

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-butanefulfonate (III) at 160° for 3 hours gave somewhat greater than 30% conversion to IV, as indicated by the 30% yield of bromosulfone 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-butanefulfonate (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

bromosulfone obtained on treatment with bromine water).

2,4-Diphenyl-3-bromo- and 3-Chloro-4-butanefulfones.—Immediate colorless precipitates were formed by addition of bromine water to acetone–water solutions containing IV. The yields of bromosulfone 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 $C_{16}H_{18}O_3SBr$: 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-butanefulfone in somewhat lower yields. After several crystallizations from aqueous acetone the material melted at 199–201°.

Anal. Calcd. for $C_{16}H_{18}O_3SCl$: 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 prepared⁶ 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 -sulfone) was added to 7.9 g. (0.099 mole) of styrene, and a portion of 69.6 g. (containing 0.0644 mole of β -sulfone) 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° reported⁴) 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]

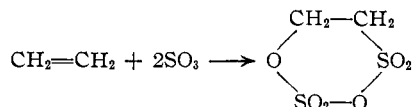
Sulfonation of Olefins. V. Formation of a Cyclic Sulfonate-Sulfate Anhydride Intermediate

BY F. G. BORDWELL AND MARVIN L. PETERSON¹

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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 -sulfone 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, $n-C_4H_9CH(NHC_6H_5)CH_2SO_3^- + NH_3C_6H_5$; with pyridine the dipolar ion, $CH_3CH_2CH_2CH_2CH(+NC_6H_5)CH_2SO_3^-$, 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

(1) Procter and Gamble Research Fellow, 1948–1951.

(2) H. V. Regnault, *Ann.*, **25**, 32 (1833); A. Michael and N. Weiner, *THIS JOURNAL*, **58**, 294 (1936).

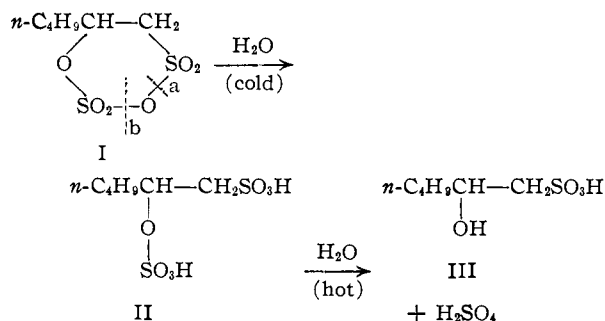
(3) C. M. Suter and F. G. Bordwell, *ibid.*, **65**, 507 (1943).

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 -hydroxy-sulfonic 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

(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).

a β -sultone rather than a sulfonate-sulfate anhydride.^{5,6} Furthermore, with styrene, use of an additional mole of sulfonating agent gave an increased yield of unsaturated sulfonic acid rather than the anhydride.^{4,7} In view of this it was decided to make a more careful investigation of an unbranched α -olefin; 1-hexene was chosen.

In the reaction of 1-hexene at 0° with twice the molar quantity of dioxane-sulfur trioxide reagent about 50% of the sulfonating reagent remained unreacted after 1.5 hr., as indicated by the quantity of sulfate ion formed by pouring the reaction mixture into ice-water. After 14 hr. at 0° only about 25% of the reagent remained, and after an additional 4 hr. at room temperature 10% was left. An additional 24 hr. at room temperature reduced the amount to about 5%. Heating the hydrolysate from the latter on the steam-bath for 48 hr. liberated an additional 45% of the original sulfur trioxide used, as sulfate. A comparable sulfonation mixture which had stood for 42 hr. was hydrolyzed with cold water and neutralized with sodium carbonate. Concentration gave the disodium salt of 2-hydrosulfato-1-hexanesulfonic acid (II), which on acid hydrolysis gave 2-hydroxy-1-hexanesulfonic acid (III) and the theoretical quantity of sulfuric acid. These results indicate that 1-hexene reacts rapidly with one mole of sulfonating agent giving an intermediate (presumably B) which reacts slowly with a second mole of sulfonating agent to give the sulfonate-sulfate anhydride (I) as the major product (80–90%), the minor product being 2-hexene-1-sulfonic acid (IV). The anhydride I was hydrolyzed rapidly by cold water to II, which can be hydrolyzed like other alkyl hydrogen sulfates by heating in acidic solution, the products in this instance being sulfuric acid and III. The struc-



ture of III was established by comparison of its S-(*p*-chlorobenzyl)-thiuronium salt with a similar derivative prepared from the sulfonate obtained by the reaction of 1-chloro-2-hexanol and aqueous sodium sulfite.

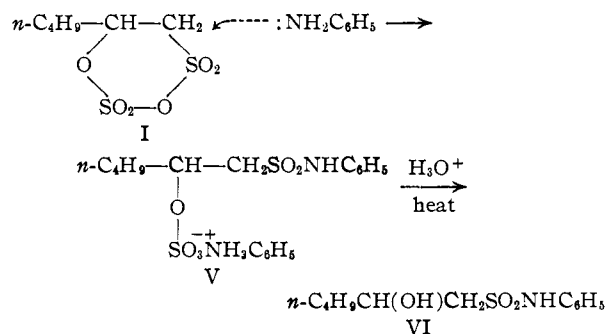
In view of the formation of II, the point of attack of water in the hydrolysis of I must be at a sulfur-oxygen rather than the carbon-oxygen bond, but no information as to which of the two anhydride type sulfur-oxygen bonds is broken (fission at a or b) can be gained from this experiment. In order to

(5) F. G. Bordwell and C. S. Rondvestedt, *THIS JOURNAL*, **70**, 2428 (1948).

(6) F. G. Bordwell, M. L. Peterson and C. S. Rondvestedt, *ibid.*, **76**, 3945 (1954).

(7) Marvin L. Peterson, Doctoral Dissertation, Northwestern University, 1951.

study this point further the reaction of I with aniline was investigated. Treatment of the ethylene chloride solution containing I with aniline gave 65% of the anilinium salt of 2-hydrosulfato-1-hexanesulfonanilide (V). The structure of V is indicated by its conversion on acid hydrolysis to 2-hydroxy-1-hexanesulfonanilide (VI) and its reaction with alkali to give 1-hexenesulfonanilide. Formation of V shows that attack on I must have occurred at the sulfonate rather than the sulfate anhydride link. The product from the latter mode of action would have been anilinium 2-(*N*-phenylsulfamoyl)-1-hexanesulfonate, $n\text{-C}_4\text{H}_9\text{CH}(\text{OSO}_2\text{NHC}_6\text{H}_5)\text{CH}_2\text{SO}_3^-\text{NH}_3^+\text{C}_6\text{H}_5$, which on acid hydrolysis would have given III rather than VI.



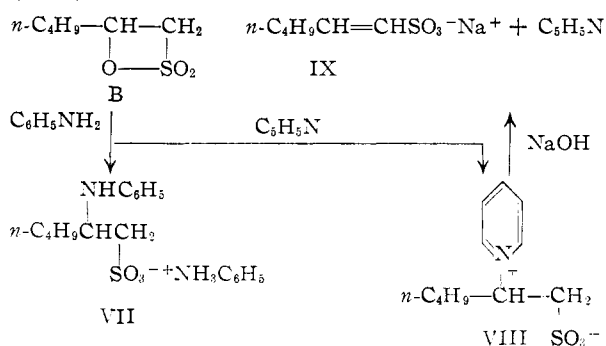
By analogy, hydrolysis of I probably involves attack by water at the sulfonate link (fission at a).

It seemed possible that I might act as a sulfonating agent, but no reaction was observed when I was allowed to stand with 1-hexene for 18 hours at room temperature.

Addition of 1-hexene to an equimolar quantity of sulfonating agent also gave some I, as was shown by the isolation of a derivative of II on hydrolysis of the reaction mixture. As determined from the amount of sulfuric acid formed on acid hydrolysis, 18% of I was formed. A titration for unsaturation indicated the presence of 15–20% of 2-hexene-1-sulfonic acid (IV). 2-Hydroxy-1-hexanesulfonic acid (III) was also shown to be present under conditions where II is not hydrolyzed, and probably represents the remainder of the product. Addition of the sulfonating agent to the 1-hexene (reverse addition) reduced the amount of I formed from 18% to less than 5%.

On the basis of the evidence gained in the sulfonation of styrene,^{5,6} III is formed in the sulfonations using equimolar quantities of reactants by hydrolysis of a β -sultone intermediate (B). The evidence presented above shows that, at most, 5–18% of III may arise from the hydrolysis of I in this reaction. In support of the hypothesis of a β -sultone intermediate, it was found that the intermediate present in the sulfonation solution from reactions with equimolar quantities of reagents underwent reactions similar to those attributed to styrene β -sultone.⁶ Thus, (1) the amount of unsaturated product, 2-hexene-1-sulfonic acid (IV) was increased by heating the sulfonation solution, (2) reaction of the sulfonation solution with aniline gave the aniline salt of 2-anilino-1-hexanesulfonic acid (VII), $n\text{-C}_4\text{H}_9\text{CH}(\text{NHC}_6\text{H}_5)\text{CH}_2\text{SO}_3^-\text{NH}_3^+\text{C}_6\text{H}_5$, and (3) reaction of the sulfonation solution with pyridine

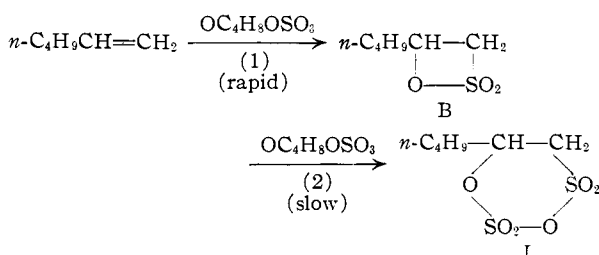
gave 2-(1-proto-1-pyridyl)-1-hexanesulfonate (VIII).⁸



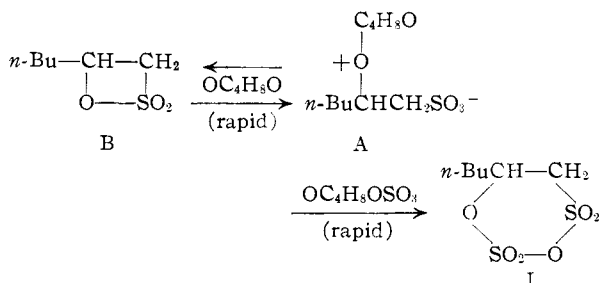
The structure of VIII was supported by a quantitative reaction with aqueous sodium hydroxide giving pyridine and sodium 1-hexene-1-sulfonate (IX). The latter was shown to differ from the isomeric salt, 2-hexene-1-sulfonic acid (IV), through their derivatives, and by the fact that IX alone gave large amounts of sulfate ion when oxidized with potassium permanganate. The structure of IV was established by the formation of *n*-butyraldehyde on ozonolysis.

It appears from the above data that 1-hexene reacts rapidly (about 90% in 1.5 hr. at 0°) with one mole of dioxane-sulfur trioxide to give a β -sulfone intermediate (B). The latter reacts slowly with an additional mole of sulfonating agent to give the cyclic sulfonate-sulfate anhydride I.

Dioxane was found to have a very marked accelerating effect on the rate of reaction 2 since use of



a 6.4:1 instead of a 1:1 molar ratio of dioxane increased the yield of I in a sulfonation with equimolar quantities of 1-hexene and sulfur trioxide from 18 to 34% (68% of the sulfur trioxide). Bromine titration of the organic layer in this experiment showed that 38% of the 1-hexene remained unreacted. Also, when a two molar portion of sulfur trioxide was used for one of olefin, the presence of excess dioxane diminished the amount of unreacted sulfonating agent present after 1.5 hours at 0° from



(8) See ref. 6 for a discussion of this nomenclature.

about 50% to about 20%.⁹ One interpretation of these results is that dioxane reacts rapidly with B to give an intermediate A, which can react more rapidly with the sulfonating agent than does B.

Omission of dioxane entirely from the sulfonating agent caused extensive polymerization.

Experimental¹⁰

Reaction of 1-Hexene with Two Moles of Sulfonating Agent.—To the dioxane-sulfur trioxide reagent prepared⁸ from 16.0 g. (0.200 mole) of sulfur trioxide, 17.6 g. (0.200 mole) of dioxane and 237 g. of ethylene chloride was added at 0°, 8.4 g. (0.100 mole) of 1-hexene. Samples (1–4) were removed after: (1) 1.5 hr. at 0°, (2) 14 hr. at 0°, (3) 14 hr. at 0° and 4 hr. at 20°, (4) 14 hr. at 0° and 24 hr. at 20°. The samples were hydrolyzed by shaking with ice-water until the acids were removed. The aqueous solutions were titrated for total acid content, and an aliquot titrated for unsaturation (by the bromide-bromate method). Barium sulfate was precipitated from the neutral solution. Table I lists the results for the 4 samples. The total sulfur trioxide accounted for is the percentage found as sulfuric acid plus monobasic acids (determined from the total acid titer and the quantity of barium sulfate precipitated) divided by the moles of sulfur trioxide in the aliquot. The hydrolysis of the sulfonate-sulfate anhydride I is not instantaneous, and three or more washings of the ethylene chloride layer were necessary to remove most of the acids. Some hydrolysis of the hydrogen sulfate ester no doubt occurs during these washings, so the amount of unreacted sulfonating agent represented by the barium sulfate is probably a maximum. An independent check on the experiment⁹ using an 8% excess of dioxane gave a value of 48% instead of 61% for the amount of unreacted sulfonating agent. Under these same conditions, use of a tenfold excess of dioxane gave only 19% of barium sulfate.

TABLE I
APPROXIMATE RATE OF FORMATION OF THE SULFONATE-SULFATE ANHYDRIDE (I) FROM 1-HEXENE

Sample no.	Mole SO ₃	Equiv. of acid	% SO ₃ as BaSO ₄	Unsatd. acid, %	% SO ₃ accounted for
1	0.0454	0.0689	61	17	91
2	.0454	.0538	26	15	92
3	.0227	.0221	11	16	87
4	.0227	.205	4	20	87

After the sulfate had been precipitated from the neutral aqueous solution of sample 4, it was acidified with hydrochloric acid and heated on the steam-bath for 48 hr., during which 2.327 g. (44% of the sulfur trioxide) of barium sulfate precipitated.

In a comparable experiment 9.8 g. (0.117 mole) of 1-hexene was added to the reagent prepared from 18.7 g. (0.234 mole) of sulfur trioxide, 20.6 g. (0.234 mole) of dioxane and 170 g. of ethylene chloride. After this mixture had stood for 18 hr. at 0°, and 24 hr. at 20°, it was hydrolyzed in cold water. The aqueous solution was neutralized with sodium carbonate. Addition of barium chloride precipitated 0.94 g. (2%) of barium sulfate. Evaporation of the filtrate yielded 37.2 g. of colorless crystalline sodium salts. Titration of a portion of these salts with bromide-bromate indicated the presence of 12% of unsaturated sulfonates. In order to get a sharp end-point in this titration excess bromate was used, and the solution was allowed to stand for several hours. Potassium iodide was then added, and the iodine liberated was titrated with standard thiosulfate solution.

Recrystallization of the sodium salts from 90% alcohol gave 27.8 g. (78%) of white crystals, which were saturated to bromine water. A sample of 3.632 g. (0.0119 mole) of recrystallized salt was hydrolyzed for 30 hr. with 1 N hydrochloric acid containing barium chloride at steam-bath tem-

(9) We wish to thank Mr. C. E. Osborne for carrying out this experiment.

(10) Melting points are uncorrected. Microanalyses were by Miss Joyce Sorenson.

perature giving 2.914 g. (0.0125 mole, 105%) of barium sulfate. Concentration of the solution and addition of S-(*p*-chlorobenzyl)-thiuronium chloride gave a derivative, which after one crystallization from water melted at 138–139°, and did not depress the melting point of a synthetic sample¹¹ of S-(*p*-chlorobenzyl)-thiuronium 2-hydroxy-1-hexanesulfonate (m.p. 138–139°). The yield of recrystallized derivative was 64%.

A sample of 1.5 g. of the sodium salt gave 2.8 g. (87%) of the bis-S-(*p*-chlorobenzyl)-thiuronium salt of 2-hydrosulfato-1-hexanesulfonic acid, m.p. 138–144°. An analytical sample, m.p. 145–146°, was obtained after three recrystallizations from water.

Anal. Calcd. for $C_{22}H_{31}O_7N_4S_4Cl_2$: N, 8.46. Found: N, 8.53.

Reaction of I with Aniline.—Twenty and five-tenths grams (0.245 mole) of 1-hexene was added to the sulfonating agent prepared from 39.1 g. (0.489 mole) of sulfur trioxide, 43.0 g. (0.489 mole) of dioxane and 100 ml. of ethylene chloride. After standing for 48 hr. at 0°, one-half the reaction mixture was treated, while cooling in an ice-bath, with 22.9 g. (0.246 mole) of aniline in 50 ml. of ethylene chloride. After standing for 2 days at 0°, 28.8 g. (54%) of colorless crystals of V, m.p. 140–151°, had separated from the yellow solution. The salt was recrystallized from water; its m.p. varied with the rate of heating. An additional 10% of the anilinium salt of 2-hydrosulfato-1-hexanesulfonanilide (V) was recovered from the original filtrate.

Anal. Calcd. for $C_{18}H_{26}O_6N_2S_2$: C, 50.21; H, 6.09. Found: C, 49.98, 50.73; H, 6.08, 6.16.

When a 2.8-g. portion of this salt was dissolved in 2 *N* hydrochloric acid and the solution heated to the boiling point, an oil separated rapidly. On cooling 1.6 g. (96%) of colorless crystals, m.p. 80–84°, was obtained. This material was insoluble in cold water, but dissolved rapidly in cold aqueous sodium hydroxide and was reprecipitated when the solution was acidified. It was recrystallized from aqueous alcohol to give 2-hydroxy-1-hexanesulfonanilide, m.p. 83–84°.

Anal. Calcd. for $C_{12}H_{18}O_3NS$: C, 56.23; H, 7.07. Found: C, 56.48, 56.68; H, 7.20, 7.38.

When the anilinium salt of 2-hydrosulfato-1-hexanesulfonanilide (V) was heated in neutral aqueous solution for 12 hr. on the steam-bath, no sulfate ion was released. A 0.918-g. sample heated for 18 hr. on the steam-bath in 1 *N* hydrochloric acid containing barium chloride gave 0.493 g. (99.4%) of barium sulfate.

A solution of 2.3 g. (0.0052 mole) of V in 25 ml. of 1 *N* sodium hydroxide was heated on the steam-bath for 90 min. Neutralization of the solution with hydrochloric acid gave 1.2 g. (0.005 mole, 96%) of yellow crystals, m.p. 41–47°; the filtrate gave barium sulfate on addition of barium chloride. The sample was decolorized and crystallized from aqueous alcohol. After three crystallizations the sample of 1-hexene-1-sulfonanilide melted at 51–52°.

Anal. Calcd. for $C_{12}H_{17}O_2NS$: C, 60.22; H, 7.16. Found: C, 60.17, 60.79; H, 7.31, 6.66.

Attempted Reaction of I with 1-Hexene.—A sulfonating reagent prepared from 54.9 g. (0.686 mole) of sulfur trioxide, 60.4 g. (0.686 mole) of dioxane and 150 ml. of ethylene chloride was treated with 28.8 g. (0.343 mole) of 1-hexene and allowed to stand for 15 hours at 10° and 6 hours at 25°. An additional 28.8 g. of 1-hexene was then added and the mixture allowed to stand for 18 hr. at room temperature. The mixture was hydrolyzed with water, neutralized with sodium carbonate, and the aqueous layer separated and evaporated under reduced pressure to give 99.3 g. (95%) of sodium salts.

The ethylene chloride layer was dried over sodium sulfate and then distilled through a 20-cm. vacuum-jacketed Vigreux column. A fraction of 27.7 g. of 1-hexene boiling over the range 63–66° was recovered, corresponding to 96% of the olefin added to I.

Sulfonation of 1-Hexene with One Mole of Sulfonating Agent.—A 36.4-g. (0.434 mole) portion of 1-hexene was slowly added to a sulfonating reagent consisting of 34.7 g. (0.434 mole) of sulfur trioxide, 38.2 g. (0.434 mole) of dioxane and 161.5 g. of ethylene chloride. After standing for

15 min. a portion of 59.8 g. (containing the products from 0.0956 mole of sulfur trioxide) was hydrolyzed in ice-water. The aqueous solution was neutralized by 0.0940 equivalent of sodium hydroxide. Barium chloride was added to a portion of the neutralized solution precipitating 0.00771 mole (8%) of barium sulfate. When this filtrate was acidified and digested for 18 hours on the steam-bath, an additional 0.01721 mole (18%) of barium sulfate was precipitated.

When the volume of the remainder of the aqueous solution was reduced to 20 ml., 1.4 g. of white crystals separated, which gave an S-(*p*-chlorobenzyl)-thiuronium salt melting at 134–137° without further crystallization. A mixture of this salt with an authentic sample of S-(*p*-chlorobenzyl)-thiuronium 2-hydroxy-1-hexanesulfonate (m.p. 138–139°) melted at 135–138°.

Addition of 50 ml. of ethanol to the aqueous filtrate precipitated a second crop which gave the derivative of sodium 2-hydroxy-1-hexanesulfonate. Evaporation to 10 ml. gave a third crop of crystals, and complete evaporation gave a salt from which an S-(*p*-chlorobenzyl)-thiuronium salt, m.p. 145–147° (after two crystallizations from water), was prepared which was identical with that prepared from sodium 2-sodiosulfato-1-hexanesulfonate.

The amount of unsaturated sulfonic acid in sulfonations under these conditions was 15–20% (bromate–bromide titration). Of the sulfur trioxide used, 8% was accounted for as sulfate (probably unreacted reagent), 36% as sulfonate-sulfate anhydride I, and 15–20% as 2-hexene-1-sulfonic acid (IV). 2-Hydroxy-1-hexanesulfonic acid, which was also shown to be present, probably accounts for the remaining 36–40%.

A comparable sulfonation, except that the sulfonating agent was added to a solution of 1-hexene in ethylene chloride, gave only 3% of sulfuric acid on acid hydrolysis of the products.

Effect of Excess Dioxane on the Equimolar Sulfonation.—To the sulfonating reagent prepared from 11.2 g. (0.140 mole) of sulfur trioxide, 79.3 g. (0.902 mole) of dioxane and 100.2 g. of ethylene chloride, 11.8 g. (0.140 mole) of 1-hexene was added at 0°. After standing for 30 min. the mixture was hydrolyzed with cold water. Titration of the aqueous layer with sodium hydroxide showed the presence of 0.142 equivalent of acid, and bromate–bromide titration showed 0.0114 mole (8%) of unsaturated acid. From the neutral solution 0.0055 mole (4%) of barium sulfate was precipitated. When the solution was acidified and digested on the steam-bath for 18 hours, an additional 0.0480 mole (34%) of barium sulfate was precipitated. Since 38% of the sulfur trioxide which was added was obtained as sulfate, this quantity of olefin also remained unreacted and thus 15% of the olefin reacting formed unsaturated sulfonate. The ethylene chloride layer contained 38% of unreacted 1-hexene as indicated by a bromine titration. Since the accuracy in these experiments is probably no better than 5–10%, this is a fortuitous result.

Formation of 2-Hexene-1-sulfonic Acid (IV).—An equimolar sulfonation mixture containing 0.366 molar quantities of reactants was divided into two portions. The first portion, containing 0.106 mole of reactants, was hydrolyzed with water, and found to contain 19% of unsaturated sulfonic acids. A second portion, containing 0.0752 mole of reactants, was heated to 60° for 2 hr. and then hydrolyzed with water. Analysis of this product showed the presence of 0.0615 equivalent of acids, 0.0032 mole (4%) of sulfuric acid and 0.0323 mole (43%) of unsaturated sulfonic acids. The solution was neutralized with barium carbonate, and the filtrate concentrated to give 4 crops of barium salts of the following weights and percentage unsaturation: (1) 0.85 g. (99%), (2) 1.29 g. (89%), (3) 2.38 g. (65%) and (4) 5.78 g. (43%). The end-point in the bromate–bromide titration of these samples was not sharp (as it is for titration of α,β -unsaturated sulfonic acids), and analyses were made by adding excess bromate, allowing the solution to stand for several hours, adding potassium iodide and back-titrating with thiosulfate. The samples gave only slight tests for sulfate after oxidation with potassium permanganate, indicating the presence of only small amounts of barium 1-hexenesulfonate.

A quantitative experiment with sodium 1-hexene-1-sulfonate showed 75% of sulfate to be formed by oxidation under these conditions. From the amount of sulfate obtained on oxidation of the sulfonates obtained after heating the sulfonation mixture, it is estimated that the unsaturated

(11) R. S. Schiefelbein, Doctoral Dissertation, Northwestern University, 1951.

sulfonates consist of about 10% of 1-hexene- and 90% of 2-hexene-1-sulfonate.⁹

From 0.68 g. of the first crop of barium salts dissolved in 15 ml. of water a 55% yield of an S-(*p*-chlorobenzyl)-thiuronium derivative, m.p. 126–130°, was obtained. After three recrystallizations from hot water the sample of S-(*p*-chlorobenzyl)-thiuronium 2-hexene-1-sulfonate melted at 130–131°, and its mixed m.p. with S-(*p*-chlorobenzyl)-thiuronium 2-hydroxy-1-hexanesulfonate (m.p. 138–139°) was 116–123°.

Anal. Calcd. for C₁₄H₂₁O₃N₂S₂Cl: C, 46.08; H, 5.80. Found: C, 46.36; H, 5.82.

A portion of the fourth crop was converted to the sodium salt in aqueous solution with an equimolar quantity of sodium sulfate. Crystallization of the sodium salt from 90% alcohol gave a salt which was only slightly unsaturated, and which gave an S-(*p*-chlorobenzyl)-thiuronium salt melting at 135–137°, which did not depress the m.p. of that of 2-hydroxy-1-hexanesulfonate.

When a sulfonation mixture comparable to that above was allowed to stand for 40 hours at room temperature and then refluxed for 1 hour, the amount of unsaturated sulfonic acids was 59%. Five crops of crystalline barium salts were collected: (1) 1.7 g. (98% unsaturated), (2) 3.0 g. (95%), (3) 2.0 g. (79%), (4) 6.5 g. (90%) and (5) 9.6 g. (60%).

A slow stream of ozone was passed into a solution of 0.649 g. of the first crop in 50 ml. of acetic acid for 25 min. The solution was then added to 150 ml. of water containing 0.5 g. of zinc dust. The zinc dust was removed, the solution brought almost to the neutral point with sodium hydroxide and 0.75 g. of 5,5-dimethyldihydroresorcinol in 5 ml. of alcohol added. On cooling, 17% of derivative identical with that from *n*-butyraldehyde (m.p. 133–134°) was obtained. The sodium salt gave 33% of the crude derivative under comparable conditions.

The Aniline Salt of 2-Anilino-1-hexanesulfonic Acid (VII).—The sulfonation mixture, prepared by adding 21.5 g. (0.256 mole) of 1-hexene to 20.5 g. (0.256 mole) of sulfur trioxide, 22.6 g. (0.256 mole) of dioxane and 75 ml. of ethylene chloride, was allowed to stand for 30 min. at 0°, and then cautiously treated at 0° with 50.0 g. (0.538 mole) of aniline. After standing for 2 days 20.6 g. (23%) of colorless solid, m.p. 105–110°, separated from the yellow solution (analysis by hydrolysis suggests the presence of only about 40% of 1-hexene- β -sultone, so this is a 57% yield on this basis). Recrystallization of this aniline salt failed to raise the melting point. A portion of the salt was heated with aqueous sodium hydroxide to remove the aniline. The aniline-free solution was acidified with hydrochloric acid and a saturated aqueous S-(*p*-chlorobenzyl)-thiuronium chloride solution was added. Recrystallization gave S-(*p*-chlorobenzyl)-thiuronium 2-anilino-1-hexanesulfonate, m.p. 143–144°.

Anal. Calcd. for C₂₀H₂₅O₃N₂S₂Cl: C, 52.44; H, 6.16. Found: C, 52.40; H, 6.24.

2-(1-Proto-1-pyridyl)-1-hexanesulfonate (VIII).—A sulfonation mixture containing 75 ml. of ethylene chloride, 15.8 g. (0.197 mole) of sulfur trioxide, 17.4 g. (0.198 mole) of dioxane and 16.6 g. (0.197 mole) of 1-hexene was allowed

to stand for 30 min. at 0° and then treated with 31.6 g. (0.400 mole) of dry pyridine. After this solution had stood for 2 weeks at room temperature, it had turned red-brown and 7.7 g. of a slightly yellow crystalline solid, m.p. 245–250°, had precipitated, which was free of pyridinium sulfate. Addition of 30 ml. of ethylene chloride to the filtrate precipitated an additional 4.6 g. of VIII, which was contaminated with 15% of pyridinium sulfate. This sample of VIII was 81% pure as judged by treatment with aqueous sodium hydroxide and titration with bromate–bromide (see below). Addition of another 50 ml. of ethylene chloride produced 1.6 g. of solid, which analysis showed to consist of 30% pyridinium sulfate and 70% of VIII. Concentration to a small volume gave 2.0 g. of pure pyridinium sulfate.

The organic solvent was completely removed under reduced pressure to give a dark red oil, which was hydrolyzed with water. The hydrolysate was neutralized with barium carbonate. The residue yielded 4.9 g. of barium sulfate. The filtrate contained 50–60% of unsaturated barium sulfonates, but pure products or derivatives were not obtained from these.

A total of 0.052 mole (27%) of VIII was accounted for. Assuming the presence of about 40% of 1-hexene- β -sultone in the sulfonation mixture (see above), this is a 67% yield. A total of 17% of hydrolyzable sulfate and 27% of unsaturated sulfonates (presumably pyridinium 2-hexene-1-sulfonate) were also present.

The first crop of VIII was recrystallized from a mixture of ethanol and acetone (it is very slightly soluble in acetone) to give material melting at 250–251°.

Anal. Calcd. for C₁₁H₁₇O₃NS: C, 54.29; H, 7.04; neut. equiv., 243. Found: C, 54.14, 54.85; H, 7.02, 7.24; neut. equiv., 247.

In the determination of the neutral equivalent a sample of VIII was heated for 30 min. with about 0.2 *N* standard sodium hydroxide and then back-titrated with standard hydrochloric acid. Titration of an aliquot of this solution with bromate–bromide gave a sharp end-point (characteristic of α,β -unsaturated sulfonates), and 97% of the theory was consumed.

A portion of the aqueous solution was oxidized with potassium permanganate, the manganese dioxide removed in acid solution by adding 30% hydrogen peroxide, and barium chloride added. A copious precipitate of barium sulfate was obtained, which is not the case for β,γ -unsaturated sulfonates,³ such as salts of 2-hexene-1-sulfonic acid (see above).

Another aliquot of the solution was treated with S-(*p*-chlorobenzyl)-thiuronium chloride solution to give a 67% yield of salt. The sample of S-(*p*-chlorobenzyl)-thiuronium 1-hexene-1-sulfonate melted at 135–136° after recrystallization from water. The m.p. of a mixture of this salt with S-(*p*-chlorobenzyl)-thiuronium 2-hexene-1-sulfonate (m.p. 130–131°) was 119–125°, and that with S-(*p*-chlorobenzyl)-thiuronium 2-hydroxy-1-hexanesulfonate (m.p. 138–139°) was 120–128°.

Anal. Calcd. for C₁₄H₂₁O₃N₂S₂Cl: C, 46.08; H, 5.80. Found: C, 46.34, 45.73; H, 5.79, 5.54.

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