).

diphenyl-1,4-butanesultone (insoluble in water). Recrystallization from acetone gave a pure salt, m.p. 115–116°.

Anal. Calcd. for $C_{14}H_{16}O_4NS$: C, 56.93; H, 5.80. Found: C, 56.96; H, 5.85.

Addition of S-(*p*-chlorobenzyl)-thiuronium chloride solution to the pyridine salt of III gave the thiuronium salt, m.p. 175–176°.

Hydrolysis of **Pyridinium 2-Methoxy-2-phenyl-1-ethanesulfonate.**—An experiment simulating that above in which the methanol treated sulfonation solution was poured into water was conducted by dissolving the pyridine salt of III in dioxane–ethylene chloride, saturating with a 10 molar portion of hydrogen chloride and pouring into water. No hydrolysis to II was observed under these conditions.

The pyridine salt of III also was not affected by treatment with 1 *N* sodium hydroxide at steam-bath temperature for 24 hours.

A solution of 3.2 g. (0.01 mole) of pyridinium 2-methoxy-2-phenyl-1-ethanesulfonate in 50 ml. of 1 *N* hydrochloric acid was heated on the steam-bath for 48 hours. Titration of a 33% aliquot with bromate–bromide showed the presence of 14% of I. The remainder of the solution was neutralized with sodium hydroxide and evaporated to dryness under reduced pressure. The salts were dissolved in 5 ml. of water, the solution treated with 75 ml. of hot 95% alcohol, and the precipitated sodium chloride removed by filtration. On cooling 1.0 g. (70%) of sodium 2-hydroxy-2-phenyl-1-ethanesulfonate was obtained. The S-(*p*-chlorobenzyl)-thiuronium salt, m.p. 176–179°, depressed the m.p. of the derivative of III to 155–160°, but was not depressed in m.p. by mixture with the derivative of II, m.p. 179–180°.

Products from the Reaction of the Sulfonation Solution with Aniline.—Twenty-four grams (0.258 mole) of aniline was added at 0° to a sulfonation mixture prepared from 10.1 g. (0.127 mole) of sulfur trioxide, 11.1 g. (0.127 mole) of dioxane, 13.2 g. (0.127 mole) of styrene and 75 ml. of ethylene chloride. After standing at 0° for 2 days the 36.8 g. of crystalline product was collected on a filter and then suspended in 200 ml. of benzene.

A. Anilinium 2-Anilino-2-phenyl-1-ethanesulfonate (IV).—The orange benzene suspension was filtered leaving 24 g. of colorless salts. These were suspended twice in 180-ml. portions of cold water and 20.2 g. (43%) of a colorless salt, m.p. 206–208°, remained. After two recrystallizations from methanol the sample of IV melted at 216–217°.

Anal. Calcd. for $C_{20}H_{22}O_3N_2S$: C, 64.96; H, 5.95. Found: C, 64.90; H, 6.29.

A sample of IV was neutralized with aqueous sodium hydroxide. The aniline liberated was extracted with isopropyl ether and identified by conversion to tribromoaniline. Concentration of the aqueous solution caused sodium 2-anilino-2-phenyl-1-ethanesulfonate to precipitate. A sample of the sodium salt was converted back to the less soluble aniline salt IV by reaction with aniline in acetic acid–sodium acetate buffer solution. Treatment of an aqueous solution of the sodium salt with bromine water gave sodium 2-(2,4,6-tribromoanilino)-2-phenyl-1-ethanesulfonate, which was washed with sodium bisulfite and crystallized from water.

The **S-benzylthiuronium** salt melted at 173.5–174° after three crystallizations from 30% alcohol.

Anal. Calcd. for $C_{22}H_{22}O_3N_3S_2Br_3$: N, 6.18; Br, 35.2. Found: N, 6.09; Br, 34.7.

A sample of IV titrated by the bromate–bromide method absorbed 96% of the theoretical amount of bromine (6 moles) and 94% of the theoretical quantity of tribromoaniline was recovered.

A 3.7-g. (0.01 mole) sample of the anilinium salt of IV was dissolved in 35 ml. of 0.3 *N* sodium hydroxide and the liberated aniline removed by 4 methylene chloride extractions. The solution was then treated with 25 ml. of concd. hydrochloric acid and refluxed for 4 days. After decantation from tarry material, basification and extraction yielded 64% of the theoretical quantity of aniline. Evaporation of the filtrate and extraction of the salts with 80% alcohol gave an impure sample of the sodium salt of I.

B. Anilinium Sulfate and Anilinium 2-Phenylethenesulfonate.—The benzene in which IV had been suspended was washed 3 times with water and these washings combined with the washings from solid IV. Addition of 5% barium chloride solution precipitated 3.8 g. (13%) of barium sulfate (weighed after ignition at 800° in a muffle furnace).

Evaporation of the aqueous solution under reduced pressure yielded 10.4 g. (30%) of a purple crystalline salt, which was decolorized by crystallization from water containing Norit. This salt gave the S-(*p*-chlorobenzyl)-thiuronium salt of I.

C. 2,4-Diphenyl-4-protoanilino-1-butanesulfonate (V).[6]—Washing the original ethylene chloride filtrate with two 50-ml. portions of 1 *N* hydrochloric acid converted the anilinium 2,4-diphenyl-4-anilino-1-butanesulfonate present to the insoluble dipolar ion V. One and eight-tenths grams was obtained at this point and another 1.4 g. of acetone-insoluble material was obtained on evaporation of the ethylene chloride filtrate (0.69 g., 2% of acetone-soluble 2,4-diphenyl-1,4-butanesultone was also recovered). Several crystallizations from alcohol gave a sample, m.p. 221–222°.

Anal. Calcd. for $C_{22}H_{23}O_3N$: C, 69.26; H, 6.07; S, 8.41; N, 3.67; neut. equiv., 381. Found: C, 68.86; H, 6.10; S, 8.14; N, 3.73; neut. equiv., 381.

Dipolar ion V is insoluble in aqueous acid, but dissolves in alkali or even sodium bicarbonate. It absorbed 89% of the theoretical quantity of bromine when titrated by the bromate–bromide method. A sample of V was obtained in 89% yield by allowing 2.45 g. of 2,4-diphenyl-1,4-butanesultone in 25 ml. of ethylene chloride containing 5 ml. of pure aniline to stand at room temperature, and working up the product as described above. This reaction undoubtedly accounts for the formation of V from the sulfonation solution.

After refluxing a 1-g. sample of V in a solution of 40 ml. of 25% hydrochloric acid and 20 ml. of acetic acid, 31% of V was recovered and 47% of the theoretical quantity of aniline was released (from the amount of tribromoaniline obtained).

Reaction of the Sulfonation Mixture with Ethanethiol.—Fifteen ml. of ethanethiol was added at 0° to 0.057 mole of a sulfonation mixture in 30 ml. of ethylene chloride. After 44 hours, the reaction mixture was hydrolyzed with ice-water and the aqueous portion separated and neutralized with dil. sodium hydroxide. After boiling to remove small amounts of ethanethiol, the aqueous solution was treated with 3 g. of mercuric chloride in 10 ml. of hot water. The mercuric chloride complex (2.9 g.) was suspended in water and the mercury precipitated with hydrogen sulfide. The mercuric sulfide was collected on a filter (with the aid of Celite), and the filtrate evaporated. A solution of the residue in 10 ml. of water precipitated 2.1 g. (42%) of a derivative, m.p. 139–143°, when treated with 10 ml. of S-(*p*-chlorobenzyl)-thiuronium chloride solution, containing 0.005 mole of reagent. A sample of **S-(*p*-chlorobenzyl)-thiuronium 2-ethylthio-2-phenyl-1-ethanesulfonate** melted at 149–150° after three recrystallizations from dilute alcohol.

Anal. Calcd. for $C_{18}H_{23}O_3N_2S_3Cl$: C, 48.36; H, 5.19; S, 21.5. Found: C, 48.19; H, 5.26; S, 20.9.

2-Phenyl-2-(1-proto-1-pyridyl)-1-ethanesulfonate (VI).—Twenty-five grams (0.316 mole) of dry pyridine was added to a sulfonation reagent containing 0.122 mole of sulfur trioxide, dioxane and styrene in 75 ml. of ethylene chloride. After standing for 5 days at 0° 13.0 g. of crystalline salts was collected. One gram of this salt yielded 0.287 g. of barium sulfate on treatment with barium chloride. This represents 12% of the original sulfur trioxide (present as pyridinium sulfate) and the yield of VI is then 35% (by difference). Crystallization from ethanol gave pure VI, m.p. 235–235.5°.

Anal. Calcd. for $C_{13}H_{13}O_3NS$: C, 59.29; H, 4.97. Found: C, 59.35; H, 4.85.

The ethylene chloride filtrate was evaporated giving an oil which was dissolved in water and treated with barium carbonate. An additional 2.5% of barium sulfate was precipitated. The salts obtained on evaporation contained 37% of I (by titration; this is 16% of the original sulfur trioxide). Extraction of 2 g. of the salts with 50 ml. of methanol and evaporation gave 1.3 g. of crude VI, bringing the total yield of VI to 61%.

Treatment of VI with 1 *N* sodium hydroxide for 30 min. gave pyridine and 98.5% of I (determined by titration and identified by derivative).

Heating VI for 24 hours in an aqueous solution on the steam-bath with or without pyridine present failed to produce any unsaturation. Only starting material was isolated from experiments in which VI was refluxed with potassium iodide in methanol for 18 hours, or heated at steam-bath temperature in aqueous solution with thiourea for 24 hours.

Sulfonation of Styrene with Pyridine–Sulfur Trioxide.—The reagent was prepared by adding 12.2 g. (0.153 mole) of dry pyridine to a solution of 12.2 g. (0.153 mole) of sulfur trioxide in 100 ml. of ethylene chloride. The white granular precipitate formed after about two-thirds of the pyridine had been added remained unaffected by the addition of 15.9 g. (0.153 mole) of styrene. After standing at room temperature for 10 hours and refluxing for 16 hours, 10.5 g. (0.064 mole, 41%) of the reagent still precipitated on cooling (hydrolysis with boiling water was quantitative). An additional 20% of reagent remained in the ethylene chloride filtrate, as indicated by the amount of sulfate ion obtained on hydrolysis. Styrene and a 26% yield of the S-(*p*-chlorobenzyl)-thiuronium salt of I were also obtained from this filtrate.

Formation of 4,8-Diphenyl-1,5-dioxa-2,6-dithiacycloöctane 2,2,6,6-Tetraoxide (VII).—The sulfonating reagent was prepared from 37.3 g. (0.466 mole) of sulfur trioxide, 41.0 g. (0.466 mole) of dioxane and 125 ml. of ethylene chloride. To this reagent 48.5 g. (0.466 mole) of styrene was added at such a rate and with appropriate cooling in cold water so that the temperature was maintained at 40–42°. A clear solution resulted which was cooled to 0° for one hour and then hydrolyzed by the slow addition of water at 10–15°. After the two-layer system had stood for 10 min. a white solid began to separate from the ethylene chloride layer; weight 2.0 g., m.p. 94° dec. The ethylene chloride layer was washed with water once more and then 100 ml. of petroleum–hexane was added giving 2.2 g. of colorless crystals, m.p. 96° dec. Addition of 100 ml. more of hexane gave 1.6 g., m.p. 91–93° dec. Addition of 150 ml. more hexane gave no immediate precipitate, but on standing for 12 hours at 0°, 10.6 g. of material, m.p. 84–96° dec., was obtained. Recrystallization of the latter gave 2,4-diphenyl-1,4-butanesultone. Evaporation of the filtrate gave an additional 2.5 g. of the latter bringing the total yield to about 9%. The total yield of VII was about 6%. It was crystallized by preparing a nearly saturated acetone solution at room temperature and adding water.

Anal. Calcd. for $C_{16}H_{16}O_6S_2$: C, 52.16; H, 4.37; neut. equiv., 184. Found: C, 51.92; H, 4.19; neut. equiv., 185, 181.

A similar sulfonation carried out at 0° and subsequent elevation of the temperature to 40° failed to produce any VII.

Reactions of VII. A. Decomposition.—Samples of VII decomposed in a few days at room temperature, but could be kept for several weeks at 0°. After 2.5 days at room temperature only 0.07 g. of a 1.5-g. sample was still water insoluble. A 32% yield of the S-(*p*-chlorobenzyl)-thiuronium derivative of I was obtained from this solution.

B. With Water.—A suspension of 0.5 g. of VII in 10 ml. of water failed to develop an acid reaction in 3 days at 0°, and 0.4 g. of starting material was recovered. A 1 *N* hydrochloric acid solution was equally ineffective.

A sample of 0.5 g. (0.0027 mole) of VII was dissolved in 15 ml. of acetone, 10 drops of water added and the solution refluxed for 2 hours. Addition of an aqueous solution of S-(*p*-chlorobenzyl)-thiuronium chloride gave a nearly quantitative yield of the derivative of II, from which 0.9 g. (0.0023 mole, 90%), m.p. 179–181°, was obtained by one crystallization from water.

C. With Methanol.—A suspension of 0.5 g. of VII in 5 ml. of methanol was refluxed for 2 hours giving a clear solution. Evaporation gave material which yielded 0.8 g. (70%) of a S-(*p*-chlorobenzyl)-thiuronium derivative, m.p. 159–169°. The crystals, which melted at 176–177° after several crystallizations from water, also melted at 176–177° when mixed with the derivative of III.

D. With Aniline.—To a solution of 2.0 g. (0.011 mole) of VIII in 25 ml. of ethylene chloride 2.0 g. (0.22 mole) of aniline was added. A white solid began to form after 15 min., and after 24 hours 3.5 g. (0.0094 mole, 86%) of white crystals, m.p. 205–213°, had formed. Two crystallizations from methanol gave material, m.p. 215–217°, identical, as shown by mixed m.p., with IV.

E. With Pyridine.—After standing for 2 days at room temperature, the solvent was evaporated under reduced pressure from a solution of 1.6 g. (0.0087 mole) of VII, 50 ml. of ethylene chloride and 0.7 g. of dry pyridine. An aqueous solution of the residue yielded 72% of the S-(*p*-chlorobenzyl)-thiuronium salt of I, m.p. 190–198°. One crystallization (90% recovery) gave material with m.p. 197–200°.

When a comparable reaction mixture containing 40% less ethylene chloride stood for 9 days at 0°, 0.4 g. of VI, m.p. 229–232°, crystallized from the solution.

F. With Thiourea.—After standing for 5 days at 0°, a solution of 0.5 g. (0.0027 mole) of VII in 15 ml. of acetone containing 0.2 g. (0.0026 mole) of thiourea deposited 0.4 g. of white crystals. Partial evaporation of the acetone gave more of the same material (m.p. 230° dec.). Recrystallization from 80% methanol gave colorless crystals, m.p. 232° dec.

Anal. Calcd. for $C_9H_{12}O_3N_2S_2$: C, 41.52; H, 4.65. Found: C, 41.88; H, 5.03.

Molecular Weight of VII.—A solution of 0.125 g. of VII in 34.3 g. of benzene gave a f.p. lowering of 0.05° (mol. wt. 370). Higher concentrations could not be used due to solubility limitations. Determinations in nitrobenzene were more reliable; 0.270 g. of VII in 17.74 g. gave f.p. lowering of 0.34° (mol. wt. 310); 0.099 g. of VII in 20.33 g. gave f.p. lowering of 0.10° (mol. wt. 340).

Isolation of the β-Sultone Intermediate (B).[14]—A sulfonation reagent prepared from 23.2 g. (0.29 mole) of sulfur trioxide, 25.5 ml. of dioxane and 200 ml. of ethylene chloride was treated with a solution of 30.2 g. (0.29 mole) of styrene in 100 ml. of ethylene chloride at 0°, and the solution stirred for 30 min. The solution was then diluted with 500 ml. of hexane and the flask placed in a dry-box equipped for a low temperature crystallization. The dry-box was swept with dry nitrogen for 30 min. and the precipitate in the flask collected. The product was but slightly soluble in cold dioxane, ether, benzene, carbon tetrachloride, hexane or chloroform but dissolved in ethylene chloride or methylene chloride. It was washed with dry ether and recrystallized by dissolving in methylene chloride–pentane solution and cooling and filtering in a Dry Ice-bath in a crystallizer designed for this purpose. Samples of the crude ether-washed material and the recrystallized material were dried in vacuum at −78° and the neutral equivalent determined.

Anal. Calcd. for $C_8H_8O_3S$: neut. equiv., 184. Found: neut. equiv., 228 (crude ether-washed material); 175, 169 (recrystallized material).

A molecular weight determination was carried out by weighing 518.0 mg. in 52.98 g. of methylene chloride and observing a b.p. elevation of 0.120° (mol. wt. calcd. 184, found 215).

In two separate experiments the yield of β-sultone was estimated to be in the order of 80% by drying and weighing an aliquot of the sample precipitated.

The β-sultone was precipitated from a 0.518 mole sulfonation by addition of pentane at 0°. The pink solid was washed 3 times with pentane, added to 50 ml. of ethanol, and the mixture neutralized with 0.28 mole of sodium methoxide in methanol. The 60 g. of precipitated sodium salts were collected on a filter and washed with pentane. The filtrate and washings were combined and distilled through a 20-cm. vacuum-jacketed Vigreux column. No material boiling above 80° was obtained. The ethylene chloride layer containing pentane was also distilled. By extraction of the distillate boiling above 87° with water and saturating the aqueous solution with potassium carbonate 15.6 g. (33%) of dioxane was recovered.

Reactions of the β-Sultone (II). A. Decomposition.[14]—The solid intermediate begins to liquefy and darken within a few minutes at room temperature. Under pentane at 0° it decomposed more slowly. A sample allowed to decompose at room temperature for several days was dissolved in water filtered from a small residue and an aliquot titrated with standard base. Addition of a S-(*p*-chlorobenzyl)-thiuronium chloride solution precipitated a 46% yield (based on the acids formed by titration) of salt, m.p. 180–185°. After recrystallization from water (50% recovery) the product, m.p. 200–202°, did not depress the m.p. of an authentic sample of S-*p*-chlorobenzylthiuronium 2-phenylethene-1-sulfonate, m.p. 200–202°.

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[14] We wish to thank Dr. Richard D. Chapman for carrying out this experiment.

B. Hydrolysis.[14]—Attempts to measure the rate of hydrolysis of the β-sultone by dissolving a small sample in dry dioxane at 0° and mixing with a large volume of water at 0° (final concn. of dioxane was 2.75% by volume) pouring into a conductivity cell and measuring the resistance as rapidly as possible (initial readings may be taken in less than 30 sec.) were unsuccessful, apparently because the reaction was complete within that time.

Titration of one hydrolysate from precipitated crude β-sultone for total acids and unsaturated material indicated the presence of 17% of 2-phenylethene-1-sulfonic acid and 72% of 2-hydroxyphenylethanesulfonic acid. The presence of the latter was confirmed by isolation of its S-p-chlorobenzylthiuronium salt.

C. With Methanol.—A sample of precipitated crude β-sultone was suspended in methanol at 0° for 2 hours and dry pyridine was then added. After 4 days the solvent was removed under reduced pressure giving an oil which slowly crystallized. Crystallization from acetone gave a colorless salt which gave a S-(p-chlorobenzyl)-thiuronium salt of III m.p. and mixed m.p. 174–176°. The acetone filtrate gave salts yielding derivatives of both I and III.

Evanston, Illinois

[Contribution from the Chemical Laboratory of Northwestern University]

Sulfonation of Olefins. IV. A δ-Sultone from Styrene

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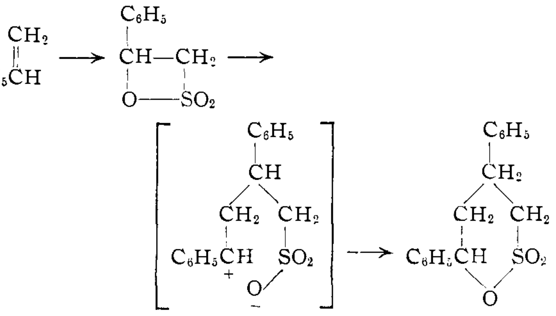
The structure 2,4-diphenyl-1,4-butanesultone (I), assigned[3] to a sultone formed in the sulfonation of styrene, has been supported by its reactions, particularly hydrogenolysis to 2,4-diphenylbutanesulfonic acid (II), the structure of which was established by an independent synthesis.

The presence of about 10% of a sultone, $C_{16}H_{16}O_3S$, described as 2,4-diphenyl-1,4-butanesultone has been mentioned in several previous papers.[3,4,5] The structure tentatively assigned (I)[4] appeared logical since the sulfonation intermediate, now believed to be a β-sultone,[5] might be expected to react with more styrene in the manner



I

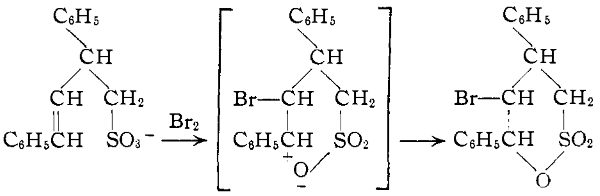
Structure I for the sultone from styrene has now been supported by hydrogenolysis to 2,4-diphenyl-1-butanesulfonic acid (II), and synthesis of the sodium salt of II by the independent route shown. Identity of the samples was established through the melting points of p-toluidine and S-benzylthiuronium salts. This synthesis establishes the carbon skeleton and point of attachment of sulfur to the carbon skeleton; it does not show the point of attachment of oxygen to the carbon chain, but this follows from the mode of formation and the reactions described below.

$$C_6H_5CH_2CH_2CH(C_6H_5)COOH \xrightarrow{LiAlH_4}$$
$$C_6H_5CH_2CH_2CH(C_6H_5)CH_2OH \xrightarrow[C_5H_5N]{SOCl_2}$$
$$C_6H_5CH_2CH_2CH(C_6H_5)CH_2Cl \xrightarrow[200^\circ]{Na_2SO_3}$$
$$C_6H_5CH_2CH_2CH(C_6H_5)CH_2SO_3^-Na^+$$

Hydrolysis of I was readily accomplished with aqueous barium hydroxide to give barium 4-hydroxy-2,4-diphenyl-1-butanesulfonate (III). Dehydration of III by pyrolysis of the salt gave barium 2,4-diphenyl-3-butene-1-sulfonate (IV). Since a comparable dehydration could be effected with sodium 2-hydroxy-2-phenylethane-1-sulfonate, but not with sodium 2-hydroxy-2-methyl-3-phenyl-1-propanesulfonate, evidence is provided for the hydroxyl of III being on the 4- rather than the 3-position.

The sultone ring was reformed by concentration of acid solutions of the salts of III *in vacuo.* The sultone I also was obtained by heating salts of III with 50% sulfuric acid. The ready formation of I from III also suggests a reactive (benzyl-type) hydroxyl, since sultone rings are usually formed from hydroxysulfonic acids only under more drastic conditions.[6]

The sultone ring also was reformed readily by reaction of IV with bromine water, giving the bromosultone V, or with chlorine water, giving a chlorosultone.



IV V

The formation of anilinium 2,4-diphenyl-4-anilino-1-butanesulfonate (VI) and the dipolar ion 2,4-diphenyl-4-protanilino-1-butanesulfonate[7] (VII)

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[1] Winthrop Chemical Company Fellow, 1945–1946.

[2] U. S. Public Health Fellow. 1947–1948.

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[5] F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, *ibid.*, **76**, 3945 (1954).

[6] T. Nilsson, Doctoral Dissertation, University of Lund, Sweden, 1946.

[7] See ref. 5 for a discussion of this nomenclature.