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]

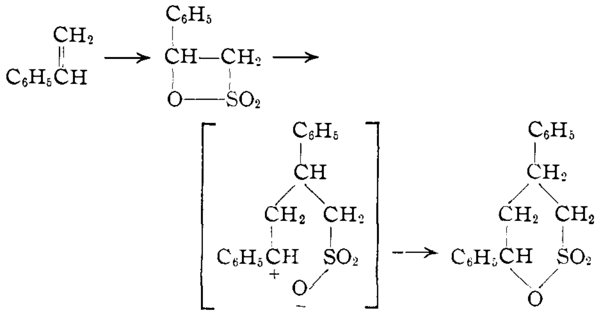
Sulfonation of Olefins. IV. A δ-Sultone from Styrene

By F. G. Bordwell, Frank B. Colton[1] and Martin Knell[2]

Received September 8, 1953

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.

$$C_6H_5CH_2CH_2CH(C_6H_5)COOH \xrightarrow{LiAlH_4}$$

$$C_6H_5CH_2CH_2CH(C_6H_5)CH_2OH \xrightarrow[C_5H_5N]{SOCl_2}$$

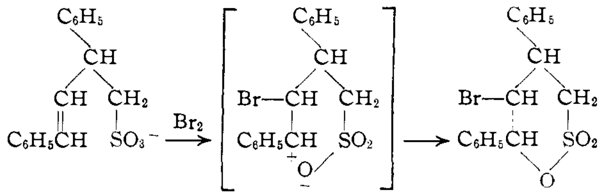
$$C_6H_5CH_2CH_2CH(C_6H_5)CH_2Cl \xrightarrow[200^\circ]{Na_2SO_3}$$

$$C_6H_5CH_2CH_2CH(C_6H_5)CH_2SO_3^-Na^+$$

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)

---

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

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

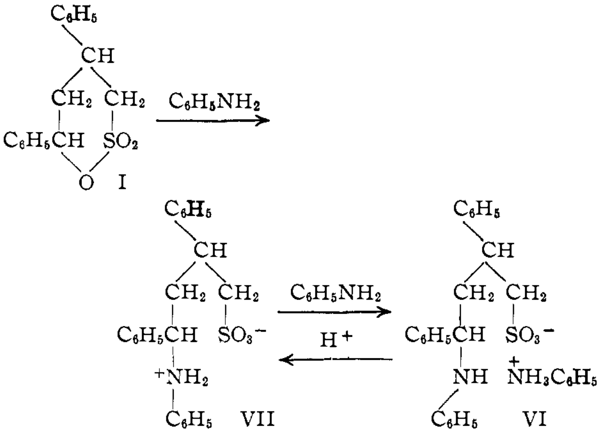
[3] F. G. Bordwell and C. S. Rondestvedt, This Journal, **70**, 2431 (1948).

[4] F. G. Bordwell, C. M. Suter, J. M. Holbert and C. S. Rondestvedt, *ibid.*, **68**, 139 (1946).

[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.



from the reaction of I with aniline has been described previously.[5]

According to the equations written for the formation of I during the sulfonation, increased yields of I would be expected from a reverse addition (sulfonating agent added to styrene), and from experiments where styrene was used in excess. Inverse addition increased the yield of I from 10 to 15%. Addition of a 1.5 molar portion of styrene to the sulfonation solution (containing styrene-β-sultone[5]) increased the yield of I (based on sulfur trioxide) to 39%. Polystyrene is also formed in these reactions, which places a practical limitation on the amount of I that can be prepared in this way.

Experimental[8]

Hydrogenolysis of 2,4-Diphenyl-1,4-butanesultone (I).—When a solution of 10.0 g. (0.035 mole) of I in 100 ml. of warm dioxane was hydrogenated under low pressure using 1.0 g. of 5% palladium-on-charcoal catalyst, the theoretical amount of hydrogen was absorbed in 9 minutes. The catalyst was removed, the filtrate neutralized by titrating with standard sodium hydroxide and the solution evaporated under reduced pressure to give the sodium salt of II.[9]

Two grams (0.0064 mole) of this salt was mixed with 1.7 g. (0.0078 mole) of phosphorus pentachloride, and after the spontaneous reaction had subsided 20 g. of ice was added. The oil was extracted with pentane. After evaporation, a solution of the residue in pentane slowly crystallized giving 0.84 g. (43%) of product, m.p. 56–64°. Several further crystallizations gave **2,4-diphenyl-1-butanesulfonyl chloride**, m.p. 67.5–68.5°.

Anal. Calcd. for $C_{16}H_{17}O_2SCl$: C, 62.22; H, 5.55. Found: C, 62.57; H, 5.76.

A solution of a sample of crude 2,4-diphenyl-1-butanesulfonyl chloride in liquid ammonia was allowed to evaporate and the oily residue dissolved in absolute alcohol. Water was added to the turbidity point, and 57% of product, m.p. 90–92°, obtained on cooling. Crystallization from alcohol–water gave 2,4-diphenyl-1-butanesulfonamide, m.p. 92–93.5°.

Anal. Calcd. for $C_{16}H_{19}O_2NS$: N, 4.84. Found: N, 4.91.

1.55 g. (0.005 mole) of the sodium salt of II was dissolved in a minimum quantity of hot water and added to a solution of 1.5 g. (0.086 mole) of S-benzylthiuronium chloride in 5 ml. of water gave 2.0 g. (93%) of material, m.p. 120–124°. After crystallization from alcohol–water and dioxane–water the sample of S-benzylthiuronium 2,4-diphenyl-1-butanesulfonate melted at 126–127°.

Anal. Calcd. for $C_{24}H_{23}O_3N_2S_2$: C, 63.19; H, 6.05. Found: C, 63.09; H, 6.08.

The oil obtained on mixing a solution of 0.97 g. (0.003 mole) of the sodium salt of II in a minimum quantity of hot water, 0.6 g. (0.0056 mole) of *p*-toluidine and 2 ml. of concd. hydrochloric acid gradually crystallized on standing. Crystallization from alcohol–water gave 0.76 g. (63%) of material, m.p. 148–154°. After two further crystallizations from alcohol–water the sample of ***p*-toluidinium 2,4-diphenyl-1-butanesulfonate** melted at 151–153°.

Anal. Calcd. for $C_{23}H_{27}O_3NS$: C, 69.49; H, 6.85. Found: C, 69.17; H, 6.80.

2,4-Diphenyl-1-butanol.—A solution of 31.1 g. (0.13 mole) of 2,4-diphenylbutyric acid, prepared by the method of Newman,[10] in 150 ml. of dry ether was added slowly to a solution of 11.0 g. (0.29 mole) of lithium aluminum hydride in 300 ml. of dry ether. The resulting product was worked up according to the procedure of Nystrom and Brown,[11] and on distillation 24.5 g. (83.5%) of 2,4-diphenyl-1-butanol, b.p. 166–167° at 2 mm., $n^{20}D$ 1.5671, was obtained.[12]

The α-naphthylurethan melted at 102–103° after crystallization from absolute alcohol and from petroleum ether.

Anal. Calcd. for $C_{27}H_{25}O_2N$: C, 82.04; H, 6.33. Found: C, 82.14; H, 6.47.

2,4-Diphenyl-1-chlorobutane.—To a solution of 18.6 g. (0.082 mole) of 2,4-diphenyl-1-butanol and 64 g. (0.082 mole) of dry pyridine in 50 ml. of dry benzene at 5°, 14.4 g. (0.121 mole) of thionyl chloride was added slowly with stirring so as to keep the temperature below 15°. The solution was allowed to come to room temperature, and then heated for 2 hours at 55–60°. The two liquid layers were poured into a mixture of 50 ml. of concentrated hydrochloric acid and 50 g. of cracked ice. The layers were separated and the benzene layer washed with 50 ml. of water, 30 ml. of saturated sodium carbonate, and again with 50 ml. of water. The water layer was extracted with benzene and the benzene layers combined, dried, and the solvent distilled. Distillation of the residue *in vacuo* gave 11.8 g. (59%) of 2,4-diphenyl-1-chlorobutane, b.p. 161.5–162° at 2 mm. An analysis of this material was 1% high in carbon so it was washed twice with 5 ml. of concentrated sulfuric acid to remove any unchanged alcohol, and then with aqueous bicarbonate and water. The material was then extracted with ether, and the extract dried and distilled, giving material boiling at 131–133° at 0.5 mm.

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00. Found: C, 79.09; H, 7.15.

Synthesis of Sodium 2,4-Diphenyl-1-butanesulfonate.—A mixture of 2.0 g. (0.0082 mole) of 2,4-diphenyl-1-chlorobutane, 5.0 g. (0.04 mole) of anhydrous sodium sulfite and 5 ml. of water was sealed in a tube and placed in a Carius furnace at 200° for 3 days, and, since two layers remained, in a rocking autoclave for 15 hours. The tube was opened (two layers still present), 15 ml. of water added and the mixture extracted with 10 ml. of ether (1.0 g. of oil was recovered from the ether layer). The water layer was evaporated with the aid of an air stream, and the residue dried in a vacuum evaporator. The salts were extracted with 30 ml. of absolute alcohol in a 2-hour reflux and the extract separated by filtration and evaporated. The resulting oil was dissolved in water and an S-benzylthiuronium salt, m.p. 124–125°, and a *p*-toluidine salt, m.p. 151–152°, prepared from aliquots of the solution. The m.p.'s of these derivatives were not depressed by mixture with the corresponding salts prepared from the hydrogenolysis of I (see above).

In a second experiment the yield of product, isolated as the S-benzylthiuronium salt, was found to be 48%.

Barium 4-Hydroxy-2,4-Diphenyl-1-butanesulfonate (III).—Thirty and eight-tenths grams (0.107 mole) of I was hydrolyzed by refluxing with an excess of 1 *M* barium hydroxide for two hours. Carbon dioxide was passed in until the excess barium hydroxide had been precipitated, and the filtrate evaporated with the aid of a stream of air. The residue was extracted with two 180-ml. portions of 95% alcohol and the combined extracts evaporated and dried to a constant weight to yield 29 g. (73%) of product. The salt was crystallized for analysis from 95% alcohol.

---

(8) Melting points are uncorrected. Microanalyses were by Miss Patricia Craig and Miss Joyce Sorenson.

(9) Since completing this investigation preparation of this compound and the corresponding *p*-toluidine salt, acid chloride and amide has been reported by W. E. Truce, D. D. Emrick and R. E. Miles, This Journal, **75**, 3359 (1953). Our melting points are in good agreement with those reported.

(10) M. Newman, *ibid.*, **62**, 870 (1940).

(11) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

(12) L. Marion, *Can. J. Research*, **16B**, 215 (1938), gives a boiling point 174–180° at 1 mm.

Anal. Calcd. for $C_{32}H_{34}O_8S_2Ba$: Ba, 18.38. Found: Ba, 17.93.

The S-benzylthiuronium and *p*-toluidine salts of this hydroxy sulfonate were not obtained as solid derivatives.

Barium 2,4-Diphenyl-3-butene-1-sulfonate (IV).—Direct pyrolysis of barium 4-hydroxy-2,4-diphenyl-1-butanesulfonate (III) at 160° for 3 hours gave somewhat greater than 30% conversion to IV, as indicated by the 30% yield of bromosultone formed by treatment with bromine water (see below). Similar results were obtained by refluxing a toluene suspension for 3 hours. The S-benzylthiuronium and *p*-toluidine salts of IV could be obtained from this mixture. After crystallization from aqueous methanol and ethanol solutions, the S-benzylthiuronium salt of IV melted at 172–173°.

Anal. Calcd. for $C_{24}H_{26}O_3N_2S_2$: C, 63.41; H, 5.76. Found: C, 63.88; H, 5.73.

Conversion of I to IV was best effected by pyrolysis of the *p*-toluidine salt. A 31.7-g. (0.11 mole) sample of I was hydrolyzed with 1 *N* sodium hydroxide by refluxing for one hour and excess concentrated hydrochloric acid and 15 g. (0.14 mole) of *p*-toluidine added. The resulting oil was separated and 18 ml. of water distilled off. Crystallization of the residue from alcohol gave 16.4 g. of the *p*-toluidine salt of IV. The alcohol filtrate was evaporated and the resulting residue again pyrolyzed. Crystallization of the residue from alcohol gave an additional 8.4 g. of *p*-toluidine salt of IV (total yield 57%), m.p. 220–222°.

Anal. Calcd. for $C_{23}H_{25}O_3NS$: neut. equiv., 396. Found: neut. equiv., 399, 397.

Formation of I from III.—Treatment of an aqueous solution of barium 4-hydroxy-2,4-diphenyl-1-butanesulfonate (III) with an equivalent amount of aqueous sulfuric acid and evaporation of the filtrate under vacuum gave up to 85% yield of I. Evaporation of concentrated hydrochloric acid from the barium salt gave up to 75% yields. Heating a solution of the sodium or barium salt of III for a few minutes in 50% sulfuric acid at the boiling point also produced about 80% of I. Samples containing IV gave much lower yields, only 14% of I being obtained from a mixture of III and IV containing a minimum of 30% of IV, and 6% was formed from a mixture containing at least 80% of IV (yield of bromosultone obtained on treatment with bromine water).

2,4-Diphenyl-3-bromo- and 3-Chloro-4-butanesultones.—Immediate colorless precipitates were formed by addition of bromine water to acetone–water solutions containing IV. The yields of bromosultone from the barium salt pyrolysis products varied from 30–80%, m.p. 197–199° (crude products). Four crystallizations from aqueous acetone gave material melting at 204.5–205.0°.

Anal. Calcd. for $C_{16}H_{15}O_3SBr$: C, 52.33; H, 4.12. Found: C, 52.72; H, 4.04.

Treatment of aqueous solutions of the barium salt of IV with chlorine gave **2,4-diphenyl-3-chloro-1,4-butanesultone** in somewhat lower yields. After several crystallizations from aqueous acetone the material melted at 199–201°.

Anal. Calcd. for $C_{16}H_{15}O_3SCl$: C, 59.53; H, 4.68. Found: C, 59.38; H, 4.74.

Formation of I in Sulfonations Using Excess Styrene.[13]—From the sulfonation solution prepared[5] from 10.3 g. (0.129 mole) of sulfur trioxide, 11.4 g. (0.130 mole) of dioxane, 13.5 g. (0.129 mole) of styrene and 104.2 g. of ethylene chloride, a portion of 69.8 g. (presumably containing 0.0646 mole of β-sultone) was added to 7.9 g. (0.099 mole) of styrene, and a portion of 69.6 g. (containing 0.0644 mole of β-sultone) was added to 14.1 g. (0.176 mole) styrene. After standing at 0° for 21 days, these mixtures were added to cold water. The ethylene chloride layers were separated, washed with water and evaporated at room temperature with the aid of an air jet. From the mixture containing the 0.5 molar additional portion of styrene a crystalline solid was obtained, but the solution containing a 1.7 molar additional portion of styrene gave a heavy oil. Both of these products were dissolved in acetone, and water added carefully until precipitation of the less soluble constituent (polystyrene) was complete. Addition of a further quantity of water to each solution gave I; 7.2 g. (39%) from the 1.5 molar styrene run and 6.3 g. (34%) from the 2.7 molar run. The melting point of I (152–153° reported[4]) was found to depend appreciably on the rate of heating.

---

[13] This experiment was carried out by C. S. Rondestvedt and M. L. Peterson.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

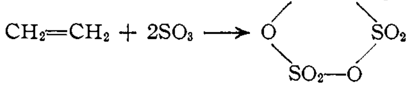
Sulfonation of Olefins. V. Formation of a Cyclic Sulfonate-Sulfate Anhydride Intermediate

BY F. G. BORDWELL AND MARVIN L. PETERSON[1]

RECEIVED FEBRUARY 22, 1954

The sulfonation of 1-hexene with an equimolar quantity of dioxane–sulfur trioxide reagent followed by hydrolysis gave 2-hydroxy-1-hexanesulfonic acid as the principal product. Evidence is presented to show that this material probably arises from the hydrolysis of a β-sultone B and to a lesser extent a cyclic sulfonate–sulfate anhydride I. Reaction of this sulfonation mixture with aniline (instead of water) gave the aniline salt of 2-anilino-1-hexanesulfonic acid, $n\text{-}C_4H_9CH(NHC_6H_5)CH_2SO_3^{-}\,{}^{+}NH_3C_6H_5$; with pyridine the dipolar ion, $CH_3CH_2CH_2CH_2CH({}^{+}NC_5H_5)CH_2SO_3^{-}$, was formed. These products are believed to arise by reactions with B. When an excess of dioxane or two moles of sulfonating agent was used, compound I became the principal intermediate and hydrolysis gave a good yield of 2-hydrosulfato-1-hexanesulfonic acid (II). Reaction of I with aniline occurred with fission of the sulfonate–oxygen bond rather than the sulfate–oxygen bond.

The formation of the cyclic sulfonate–sulfate anhydride "carbyl sulfate" from ethylene and sulfur



trioxide was observed at a very early date.[2] Since that time only one other compound of this type appears to have been isolated,[3] but such compounds have been suggested as intermediates in a number of olefin sulfonations.[4] The evidence for cyclic sulfonate–sulfate anhydrides as olefin sulfonation intermediates is rather meager, being based on the formation of β-hydroxysulfonic acids on hydrolysis of the reaction mixtures, and isolation of salts analyzing as the hydrogen sulfate esters of β-hydroxysulfonic acids from the sulfonation of 1-nonene[4b] and *p*- and *m*-nitrostyrenes.[4c] For styrene, itself, it has been shown that the major portion of the β-hydroxy sulfonic acid was formed by hydrolysis of

---

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

[2] H. V. Regnault, *Ann.*, **25**, 32 (1838); A. Michael and N. Weiner, THIS JOURNAL, **58**, 294 (1936).

[3] C. M. Suter and F. G. Bordwell, *ibid.*, **65**, 507 (1943).

[4] (a) H. Pepouse, *Bull. soc. chim. Belg.*, **34**, 133 (1925); (b) C. M. Suter, P. B. Evans and J. M. Kiefer, THIS JOURNAL, **60**, 538 (1938); (c) W. E. Truce and P. F. Gunberg, *ibid.*, **72**, 2401 (1950).