

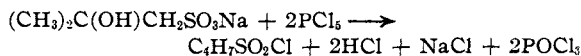
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## The Sulfonation of Isobutylene. II. Methyl-2-propene-1-sulfonic Acid<sup>1</sup> and Related Compounds

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Recently it was reported<sup>3</sup> that the action of excess dioxane sulfotrioxide upon isobutylene gives methylpropene-1,3-disulfonic acid in considerable amounts. The monosulfonation products of this olefin have now been studied. The disulfonation of isobutylene proceeds at a moderate rate at about 0° in the presence of dioxane<sup>3</sup> without serious interference from polymer formation. It seemed possible that in the absence of the dioxane sulfonation might occur at a much lower temperature where polymerization would be unimportant. However, the addition of chlorosulfonic acid to a large excess of isobutylene at -70° resulted in the formation of a mixture of polymers and no definite sulfonation product was isolated. The addition of dioxane sulfotrioxide or chlorosulfonate to isobutylene dissolved in ethylene chloride at 0° also caused appreciable polymerization unless the reaction time was brief. In one experiment where dioxane chlorosulfonate was used there was isolated, in addition to *t*-butyl chloride and diisobutylene, a considerable quantity of a sodium octylenesulfonate; this gave a benzylthiuronium salt with a sharp melting point but has not been studied further.

The crude sodium isobutylenesulfonate obtained by the rapid sulfonation of isobutylene with dioxane sulfotrioxide contained an appreciable quantity of a hydroxysulfonate, probably (CH<sub>3</sub>)<sub>2</sub>C(OH)CH<sub>2</sub>SO<sub>3</sub>Na. This was indicated by analysis and by the evolution of hydrogen chloride upon treatment with phosphorus pentachloride or oxychloride. The hydroxysulfonate prepared from isobutylene oxide and sodium bisulfite gave a sulfonyl chloride identical with that obtained from the sulfonation product. This sulfonyl chloride was also identical with that obtained



from the sodium methylpropenesulfonate synthesized from methallyl chloride and sodium sulfite. These identities were established by comparison

(1) Much of the material in this paper was presented before the Organic Division of the American Chemical Society at St. Louis, April 9, 1941.

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(3) Suter and Malkemus, *THIS JOURNAL*, **63**, 978 (1941).

of physical properties and conversion of the chloride into the benzylanilide. However, this evidence was believed to be inconclusive in distinguishing between I and II as structures for the



isobutylene sulfonation product since there was the possibility of the olefinic linkage shifting during formation of the sulfonyl chloride. Furthermore, the hydroxysulfonate might be expected to give the sulfonyl chloride of II rather than of I. It was then found that a pure benzylthiuronium sulfonate readily obtained from the isobutylene sulfonation product was identical with the corresponding derivative of the sulfonic acid prepared from methallyl chloride. Inasmuch as  $\beta$ -unsaturated carboxylic acids readily rearrange to the  $\alpha$ -isomers in alkaline solution<sup>4</sup> there still remained the possibility that in the action of methallyl chloride upon sodium sulfite the product formed was II rather than I. An attempt to prepare II by the action of isocrotyl chloride<sup>5</sup> upon aqueous sodium sulfite at a high temperature was unsuccessful. It was then found that the isobutylene sulfonation product reacted with a mixture of phosphorus pentabromide and tribromide to give 1,2,3-tribromo-2-methylpropane. The loss of the sulfonate group from I would be expected since it is known<sup>6</sup> that sodium  $\omega$ -toluenesulfonate undergoes cleavage in this manner forming benzyl bromide. If the compound II reacted with loss of the sulfonate group, only 1,1,2-tribromo-2-methylpropane could result. The structure of the 1,2,3-tribromo-2-methylpropane was established by comparing it with a sample obtained by bromination of isobutylene<sup>7</sup> and by conversion into 1-bromo-3-acetoxy-2-methyl-1-propene through the action of potassium acetate. This reagent produces 1,1-dibromo-2-methyl-1-propene from 1,1,2-tribromomethylpropane.<sup>7</sup>

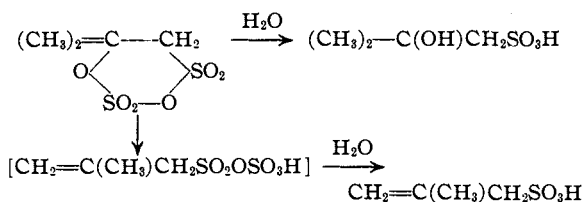
(4) Linstead and Noble, *J. Chem. Soc.*, 615 (1934); Kon, Linstead and Wright, *ibid.*, 599 (1934).

(5) We are grateful to the Shell Development Company for a sample of isocrotyl chloride.

(6) Hunter and Sorenson, *THIS JOURNAL*, **54**, 3364 (1932).

(7) Mereshkowsky, *Ann.*, **431**, 113 (1923).

Reduction of the methylpropenesulfonyl chloride with zinc and 15% sulfuric acid gave almost entirely gaseous products including hydrogen sulfide. No thiol was isolated. Hydrolysis of the sulfonyl chloride gave the original sodium sulfonate and refluxing of this with aqueous alkali caused no detectable isomerization. The evidence is, therefore, conclusive that in the monosulfonation of isobutylene, methylpropene-2-sulfonic acid is an important product; this is accompanied by 2-hydroxy-2-methylpropane-1-sulfonic acid or an intermediate which yields this on hydrolysis. This suggests immediately that both of these compounds arise from the same intermediate, a primary addition product of the carbonyl sulfate type,



This mechanism calls for the formation of one mole of sulfuric acid for each mole of hydroxy or olefinsulfonic acid. Actually in one experiment only about 12% of the sulfur trioxide originally added to the isobutylene was recovered as barium sulfate. The remainder was in the form of sulfonic acids. Hence it must be concluded that in the sulfonation of isobutylene as in halogenation<sup>8</sup> addition is not the first step.

### Experimental

**Sulfonation of Isobutylene with Dioxane Sulfotrioxide.**—To 25.1 g. (0.45 mole) of isobutylene in 100 g. of ethylene chloride at 0° was added a suspension of dioxane sulfotrioxide<sup>9</sup> in the same solvent equivalent to 27.5 g. (0.344 mole) of sulfur trioxide. The resulting clear solution was neutralized with excess aqueous barium hydroxide (about 60 g. of base), the ethylene chloride and dioxane removed by steam distillation and carbon dioxide passed into the residual mixture until the solution became neutral. Filtration and treating the solid with dilute hydrochloric acid left 8.4 g. of barium sulfate corresponding to 3.46 g. of sulfur trioxide or 12.6% of that present in the sulfonating mixture. Evaporation of the filtrate from the barium carbonate and sulfate gave 68.7 g. of barium salt or 98% of the amount expected from the sulfur trioxide used.

*Anal.* Calcd. for C<sub>3</sub>H<sub>14</sub>O<sub>6</sub>S<sub>2</sub>Ba: Ba, 33.70. Found: 34.22, 33.93.

Since 12.6% of the sulfur trioxide was accounted for as barium sulfate, the yield should have been 88%. The discrepancy may be accounted for in several ways including inaccuracy in determining the amount of sulfur trioxide

(8) Burgins, Engs, Groll and Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

originally present. Conversion of the barium salt to the sodium salt by addition of sodium sulfate followed by crystallization several times from absolute alcohol gave a product analyzing slightly low in sodium, which may, therefore, have contained some hydroxysulfonate, (CH<sub>3</sub>)<sub>2</sub>-COHCH<sub>2</sub>SO<sub>3</sub>Na, or diisobutylene sulfonate as an impurity.

*Anal.* Calcd. for C<sub>4</sub>H<sub>7</sub>O<sub>3</sub>SNa: Na, 14.55. Found: Na, 14.00, 13.93.

In another experiment run on a larger scale in which the dioxane sulfotrioxide was added to the isobutylene over a four hour period, the weight of mixed sodium sulfonates was considerably greater than expected if sodium isobutyl-ene-sulfonate were the only product. Analysis indicated that the material corresponded fairly closely to a diisobutyl-ene-sulfonate.

*Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>SO<sub>3</sub>Na: Na, 10.75. Found: Na, 11.11, 11.25.

Since a rapid sulfonation should decrease polymer formation another experiment was carried out as follows.

A sludge of dioxane sulfotrioxide made from 30 ml. of ethylene chloride, 14 g. of dioxane and 15.2 g. (0.19 mole) of sulfur trioxide was added during five minutes to a solution of 22 g. (0.39 mole) of isobutylene in 48 ml. of ethylene chloride at 0 = 5°. About 100 ml. of water was added and the aqueous solution neutralized with sodium hydroxide. After warming on the steam-bath a little more alkali was required, indicating hydrolysis of an intermediate sulfate sulfonate. Evaporation to dryness gave 28.1 g. of sodium salts weighed after drying at 100° (20 mm.) for six hours. Extraction of a 7-g. sample of this product with 100 ml. of absolute alcohol in a Soxhlet left 0.7 g. of insoluble residue. (Sodium sulfate and sodium 2-methylpropene-1,3-disulfonate are practically insoluble in absolute alcohol under these conditions.) The salt which crystallized from the alcohol weighed 4.3 g. After drying at 100° (20 mm.) this gave an analysis indicating a mixture of 2-methylpropenesulfonate and 2-methyl-2-propanolsulfonate in the ratio of about two to one.

*Anal.* Calcd. for C<sub>4</sub>H<sub>7</sub>O<sub>3</sub>SNa: Na, 14.55. Found: Na, 13.95, 14.02.

Upon adding a solution of benzylthiuronium chloride<sup>9</sup> to a solution of the sodium sulfonate, the derivative crystallized in a nearly pure state in a few minutes. After recrystallization this melted at 155–156°. Pure benzylthiuronium 2-methylpropene-1-sulfonate melted at 155.8–156.6° (cor.) and a mixed m. p. showed no depression.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub>S<sub>2</sub>: N, 9.26. Found: N, 9.15.

**Sulfonation of Isobutylene with Dioxane Chlorosulfonate.**—Experiments were performed under a variety of conditions. Three significant ones are described.

A. A solution prepared by adding 350 g. (3 moles) of freshly distilled chlorosulfonic acid to 264 g. (3 moles) of dioxane and 100 ml. of ethylene chloride was added slowly with stirring to 333 g. (5.95 moles) of isobutylene in 400 ml. of ethylene chloride kept below 0°. The reaction mixture was then distilled under reduced pressure from a water-bath kept at 60°. The first fraction collected at a pressure down to 250 mm. weighed 412 g., and on fractionation

(9) Donleavy, *This Journal*, **56**, 1004 (1936).

through a 60-cm. column packed with  $3/32$ " wire helices gave 188 g. of material distilling at 49.5–50.5°,  $n_D^{20}$  1.3850,  $d_4^{20}$  0.8469. This is 64% of the theoretical amount of *t*-butyl chloride. In another experiment it was shown that the loss of hydrogen chloride from the reaction mixture was negligible.

Continued heating of the reaction mixture at 60° gave as a final fraction between 5 mm. and 1 mm. 88 g. which was chiefly dioxane. One-sixth of the residue upon neutralization with aqueous sodium hydroxide gave 7 g. of a crude sodium salt corresponding in properties to a sodium diisobutylenesulfonate isolated in a pure state in another experiment.

B. Several sulfonations were carried out in the absence of the ethylene chloride solvent. One is described. A mixture of 77 g. (0.88 mole) of dioxane and 102 g. (0.88 mole) of chlorosulfonic acid was semi-solid at 0–5° but liquefied at 25–30°. This was slowly added to 149 g. (2.66 moles) of liquid isobutylene with stirring. Two layers formed at –10° and reaction was very slow. The major part of the dioxane chlorosulfonate was added at the reflux temperature of the mixture which gradually rose. The isobutylene was returned by means of a spiral condenser cooled with acetone and dry-ice. After the temperature had risen to 35°, addition of sulfonating agent was discontinued; 0.76 mole had been added. The reaction mixture consisted of an upper layer of 65 g. and a lower acid layer of 207 g. which were worked up separately. The upper layer contained 39 g. of *t*-butyl chloride, b. p. 50–55°; the remainder was chiefly diisobutylene. Neutralization of the lower layer with aqueous sodium hydroxide and dilution to 500 ml. gave 20 g. of a white crystalline precipitate which was recrystallized from water and absolute alcohol and then analyzed.

*Anal.* Calcd. for  $C_8H_{16}SO_2Na$ : Na, 10.75. Found: Na, 10.76, 10.79.

The filtrate from which this product was obtained upon evaporation to dryness gave 129 g. of mixed sodium salts from which no other pure product was isolated.

C. Sulfonations carried out rapidly on a small scale gave a product similar to that described under sulfonation with dioxane sulfotrioxide. For example, from the addition during fifteen minutes of a mixture containing 10 g. of dioxane, 11.7 g. (0.1 mole) of chlorosulfonic acid and 10 ml. of ethylene chloride to 23 g. (0.41 mole) of isobutylene in 52 ml. of ethylene chloride at 0–10° was obtained 14.8 g. of dry sodium salts. One-half of this was extracted continuously with absolute alcohol for five hours leaving a residue of 1.1 g. The solid that separated from the alcohol extract after treatment with boneblack in aqueous solution and evaporation of the solution to dryness amounted to 4.9 g. After drying at 100° (20 mm.) it was analyzed for sodium and for chlorine since a trace of sodium chloride was present. The net sodium of the sodium sulfonates is given herewith.

*Anal.* Calcd. for  $C_4H_7O_2SNa$ : Na, 14.55. Calcd. for  $C_4H_9O_2SNa$ : Na, 13.07. Found: Na, 13.63, 13.67.

It is evidently simpler to obtain a pure sodium isobutylenesulfonate from a sulfonation with dioxane sulfotrioxide than with the chlorosulfonate.

**Preparation of Sodium 2-Methyl-2-propene-1-sulfonate from Methallyl Chloride.**—To an aqueous solution of 252

g. (2.0 moles) of sodium sulfite in 1 l. of water at 55° was added gradually 181 g. (2.0 moles) of freshly distilled methallyl chloride, b. p. 70.5–71.5°. The mixture was stirred vigorously, heat was evolved and the temperature rose to 65°. The reaction was practically complete in two hours but stirring was continued overnight and the mixture then evaporated to dryness on the steam-bath. (This mixture was used in preparing the sulfonyl chloride; see next experiment.) Repeated extraction with hot 95% ethyl alcohol gave 170 g. of flaky white crystals of sodium 2-methyl-2-propene-1-sulfonate. (The yield could be increased by complete extraction of the sulfonate.) The material decomposes without charring at 260° (cor.).

*Anal.* Calcd. for  $C_4H_7O_2SNa$ : Na, 14.55. Found: Na, 14.57, 14.59.

The sulfonate rapidly decolorizes neutral permanganate, is very soluble in water and soluble in hot 95% alcohol.

**2-Methyl-2-propene-1-sulfonyl Chloride.**—To 162 g. of a crude mixture of salts from methallyl chloride and sodium sulfite theoretically equivalent to 0.75 mole of sodium 2-methylpropene-1-sulfonate was added 345 g. (2.25 moles) of phosphorus oxychloride. After stirring and heating under a reflux condenser in an oil-bath kept at 120–130° for three hours the excess phosphorus oxychloride was distilled off under reduced pressure. Up to 100° (35 mm.) 159 g. was recovered. The gummy residue was extracted with chloroform, then water added and the mixture extracted again with chloroform. The chloroform extracts were combined, washed with ice water three times, dried and distilled. The residue (101 g.) after removal of the chloroform gave 79.4 g., b. p. 68–70° (8 mm.), of colorless liquid besides a small forerun and 9 g. of residue. The sulfonyl chloride had  $n_D^{20}$  1.4779 and  $d_4^{20}$  1.2704. The yield was 69% based on the methallyl chloride used in making the sulfonates. Starting with the pure sulfonate the yield of chloride was 89%. Hydrolysis of a 2-g. sample of the sulfonyl chloride with water and oxidation of the acid solution with excess permanganate did not yield a detectable amount of acetone, using 2,4-dinitrophenylhydrazine as the test reagent.

*Anal.* Calcd. for  $C_4H_7O_2ClS$ : Cl, 22.99. Found: Cl, 23.38, 22.89.

The sodium salt (41.6 g.) obtained by sulfonating 31.4 g. (0.562 mole) of isobutylene with 22.2 g. (0.278 mole) of sulfur trioxide in the usual manner was converted into the sulfonyl chloride by heating with 107 g. (0.7 mole) of phosphorus oxychloride on the steam-bath for five hours. Hydrogen chloride was evolved at first. The reaction mixture was worked up as in the preceding experiment giving 21.1 g. or 52%, based on the sulfur trioxide, of sulfonyl chloride most of which on redistillation came over at 65–66° (7 mm.) and had  $n_D^{20}$  1.4780; this corresponds closely to the product obtained in the preceding experiment.

**2-Methyl-2-propene-1-sulfonbenzylanilide.**—To 3.1 g. (0.02 mole) of the sulfonyl chloride (obtained from the isobutylene sulfonation product) in 50 ml. of dry benzene was added 7.3 g. (0.04 mole) of benzyaniline and the mixture refluxed for twelve hours. The benzyaniline hydrochloride was removed by filtration, the benzene solution washed several times with dilute hydrochloric acid and the benzene evaporated. The residual oil (3.9 g.) was crystallized from 30 ml. of hot 95% alcohol to give 2.9 g. of

crystals melting at 78.5–79.5°. This amide was identical with that obtained from the sulfonyl chloride made from the sodium sulfonate synthesized by the Strecker reaction from methallyl chloride.

*Anal.*<sup>10</sup> Calcd. for  $C_{17}H_{19}O_2NS$ : N, 4.65. Found: N, 5.04, 5.07.

**2-Hydroxymethylpropanesulfonic Acid.**—A mixture of 36 g. (0.5 mole) of isobutylene oxide and 52 g. (0.5 mole) of sodium bisulfite in 150 ml. of water was shaken in a pressure bottle for four hours. Evaporation to dryness and extraction of the residue with hot ethyl alcohol many times gave 29 g. of the sodium sulfonate. For analysis the material was again crystallized from alcohol.

*Anal.* Calcd. for  $C_4H_9O_4SNa$ : Na, 13.07. Found: Na, 12.78.

A mixture of 17.6 g. of the salt was heated on the steam-bath for two hours with 45 g. of phosphorus oxychloride. After standing overnight chloroform was added and the whole poured into ice water. The chloroform layer was then dried over sodium sulfate and distilled. This gave 8.5 g. (55%) of methyl-2-propene-1-sulfonyl chloride, b. p. 83–84° (15 mm.),  $n_D^{20}$  1.4780. Heating 2.4 g. of the acid chloride with 10 ml. of 4 *N* sodium hydroxide produced hydrolysis in fifteen minutes. The residue after evaporating the water was treated with alcohol and a 10% solution of benzylthiuronium chloride added. The resulting derivative melted at 154° (uncor.) after recrystallization. A mixed melting point with the derivative from a sample of methylpropenesulfonic acid made from methallyl chloride was 154–155°. Refluxing a sample of the sodium methylpropenesulfonate with 5% alkali for thirty minutes brought about no change as indicated by obtaining the benzylthiuronium derivative from the mixture.

**Reduction of Methyl-2-propene-1-sulfonyl Chloride.**—To a mixture of 360 g. of ice, 65 g. of 95% sulfuric acid and 25 g. of the sulfonyl chloride was added 60 g. of granulated zinc and the mixture kept at –5° for two hours. Hydrogen sulfide was evolved continuously. The mixture was then refluxed for three hours and steam distilled.

(10) Microanalysis by Dr. Leo K. Roehen, to whom our thanks are due.

Practically no oily material appeared in the filtrate and none was obtained by ether extraction.

**Reaction of Phosphorus Bromides with Sodium Methyl-2-propene-1-sulfonate.**—To 107 ml. (1.13 moles) of phosphorus tribromide was added 17.2 ml. (0.33 mole) of bromine. While the mixture was kept in ice 50 g. of the sodium sulfonate was added during thirty minutes. A vigorous reaction and considerable charring occurred. The mixture was heated at 85° for one hour, cooled, and then 250 ml. of ether and finally ice added slowly. After further washing with water the ether layer was heated to remove the solvent and then steam distilled. The oil, when dried and distilled, came over at 100–104° (17 mm.). The yield was 18.7 g. After fractionation the product had b. p. 88.5° (9 mm.),  $n_D^{20}$  1.5652,  $d_4^{20}$  2.1750; molecular refraction calcd., 44.03; found, 44.10. The bromination of isobutylene<sup>7</sup> gave a 31.4% yield of tribromo compound which upon refractionation had the properties b. p. 75.5° (5 mm.),  $n_D^{20}$  1.5659 and  $d_4^{20}$  2.1888. Since the agreement left something to be desired 9.5 g. of the bromo compound (from the sodium sulfonate) was refluxed with 9 g. of potassium acetate in 10 ml. of acetic acid for four hours which gave 5 g. (81%) of 1-bromo-3-acetoxymethyl-1-propene,<sup>7</sup> b. p. 84–85° (13 mm.), 192–196° (750 mm.),  $n_D^{20}$  1.4775.

### Summary

1. The sulfonation of isobutylene with dioxane sulfotrioxide in ethylene chloride gives chiefly methyl-2-propene-1-sulfonic acid. 2-Hydroxymethylpropane-1-sulfonic acid and a derivative of diisobutylene were also identified.

2. The sulfonation of isobutylene is comparable to chlorination in that the formation of a carbyl sulfate type of compound is not the first step in the reaction.

3. Treatment of methyl-2-propene-1-sulfonic acid with boiling alkali does not result in shifting the olefin linkage nearer the sulfo group.

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