[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Sulfonation of Isobutylene. I. 2-Methylpropene-1,3-disulfonic Acid and Related Compounds

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Recently it has been shown that the action of dioxane sulfotrioxide[1] upon propylene gives a product that hydrolyzes to 2-hydroxypropane-1-sulfonic acid. In contrast to this behavior, isobutylene yields chiefly unsaturated mono- and disulfonic acids. The action of dioxane sulfotrioxide is therefore analogous to that of chlorine.[2] The present communication deals with the structure and reactions of one of the sulfonation products.

When isobutylene was passed into a suspension of dioxane sulfotrioxide in ethylene chloride at 0° the solid phase disappeared. If the resulting solution was allowed to stand for several days or was heated to about 60° a granular white hygroscopic solid precipitated. This had a neutral equivalent of 152, gave no barium sulfate with barium hydroxide and readily reduced potassium permanganate. These properties indicated that the product was an unsaturated sulfonic acid but the amount of barium sulfonate obtained from a weighed sample was about 27% less than the neutral equivalent predicted. This discrepancy was found to be due to dioxane, the sulfonation product precipitating as the dioxane salt, $C_4H_6(SO_3H_2)\cdot C_4H_8O_2$. The barium salt, even after long drying at 115° and 10 mm. pressure, analyzed correctly for a hydroxybutanedisulfonate, $C_4H_8O(SO_3)_2Ba$; however, it was unsaturated toward permanganate and with sodium sulfate gave a sodium salt that had the formula of the unsaturated disulfonate. The barium salt exists therefore as an unusually stable monohydrate. This was further confirmed by preparing the ammonium and aniline salts of the disulfonic acid, which were readily obtained in the anhydrous state.

Refluxing the dioxane salt with thionyl chloride converted it into the sulfonic anhydride. Aromatic sulfonic acids have been observed to give

$$C_4H_6(SO_3H)_2\cdot C_4H_8O_2 + SOCl_2 \longrightarrow C_4H_6(SO_2)_2O + 2HCl + SO_2 + C_4H_8O_2$$

anhydrides with this reagent.[3] The anhydride was found to be surprisingly stable toward hydrolysis, dissolving only slowly in cold water or dilute alkali and hydrating slowly on exposure to the atmosphere. From the anhydride were obtained salts identical in properties with those resulting from the dioxane salt, hence the thionyl chloride treatment caused no change in the molecule other than anhydride formation.

Heating the dioxane salt, a metal salt, or the sulfonic anhydride with phosphorus pentachloride at 100° gave the disulfonyl chloride which crystallized in long needles that exhibit parallel

$$C_4H_6(SO_2)_2O + PCl_5 \longrightarrow C_4H_6(SO_2Cl)_2 + POCl_3$$

extinction and negative elongation. The disulfonyl chloride reacts with bromine only slowly in warm carbon tetrachloride, the rate increasing in the presence of light. Ammonia and aniline gave the amide and anilide normally.

Kohler[4] found that ethylenesulfonic acid when treated with bromine in aqueous solution gave first 1-bromoethylene-1-sulfonic acid which then oxidized to sulfuric acid and carbon dioxide. Adding excess bromine water to a solution of the barium isobutylenedisulfonate precipitated somewhat less than one-half of the sulfur as barium sulfate. Since a compound with the structure $CH_2{=}C(CH_2SO_3)_2Ba$ or $CH_2{=}C(CH_3)CH(SO_3)_2Ba$ should give little or no sulfate this behavior is best explained by the structure $(O_3SCH_2C(CH_3){=}CHSO_3)Ba$.

Pyrolysis of the isobutylenedisulfonyl chloride at 180–210° gave a small yield of a sulfur-free oil whose properties were in only fair agreement with those of 1,3-dichloro-2-methylpropene.[5] Attempts to convert the chlorine compound into a 3,5-dinitrobenzoate gave two products neither of which was identical with either of the dinitrobenzoates from the *cis* and *trans* 1-chloro-3-hydroxy-2-methylpropene.[6] The products were not further investigated because of the small amounts available and because the drastic nature of the pyrolysis treatment reduces the significance of the results.

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(1) Suter, Evans and Kiefer, THIS JOURNAL, **60**, 538 (1938).

(2) Chechoukoff, *Ber.*, **16**, 1869 (1883); *Bull. soc. chim.*, [2] **41**, 253 (1884); **43**, 127 (1885); Groll, Hearne, Rust and Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939); Burgin, Engs, Groll and Hearne, *ibid.*, **31**, 1413 (1939).

(3) Meyer and Schlegl, *Monatsh.*, **34**, 561, 705 (1913).

(4) Kohler, *Am. Chem. J.*, **20**, 680 (1898).

(5) Pogorshelski, *Chem. Zentr.*, **76**, I, 668 (1905).

(6) Rogers and Nelson, THIS JOURNAL, **58**, 1029 (1936). We are greatly indebted to Professor Ed. F. Degering of Purdue University for supplying us with samples of these dinitrobenzoates.

The isobutylenedisulfonyl chloride was synthesized from methallyl chloride by the steps indicated in the equations. While the action of phosphorus pentachloride on the hydroxydisulfonate might give the compound $CH_2{=}C(CH_2SO_2Cl)_2$ this structure already has been eliminated.

$$CH_2{=}C(CH_3)CH_2Cl \xrightarrow{HOCl}$$
$$ClCH_2C(OH)(CH_3)CH_2Cl \xrightarrow{Na_2SO_3}$$
$$NaO_3SCH_2C(OH)(CH_3)CH_2SO_3Na \xrightarrow{PCl_5}$$
$$ClO_2SCH_2C(CH_3){=}CHSO_2Cl$$

In an unsuccessful attempt to provide further proof of the structure of the disulfonic acid, 2-methylpropane-1,3-disulfonanilide was prepared from 1,3-dichloro-2-methylpropane but the unsaturated disulfonanilide mentioned above could not be reduced by hydrogen and a platinum oxide catalyst or by indirect means. Efforts to obtain quantitative data by the permanganate oxidation of the unsaturated disulfonic acid likewise gave no definite results. It should be mentioned that Bistrzycki[7] prepared an unsaturated disulfonic acid by sulfonation of trimethylacetic acid. No attempt has been made to compare this with the disulfonic acid obtained from isobutylene.

The action of dioxane sulfotrioxide upon an excess of *t*-butyl alcohol at 0–5° gave dioxane hydrogen sulfate with no more than a trace of an acid yielding a soluble barium salt. It therefore may be predicted that with an excess of the reagent this and other tertiary alcohols would give chiefly unsaturated sulfonic acids.

$$C_4H_9OH + C_4H_8O_2{\cdot}SO_3 \longrightarrow C_4H_8 + C_4H_8O_2{\cdot}H_2SO_4$$

In contrast to the behavior of dioxane sulfotrioxide, the addition product of dioxane and chlorosulfonic acid does not react with isobutylene at an appreciable rate below about 20°. At this temperature hydrogen chloride is formed and the dioxane salt of the disulfonic acid again precipitates. Dioxane does not form a solid with chlorosulfonic acid; the liquid addition product is miscible with ethylene chloride in all proportions.[8]

Investigation of the sulfonation of olefins and of the resulting sulfonic acids is being continued.

Experimental

Sulfonation of Isobutylene.—To a solution of 264 g. (3 moles) of dioxane in 1050 ml. of ethylene chloride at 0° was added with stirring 350 g. (4.38 moles) of sulfur trioxide. Isobutylene was passed into the mixture until the increase in weight was 123 g. (2.2 moles); it was then warmed to 50° and shaken to dissolve a small amount of solid and left in the refrigerator overnight. The solid precipitate was filtered off under anhydrous conditions and washed with ethylene chloride. The yield of dioxane salt was 198 g. or 30% of the theoretical amount. More solid separated after long standing but the amount of this was not determined.

A portion of the dioxane salt was recrystallized from dioxane, freed from solvent in a vacuum desiccator over phosphorus pentoxide and analyzed for sulfur.

Anal. Calcd. for $C_4H_8O_6S_2{\cdot}C_4H_8O_2$: S, 21.07. Found: S, 21.07, 20.90.

The dioxane salt was titrated with standard barium hydroxide solution.

Anal. Calcd. for $C_4H_8O_6S_2{\cdot}C_4H_8O_2$: neut. equiv., 152.1. Found: neut. equiv., 152.2.

Dioxane was shown to be a constituent of the salt by neutralizing a 12-g. sample with sodium hydroxide and distilling off 10 ml. of liquid through an efficient column. This was saturated with potassium carbonate and extracted with ether. From the ether by careful fractionation was isolated 0.78 g. of material, b. p. 99–101°, $n^{25}D$ 1.4150, which was soluble in water and chloroform, decolorized bromine in chloroform and gave a hygroscopic white solid with concentrated sulfuric acid. These properties correspond to those of dioxane.

When the barium salt, obtained from barium hydroxide and the dioxane salt, was allowed to crystallize slowly from water it came out as the pentahydrate which upon heating at 99° (30–40 mm.) for six hours attained constant weight after the loss of four molecules of water. The pentahydrate crystallized as plates or prisms. The plates exhibited parallel cleavage and extinction was parallel to the edge of a small corner which appeared in several plates. The crystals were negative biaxial; the optic axial angle was apparently greater than 70°. The dispersion was V > R. No inclined dispersion could be detected. The three refractive indices were α, 1.525; β, 1.551; and γ, 1.567. The crystals probably belong to the monoclinic system.

Anal. Calcd. for $C_4H_6O_6S_2Ba{\cdot}5H_2O$: loss in weight ($4H_2O$), 16.31; ($5H_2O$), 20.39. Found: loss in weight. 16.76. Calcd. for $C_4H_6O_6S_2Ba{\cdot}H_2O$: Ba, 37.17. Found: Ba, 37.12, 37.17, 37.19.

Since the composition of the dried barium salt corresponded also to that of a hydroxymethylpropanedisulfonate several other salts were made. Precipitating the barium quantitatively from the barium salt with sodium sulfate and drying the residue from evaporation of the filtrate at 115° (15 mm.) gave the pure sodium salt.

Anal.[9] Calcd. for $C_4H_6O_6S_2Na_2$: Na, 17.69. Found: Na, 17.76, 17.77.

The ammonium salt was prepared by neutralizing the dioxane salt with ammonia and drying the product at 115° (15 mm.). *Anal.*[9] Calcd. for $C_4H_6(SO_3NH_4)_2$: NH_3, 13.61; S, 25.62. Found: NH_3, 13.12; S. 25.27, 24.92.

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[7] Bistrzycki, *Ber.*, **40**, 4374 (1907).

[8] That an addition product is produced is evident from the fact that chlorosulfonic acid reacts violently with isobutylene at −80° giving polymers whereas the dioxane chlorosulfonate has little effect until room temperature is approached.

[9] This analysis was made by Mr. L. G. Ginger in this Laboratory.

The aniline salt was made by adding aniline sulfate to an aqueous solution of the barium compound, filtering, evaporating the filtrate to dryness, and recrystallizing from 95% ethyl alcohol. A voluminous mass of shiny plates was obtained. This was dried and titrated with standard alkali using phenolphthalein as the indicator.

Anal. Calcd. for $C_4H_6(SO_3NH_3C_6H_5)_2$: neut. equiv., 201.1. Found: neut. equiv., 201.8, 202.

Oxidation of Barium 2-Methylpropene-1,3-disulfonate with Bromine Water.—Bromine water was added gradually to 0.8945 g. of the barium salt dissolved in 20 ml. of water. The precipitation of barium sulfate was complete in about ten minutes. After standing overnight with excess bromine present the solution was heated on the steam-bath, filtered, and the precipitate washed thoroughly. The weight of barium sulfate was 0.4143 g. or 73.3% of one molecular equivalent. A check run gave 73.1%.

2-Methylpropene-1,3-disulfonic Anhydride.—A mixture of 76 g. (0.25 mole) of the dioxane salt and 120 g. (1.0 mole) of thionyl chloride was heated on the steam-bath for five hours when the evolution of sulfur dioxide and hydrogen chloride had practically ceased. Chloroform was added and the precipitate was washed several times with the same solvent. The slightly colored product weighed 41.5 g. This was recrystallized several times from ethyl acetate from which it separated as a colorless granular solid, m. p. 167–170°. The anhydride dissolved slowly in hot water or alkali and gradually hydrolyzed in contact with the air. It was little affected by bromine in carbon tetrachloride although bromine water slowly oxidized it to give sulfuric acid. It did not dissolve appreciably in the usual organic solvents except ethyl acetate and acetone.

Anal.[9] Calcd. for $C_4H_6O_5S_2$: S, 32.35; neut. equiv., 99.09. Found: S, 32.15, 31.95; neut. equiv., 98.74.

From the action of aniline upon the anhydride in ethyl acetate solution there was obtained a mixture of products from which only the aniline disulfonate already described was isolated. This was identified by its crystallographic properties and neutral equivalent. The action of barium hydroxide upon the anhydride gave the typical barium salt mentioned earlier.

2-Methylpropene-1,3-disulfonyl Chloride.—The sulfonyl chloride was prepared from the dioxane salt, the barium salt and the anhydride. This last preparation is described. A mixture of 29.5 g. (0.149 mole) of the sulfonic anhydride and 31.0 g. (0.149 mole) of phosphorus pentachloride was heated for five hours on the steam-bath. The phosphorus oxychloride was removed under reduced pressure and the residue extracted with chloroform. The weight of unchanged insoluble anhydride was 10.6 g. The chloroform soluble fraction after crystallization from carbon tetrachloride amounted to 16.6 g. or 69% of the theoretical amount, taking into account recovered anhydride. The sulfonyl chloride was insoluble in cold water but dissolved readily in hot water or alkali. It dissolved readily in chloroform and much less easily in carbon tetrachloride, benzene or petroleum ether. From these it crystallized in long needles which exhibit parallel extinction and negative elongation and melt at 79.2–79.8°.

Anal.[9] Calcd. for $C_4H_6O_4S_2Cl_2$: S, 25.43; neut. equiv., 63.27. Found: S, 25.25, 25.25; neut. equiv., 63.3, 64.0.

The addition of an ether solution of the sulfonyl chloride to excess liquid ammonia and crystallization of the product from 100% ethyl alcohol and then from alcohol–ethyl acetate gave fine, shiny bladed needles which melted at 152.5–154°. Examination with the polarizing microscope showed that the material was homogeneous, anisotropic and "length fast." The amide was soluble in water or alcohol but insoluble in non-polar organic solvents.

Anal. Calcd. for $C_4H_{10}O_4N_2S_2$: S, 29.93. Found: S, 30.10, 30.21.

Refluxing the sulfonyl chloride with aniline in benzene solution gave a 64% yield of the anilide which after crystallization from chloroform melted at 171.5–172.5°.

Anal.[9] Calcd. for $C_{16}H_{18}O_4N_2S_2$: S. 17.50. Found: S. 17.65. 17.61.

Pyrolysis of 13.5 g. of the disulfonyl chloride by heating in a small distilling flask at 180–210° gave sulfur dioxide. a little hydrogen chloride and 2.1 g. of liquid distillate. After redistillation this had the b. p. (micro) 137–138°, n^{20}_D 1.4767, d^{20}_4 1.1773. The observed molecular refraction was 29.97 and the calculated value for $C_4H_6Cl_2$ is 29.94. The liquid was readily oxidized by potassium permanganate but did not react with bromine in carbon tetrachloride appreciably. Heating 0.13 g. of the chloride with silver 3,5-dinitrobenzoate gave two products, m. p. 56–57° and 139–142°. Since these were not identical with the esters obtained from the *cis* and *trans* 1-chloro-3-hydroxy-2-methylpropene they were not further investigated. It was observed that both the latter esters exhibited parallel extinction while the solid, m. p. 56–57°, showed 24.5° extinction.

2-Methyl-1,3-dichloro-2-propanol. Structure of the Disulfonyl Chloride.—To 102.3 g. of 3-chloro-2-methylpropene (methallyl chloride, b. p. 70–71° (739 mm.), n^{20}_D 1.4340, d^{20}_4 0.9475) was added slightly less than the theoretical amount of 2.25% hypochlorous acid, prepared by the method of Coleman and Johnstone,[10] and the mixture was stirred vigorously for seventy hours at about 15°, when no hypochlorous acid remained. The mixture was steam distilled, the oil salted out with sodium chloride and extracted with ether. Fractionation of the ether solution gave 51 g. of product, b. p. 55–56° (10 mm.), 168–170.5° (751 mm.), n^{20}_D 1.4750 and d^{20}_4 1.2758. The observed molecular refraction was 31.55 and the calculated value for $C_4H_6Cl_2O$. 31.93. Henry,[11] who prepared a small amount of this compound from 1,3-dichloropropanone and methylmagnesium bromide, reported only its b. p. (174–175°).

To a solution of 54.1 g. (0.43 mole) of sodium sulfite in 300 ml. of water was added 30.7 g. (0.215 mole) of the dichloropropanol and the mixture was stirred at 70–90° for twenty-four hours. The cooled solution was extracted with ether (only 0.6 g. of a yellow oil was recovered) decolorized with Darco and evaporated to dryness on the steam-bath. A 49-g. sample of the mixture of dried salts was heated on the steam-bath with 77.5 g. of powdered

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[10] Coleman and Johnstone, "Organic Syntheses," Vol. 5, 1925, p. 31.

[11] Henry, *Compt. rend.*, **142**, 130 (1906).

phosphorus pentachloride for seven hours. After removal of the phosphorus halides under reduced pressure the residue was extracted with warm chloroform. This was evaporated to a small volume whereupon fine needles characteristic of the disulfonyl chloride separated. The yield was 3.7 g. Recrystallization gave a product, m. p. 77.5–78.5°, which showed no depression in melting point when mixed with the unsaturated disulfonyl chloride already described. From the sulfonyl chloride also was prepared the disulfonanilide identical with that obtained from the isobutylenedisulfonic acid.

Summary

The sulfonation of isobutylene with excess dioxane sulfotrioxide gives the dioxane salt of 2-methylpropene-1,3-disulfonic acid. Evidence for the structure of this compound has been presented, including the synthesis of the corresponding disulfonyl chloride from 2-methyl-1,3-dichloro-2-propanol.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF LYMAN CHALKLEY]

Organic Mercury Derivatives of Basic Triphenylmethane Dyes: Dimercuri Derivatives of Malachite Green[*]

BY LYMAN CHALKLEY

Introduction

The various structural formulas which have been proposed for the basic triphenylmethane dyes would indicate that these dyes should mercurate easily. Depending upon the system of notation, these formulas show at least one, and sometimes two or three, para-substituted aniline groups in each molecule. The para-substituted anilines are, in general, quite easy to mercurate. Thus *p*-nitroaniline,[1] *p*-nitromonomethylaniline,[2] *p*-nitromonoethylaniline,[2] *p*-bromodimethylaniline,[3] *p*-toluidine,[4] and dimethyl-*p*-toluidine[4] mercurate with ease.

Nevertheless, most of the basic triphenylmethane dyes do not mercurate readily, if at all.[5] The completely alkylated dyes react only slowly with mercuric acetate, and the observed reaction is a reduction of the mercuric ion. This end result might be produced by the intermediate formation of an inherently unstable organic mercury compound which broke down with reduction of the mercury and oxidation of the dyestuff. If such were the case it would be impossible to prepare stable mercurated dyes either by direct mercuration or some indirect process.

However, the slowness of the reaction of the dyes with mercuric acetate speaks against a mechanism which would involve the formation of an intermediate organic mercury compound. For the mercuration of aromatic amines is usually rapid, and therefore a slow reaction, if it involved a mercuration, would indicate a slow decomposition of the organic mercury derivative, and thus time to isolate this derivative. The fact that such derivatives could not be isolated[5] would then suggest that the dyes simply do not react like substituted anilines, but behave more like aromatic quaternary ammonium salts, which are extremely resistant to mercuration.[6]

A similar situation was encountered in attempts to mercurate another basic dye, methylene blue, which reacted with mercuric acetate as do the triphenylmethane dyes.[7] But in the case of methylene blue it was found that a colorless derivative of the dye, the benzoyl leuco base, mercurated smoothly under suitable conditions.

A Plan for Mercuration.—It seemed possible, then, that in the case of the triphenylmethane dyes there might also be a profound difference between the behavior of the dyes themselves and the behavior of the colorless derivatives of these dyes toward mercuric salts. There are a number of these colorless derivatives which are in the same stage of oxidation as the dyestuff. In the Fischer notation they have the following general formulas, using Doebner's violet and para-rosaniline as illustrations

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[*] A preliminary report on a portion of the work described in this paper appeared in *Science*, **91**, 300 (1940).

(1) M. S. Kharasch, F. W. M. Lommen and I. M. Jacobsohn, THIS JOURNAL, **44**, 793 (1922).

(2) M. S. Kharasch and I. M. Jacobsohn, *ibid.*, **43**, 1894 (1921).

(3) F. C. Whitmore, *ibid.*, **41**, 1841 (1919).

(4) L. Pesci, *Gazz. chim. ital.*, **28**, II, 101 (1898); see also F. C. Whitmore, "Organic Compounds of Mercury," 1921, p. 243.

(5) F. C. Whitmore and G. J. Leuck, THIS JOURNAL, **51**, 2782 (1929).

(6) Reference 2, page 1903.

(7) L. Chalkley, THIS JOURNAL, **47**, 2055 (1925).