

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Sulfonation of the Phenylpropylenes

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In continuation of previous work on the sulfonation of various olefins with a suspension or solution of the coordination compound of dioxane and sulfur trioxide in an inert solvent,¹⁻⁵ it seemed of interest to determine how the course of the sulfonation is influenced by the presence of the phenyl group adjacent to the olefinic linkage. This paper describes the results obtained with the three phenylpropylenes.

The sulfonation of α -methylstyrene occurs readily in the range of 5 to 20°. In one experiment where a molar ratio of sulfonating agent to olefin of 1.8 was used, the barium hydroxide consumed and the barium sulfate precipitated in the hydrolysis of the reaction mixture with aqueous barium hydroxide indicated that 20% of the sulfur trioxide reacted by addition, and the remainder by substitution. The yield of mixed barium sulfonates obtained was 92% of the theoretical amount. Barium analyses on mixtures of these sulfonates obtained from various experiments varied between that calculated for a hydroxydisulfonate and an unsaturated disulfonate. Fractional crystallization of one of these mixtures yielded a small quantity of material having a barium content approaching that of a monosulfonate. By adding the dioxane sulfotrioxide reagent to a solution of α -methylstyrene at 0°, monosulfonation was increased. The main fraction obtained was, however, an unsaturated disulfonate with both sulfonate groups in the side chain as evidenced by the oxidation to benzoic acid. This material yielded a pure *S-p*-chlorobenzylthiuronium salt⁶ which analyzed for *S-p*-chlorobenzylthiuronium 2-phenylpropene-1,3-disulfonate, $[\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{SO}_3)=\text{CHSO}_3](\text{ClC}_6\text{H}_4\text{CH}_2\text{SCN}_2\text{H}_4)_2$.

When ethylene chloride was largely replaced by carbon tetrachloride as the inert solvent in the sulfonation of α -methylstyrene, a large quantity of a crystalline, hygroscopic material was deposited. Dioxane was found to be a constituent of this solid. Neutral equivalent data and tests for unsaturation agreed with the material being dioxane 2-phenylpropene-1,3-disulfonate. The behavior of this material was similar to that of dioxane 2-methylpropene-1,3-disulfonate obtained from isobutylene.³ It

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

(2) J. M. Holbert, Ph.D. Thesis, Northwestern University, 1940.

(3) Suter and Malkemus, *THIS JOURNAL*, **68**, 978 (1941).

(4) Suter, Malkemus and Archer, *ibid.*, **68**, 1594 (1941).

(5) Suter and Bordwell, *ibid.*, **65**, 507 (1943). The authors are indebted to Dr. Frederick Bordwell for suggestions made during the course of the present work and for his comments on the manuscript.

(6) Donlevy, *ibid.*, **55**, 1004 (1936).

yielded a *S-p*-chlorobenzylthiuronium salt which was identical with that obtained from the hydrolysis product of the first sulfonation of α -methylstyrene. Attempts to prepare the disulfonamide from the sodium and barium salts were not successful. The dioxane salt however gave a fair yield of the corresponding disulfonamide. It analyzed correctly for 2-phenylpropene-1,3-disulfonamide, $\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{SO}_2\text{NH}_2)=\text{CHSO}_2\text{NH}_2$. Further evidence for the structure of the disulfonamide was obtained by an independent synthesis.

2-Phenyl-2-hydroxy-1,3-dichloropropane, prepared from *sym*-dichloroacetone and phenylmagnesium bromide,⁷ was converted to sodium 2-phenyl-2-hydroxypropane-1,3-disulfonate, $\text{C}_6\text{H}_5\text{COH}(\text{CH}_2\text{SO}_3\text{Na})_2$, by the Strecker reaction.⁸ The *S-p*-chlorobenzylthiuronium salt of this material was not the same as that of the principal sulfonation product of α -methylstyrene. The sodium hydroxydisulfonate was difficult to dehydrate but this was finally accomplished by prolonged treatment with hot acetic anhydride or by treatment with a mixture of phosphorus oxychloride and phosphorus pentachloride. *S-p*-Chlorobenzylthiuronium 2-phenylpropene-1,3-disulfonate was isolated from each reaction. This was the same as the corresponding derivative obtained from the principal sulfonation product of α -methylstyrene.

Allylbenzene is readily sulfonated by dioxane sulfotrioxide at 10–20°. The course of the sulfonation was not appreciably altered by the mode of addition of the reagent. An aqueous solution of the barium sulfonates resulting from subsequent hydrolysis of the sulfonation mixture deposited a hydroxysulfonate in approximately 48% yields, based on the amount of sulfur trioxide employed. A pure unsaturated monosulfonate was also obtained from the filtrate. However, the major portion of the remaining material resisted further purification by fractional crystallization. Evidence was also obtained that a fairly stable intermediate in the hydrolysis was barium β -benzylethionate, $[\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OSO}_3)\text{CH}_2\text{SO}_3]\text{Ba}$. To obtain evidence for the structure of the hydroxysulfonate 1-phenyl-2-hydroxy-3-bromopropane, $\text{C}_6\text{H}_5\text{CH}_2\text{CHOHCH}_2\text{Br}$, was prepared by treating allylbenzene with an aqueous solution of bromine and potassium bromide. This bromohydrin was treated with sodium sulfite to yield sodium 3-phenyl-2-hydroxypropane-1-sulfonate. The behavior of this material was identical with that of the sodium hydroxysulfo-

(7) Baeyer and Company, German Patent 168,941, Friedländer, "Fortschritte der Teerfarbenfabrikation," Vol. 8, p. 1043.

(8) Strecker, *Ann.*, **148**, 90 (1868).

nate obtained by the sulfonation of allylbenzene. It yielded *S*-benzylthiuronium 3-phenyl-2-hydroxypropane-1-sulfonate and sodium 3-phenyl-2-acetoxypropane-1-sulfonate which were identical with the same derivatives obtained from the sulfonation product. The unsaturated sulfonic acid was shown to be 3-phenyl-2-propene-1-sulfonic acid by a comparison of its *S*-*p*-chlorobenzylthiuronium salt with that obtained from the product of the reaction between cinnamyl chloride and sodium sulfite. The hydroxysulfonate yielded a sulfonamide which was difficult to purify, probably because of the formation of two or more of the possible isomeric 3-phenylpropene-1-sulfonamides. A pure product was obtained in low yields. This was not the same as the pure sulfonamide obtained from sodium 3-phenyl-2-propene-1-sulfonate. Both products analyzed correctly for a 3-phenylpropene-1-sulfonamide.

Sodium 3-phenyl-2-acetoxypropane-1-sulfonate pyrolyzed smoothly a little above its melting point to yield acetic acid and sodium 3-phenyl-2-propene-1-sulfonate, $C_6H_5CH=CHCH_2SO_3Na$. Since this compound also was obtained from cinnamyl chloride the original hydroxysulfonate cannot have the alternative formula, $C_6H_5CH_2CH(SO_3Na)CH_2OH$.

The sulfonation of propenylbenzene occurs readily at 15–20° by substitution; the resulting unsaturated sulfonic acid was obtained in practically theoretical yields as the barium salt. Analyses for barium gave low results, probably because of varying amounts of occluded water (the salt was difficult to dry, undergoing decomposition on prolonged heating even at 80°). Sodium analyses on the corresponding sodium salt were in agreement with the formula, $C_6H_5CH=C(CH_3)SO_3Na \cdot H_2O$. This material did not immediately reduce bromine water but did reduce a dilute solution of potassium permanganate with the formation of benzoic acid. Excellent yields (52% over-all) of the sulfonamide were obtained. It analyzed correctly for 1-phenyl-1-propene-2-sulfonamide, $C_6H_5CH=C(CH_3)SO_2NH_2$.

Attempts were made to prepare sodium 1-phenyl-1-hydroxypropane-2-sulfonate from the halohydrins obtained by treating propenylbenzene with an aqueous solution of bromine and potassium bromide or with an aqueous solution of hypochlorous acid. However, in each reaction an appreciable quantity of side products was obtained, chief among which seemed to be sodium 1-phenyl-1,2-propanedisulfonate (as indicated by sodium analyses). A pure sample of 1-phenyl-1-hydroxy-2-bromopropane was prepared by the reduction of α -bromopropiophenone.⁹ This bromohydrin was then converted to sodium 1-phenyl-1-hydroxypropane-2-sulfonate. The benzylthiuronium salt of this was not the same as that obtained from the sulfonation product of propenylbenzene. However, it yielded 1-phenyl-1-

propene-2-sulfonamide which was identical with the sulfonamide obtained from the sulfonation product of propenylbenzene. Hence propenylbenzene and styrene² sulfonate in a different manner than do other olefins so far studied. The implications of these results for the mechanism of sulfonation reactions will be discussed elsewhere.

Since the sodium salt from the sulfonation of propenylbenzene melted at about 180° (somewhat variable) a pyrolysis seemed of interest. On heating the material at 210–213° propenylbenzene (identified by some of its physical constants and its dibromide) and water were evolved. The residue consisted largely of sodium sulfate (identified through its *S*-*p*-chlorobenzylthiuronium salt). This result is not too surprising since by the principle of vinylogy, the sulfonate group in $C_6H_5CH=C(CH_3)SO_3Na \cdot H_2O$ would be expected to partake of some of the properties of the sulfo group in benzenesulfonic acid which is replaced by hydrogen on heating in a current of superheated steam at 175°. In the present reaction the water of crystallization which is released at an elevated temperature takes the place of a current of superheated steam. The yields in this experiment were rather poor and appreciable decomposition took place.

Experimental¹¹

Sulfonation of α -Methylstyrene.—One hundred and eleven grams (0.94 mole) of α -methylstyrene was added slowly and with stirring to a sludge of 176 g. (2.0 moles) of dioxane, 135 g. (1.69 moles) of sulfur trioxide and 400 g. of ethylene chloride. The temperature of the reaction mixture was kept at 20°. At the end of the addition the temperature was allowed to rise to 25°. The clear, light-orange solution was kept at 5° overnight. It was then poured into a hot solution of 145 g. (0.845 mole) of anhydrous barium hydroxide in one liter of water. Since the mixture was still acidic, an additional 40 g. (0.234 mole) of anhydrous barium hydroxide was added. Excess barium hydroxide was precipitated with carbon dioxide. The mixture was boiled with a total of three liters of water, and filtered. The white residue weighed 150 g. The filtrate was evaporated to dryness, leaving 292 g. of a light-yellow solid. A quantity of this solid was recrystallized from a water-acetone mixture.

Anal. Calcd. for $C_9H_9O_3S_2Ba$: Ba, 33.22. Found: Ba, 31.70, 31.76.

The material reduced cold, dilute, neutral potassium permanganate solution with the formation of benzaldehyde. It decolorized bromine water with the formation of barium sulfate.

The *S*-*p*-chlorobenzylthiuronium salt was prepared.⁶ This was crystallized several times from ethyl alcohol-water solutions and from methyl alcohol. This salt melted at 215–217°.

Anal. Calcd. for $C_{25}H_{23}O_4Cl_2N_4S_4$: Cl, 10.44. Found: Cl, 10.32, 10.39.

Fifty-four grams (0.46 mole) of α -methylstyrene was added dropwise to a sludge of 85 g. (0.94 mole) of sulfur trioxide, 176 g. of dioxane and 500 g. of carbon tetrachloride. The temperature of the reaction mixture was kept at 10–15°. By the end of the addition, a two-layer system was obtained. Eighty grams of ethylene chloride was added to obtain a single liquid phase. The mixture

(10) Armstrong and Miller, *J. Chem. Soc.*, **45**, 148 (1884).

(11) The melting points in this section are uncorrected.

(9) Stevens, Allenby and Dubois, *This Journal*, **62**, 1424 (1940).

was filtered. Approximately 5 g. of a crystalline, hygroscopic residue was obtained. The filtrate was chilled to 0°. The resulting mixture was filtered under anhydrous conditions and the residue was washed with 150 cc. of dry ether. The yield of the hygroscopic dioxane salt was 93 g. or 57% of the theoretical.

Anal. Calcd. for $C_{12}H_{14}C(CH_2SO_3H)=CHSO_3H \cdot C_4H_8O_2$: neut. equiv., 183. Found: neut. equiv., 181.

Dioxane was identified as a constituent by neutralizing 5.71 g. of the above material with sodium hydroxide solution and then distilling about 20 cc. of the liquid. This was saturated with potassium carbonate and extracted with ether. After drying, this was distilled. The fraction, 0.47 g., b. p. 99–101°, n_D^{20} 1.4053, was collected. It gave a heavy, white precipitate with concentrated sulfuric acid, did not decolorize bromine in carbon tetrachloride and was soluble in water and in ethylene chloride. The aqueous residue from the above distillation was evaporated to dryness. The residue was recrystallized from water, washed with ethyl alcohol and dried.

Anal. Calcd. for $C_8H_8O_6S_2Na_2$: Na, 14.26. Found: Na, 13.88, 14.13.

2-Phenylpropene-1,3-disulfonamide.—A mixture of 11.5 g. of the dioxane salt, 22 g. of phosphorus pentachloride and 50 ml. of ethylene chloride reacted immediately with the evolution of hydrogen chloride. The mixture was refluxed for three hours and allowed to stand at room temperature for three days. The clear, light-yellow solution was washed with two 50-ml. portions of cold water, dried over anhydrous sodium sulfate, filtered and excess liquid ammonia added. After evaporation of unreacted ammonia the mixture was diluted to 100 ml. with ethylene chloride, heated to boiling and filtered. Ligroin was added to the filtrate and the mixture was chilled and filtered. The residue, 3.2 g., was recrystallized several times from water. The resulting product melted at 197–200°. The yield was 36% of the theoretical.

Anal. Calcd. for $C_9H_{10}O_4N_2S_2$: S, 23.2. Found: S, 23.4.

Proof of Structure of 2-Phenylpropene-1,3-disulfonic Acid.— β -Phenyldichlorohydrin was prepared from symmetrical dichloroacetone and phenylmagnesium bromide.⁷ The yield was 72% of the theoretical amount. A mixture of 55.3 g. (0.27 mole) of β -phenyldichlorohydrin (n_D^{20} 1.5605; b. p. 161–165° (24 mm.)), 68.1 g. (0.54 mole) of anhydrous sodium sulfite, and 200 cc. of water was heated on the steam-bath for sixty hours. The resulting solution was evaporated to about 175 ml. on the steam-bath. This was chilled and filtered. The solid was recrystallized from a water-ethyl alcohol solution. The purified material weighed 62.4 g., which is 68% of the theoretical.

Anal. Calcd. for $C_9H_{10}O_7S_2Na_2$: Na, 13.53. Found: Na, 14.1, 14.2.

The *S-p*-chlorobenzylthiuronium salt was prepared. It melted at 164–166°.

Anal. Calcd. for $(C_6H_4CH_2SCN_2H_4)_2[C_6H_5CHOH(CH_2SO_3)_2]$: Cl, 10.16. Found: Cl, 9.95, 9.80.

A mixture of 1.0 g. of the sodium salt and 5 ml. of acetic anhydride was kept at a temperature close to the boiling point for ten hours. Most of the acetic anhydride was then removed under reduced pressure. The residue was dissolved in water and the solution was filtered with decolorizing charcoal. The hot filtrate (5 ml.) was added to a hot solution of 1.4 g. of *S-p*-chlorobenzylthiuronium chloride in 20 ml. of alcohol. The precipitated oil was recrystallized several times from alcohol-chloroform mixtures. The final melting point was 209–214°. A mixed melting point with the corresponding salt obtained from the sulfonation product of α -methylstyrene was 209–215°.

A mixture of 15 g. of the sodium salt, 15 g. of phosphorus pentachloride and 20 g. of phosphorus oxychloride was kept at 75° for five hours. The mixture was extracted with chloroform and this extract was washed with water. The material was heated on the steam-bath for one hour with an excess of an aqueous solution of sodium hydroxide.

The resulting solution was diluted to 100 ml. and filtered with decolorizing charcoal. The filtrate was acidified slightly with hydrochloric acid and refiltered. The hot filtrate was added to a hot solution of 5 g. of *S-p*-chlorobenzylthiuronium chloride in 20 ml. of water. The thick oil which precipitated was recrystallized from 95% ethyl alcohol. The product melted at 213.5–215°, and gave a mixed melting point with the corresponding salt obtained from a sulfonation product of α -methylstyrene of 214–215°.

Anal. Calcd. for $C_{25}H_{23}O_6S_4Cl_2N_4$: Cl, 10.44. Found: Cl, 10.4.

Sulfonation of Allylbenzene.—Ninety-two grams (0.78 mole) of allylbenzene was added slowly to a sludge of 88 g. of dioxane, 68 g. (0.85 mole) of sulfur trioxide and 300 g. of ethylene chloride. The temperature of the reaction mixture was kept below 20°. This mixture was hydrolyzed by heating with an excess of an aqueous solution of barium hydroxide. The aqueous extract (2 liters) on cooling deposited 57 g. of a white crystalline solid, product A. The filtrate was evaporated to dryness, leaving 68 g. of a resinous solid, product B. A dilute solution of product A gave no reaction with bromine water or with dilute, cold, neutral potassium permanganate solution.

Anal. Calcd. for $C_{11}H_{12}O_3S_2Ba$: Ba, 24.20. Found: Ba, 24.61, 24.57.

The *S-p*-chlorobenzylthiuronium salt was prepared. This was recrystallized from water. It melted at 156–158°.

Anal. Calcd. for $C_{17}H_{21}ClS_2N_2O_4$: S, 16.83. Found: S, 16.3, 16.4.

Thirty grams of potassium permanganate was added slowly to a solution of 10 g. of product A in 200 ml. of water. The resulting solution was heated on the steam-bath for one hour. The mixture was filtered and the filtrate was acidified. The crystalline material obtained by filtration and extraction with ether, m. p. 117–119°, 3.6 g., represents a yield of benzoic acid of 82% of the theoretical.

A mixture of 7.0 g. of product A, 15 g. of phosphorus pentachloride and 50 ml. of ethylene chloride was refluxed on a steam-bath for twelve hours. The mixture was filtered. The filtrate was washed with water and dried over anhydrous sodium sulfate. An excess of liquid ammonia was added. After excess ammonia had evaporated, the mixture was heated to boiling and filtered. This filtrate was evaporated to a thick brown oil which was heated to boiling with 25 ml. of water and filtered. On cooling, an oil was deposited which slowly crystallized (0.40 g.). This was recrystallized twice from water and then melted at 65–67°.

Anal. Calcd. for $C_9H_{11}NO_2S$: S, 16.26. Found: S, 15.8.

The above procedure was repeated with 15 g. of sodium 3-phenylpropene-1-sulfonate which was prepared by a Strecker reaction between cinnamyl chloride and sodium sulfite. This sulfonamide melted at 126–127° after crystallization from a water-ethyl alcohol mixture and weighed 1.90 g.

Anal. Calcd. for $C_9H_{11}NO_2S$: S, 16.26. Found: S, 15.9.

Sodium 3-Phenyl-2-acetoxypropane-1-sulfonic Acid.—A portion of product A was converted to the sodium salt. A mixture of 10 g. of the sodium salt and 50 ml. of acetic anhydride was heated at about 120° for one hour. The mixture was filtered hot. The filtrate was kept at 50° overnight and was then evaporated to a volume of 10 ml. under reduced pressure. About 100 ml. of ether was added and the resulting mixture was filtered. The residue was extracted with 100 ml. of boiling alcohol. This was evaporated to 60 ml.; a little ether was added and the mixture was chilled and filtered. The residue after drying at 50° for six days melted at 170–177°. It was recrystallized from an alcohol-ether mixture and dried at 78° under reduced pressure for three hours (m. p. 171–174°).

Anal. Calcd. for $C_{11}H_{13}O_6SNa$: Na, 8.21. Found: Na, 8.24, 8.24.

Four and four-tenths grams of the acetoxy derivative was kept at 210–215° for ninety minutes. Acetic acid (0.7 ml.) was evolved and identified by its anilide. The residue from the pyrolysis was dissolved in water and the solution was filtered and evaporated to 5 ml. On cooling, a white crystalline precipitate, 1.3 g., was obtained. This gave a positive Bayer test for unsaturation.

Anal. Calcd. for $C_9H_9O_3SNa$: Na, 10.44. Found: Na, 11.02, 10.90.

The *S-p*-chlorobenzylthiuronium salt of this product was formed. It crystallized well from water and melted at 196–198°.

Anal. Calcd. for $C_{17}H_{19}ClN_2O_3S_2$: Cl, 8.89. Found: Cl, 9.03, 8.80.

Cinnamyl chloride and sodium sulfite were converted to sodium 3-phenyl-2-propene-1-sulfonate. The corresponding *S-p*-chlorobenzylthiuronium salt was prepared. It melted at 196–197.5° and gave a mixed melting point with the *S-p*-chlorobenzylthiuronium salt from the pyrolysis product of 196–197.5°.

Proof of Structure of 3-Phenyl-2-hydroxypropane-1-sulfonic Acid.—A mixture of 30 g. (0.24 mole) of allylbenzene and 500 ml. of water was emulsified by vigorous stirring and kept at 90°. A solution of 45 g. (0.28 mole) of bromine and 45 g. of potassium bromide in 700 ml. of water was added dropwise. Toward the end of the addition the mixture absorbed bromine slowly. The mixture was cooled and extracted with benzene. Assuming a 70% yield of the bromohydrin (a yield of 76% of the bromohydrin from anethole was reported¹²), the above reaction product, after removal of the benzene, was stirred and heated on the steam-bath for two days with 22.1 g. (0.175 mole) of anhydrous sodium sulfite and 150 ml. of water. The mixture was cooled, enough water was added to keep the salts in solution and the mixture was extracted with ether. The ether extract yielded 23 g. of a viscous oil. The aqueous solution was evaporated to 250 ml., and chilled. Flaky, white crystals were formed. The dried material weighed 30.5 g.

Anal. Calcd. for $C_9H_{11}SO_4Na$: Na, 9.65. Found: Na, 9.40, 9.54.

It yielded an acetylated derivative by the procedure described above which melted at 172–174° and gave a mixed melting point with the sodium acetoxy sulfonate obtained from allylbenzene of 171–173°.

The corresponding *S*-benzylthiuronium salt was prepared. It melted at 158–159°. A mixed melting point with the same derivative of the allylbenzene sulfonation product (m. p., 156–158°) was 156–158°.

Identification of 3-Phenyl-2-propene-1-sulfonic Acid.—Product B from the sulfonation of allylbenzene was fractionally crystallized from water. The crystalline fractions were small. They were contaminated by product A. However, one of the fractions yielded a *S-p*-chlorobenzylthiuronium salt which, after several recrystallizations, melted at 195–197°. The *S-p*-chlorobenzylthiuronium salt of the "cinnamyl" sulfonate melted at 196–197°. A mixed melting point was 195–197°.

Sulfonation of Propenylbenzene.—Ninety grams (0.76 mole) of propenylbenzene was added slowly to a sludge of 61 g. (0.76 mole) of sulfur trioxide, 75 g. of dioxane and 300 ml. of ethylene chloride. The temperature of the reaction mixture was kept at 15–20°. It did not become clear until all the olefin had been added. An aqueous extract needed 122 g. (0.83 mole) of $Ba(OH)_2 \cdot 8H_2O$ for neutralization. The mixture was heated to boiling and filtered. The filtrate was evaporated to 500 cc., chilled and filtered. The crystalline residue, 107 g., was recrystallized twice from water. This salt had a variable decomposition point in the neighborhood of 200°. Analyses varied depending on the amount of drying.

Anal. Calcd. for $C_{10}H_{12}S_2O_6Ba$: Ba, 25.84. Found: Ba, 22.60, 22.65, 22.80, 23.65, 23.84, 23.90, 24.00.

A portion of this salt was oxidized in an alkaline solution of potassium permanganate, yielding 89% of the theoretical amount of benzoic acid.

The sodium salt was prepared. It was recrystallized from water and melted at about 180° (somewhat variable). It did not reduce bromine water but did reduce dilute, neutral potassium permanganate solution slowly with the formation of sulfate ion and benzaldehyde.

Anal. Calcd. for $C_9H_9SO_3Na$: Na, 10.45. Found: Na, 9.76, 9.66.

The *S-p*-chlorobenzylthiuronium salt was formed and recrystallized from water. It melted at 162–163°.

Anal. Calcd. for $C_{17}H_{19}O_3N_2ClS_2$: Cl, 8.88. Found: Cl, 8.56, 8.65.

Three grams of the above sodium salt was heated slowly to 230°. A volatile distillate, 0.25 ml. of water and 0.80 ml. of an organic liquid, was obtained. The mixture was extracted with ether and the ether was evaporated to a colorless oil, b. p. 170–171° (750 mm.), n_D^{20} 1.5493. It yielded a dibromide melting at 59–61°. The constants for propenylbenzene are: b. p. 176–177° (760 mm.), n_D^{20} 1.5493; and the dibromide melts at 66–67°. The residue from this pyrolysis yielded a *S-p*-chlorobenzylthiuronium salt which melted at 236–237° dec.

Anal. Calcd. for $C_{16}H_{20}O_4N_4Cl_2S_3$: Cl, 14.2. Found: Cl, 14.2, 14.7.

S-p-Chlorobenzylthiuronium sulfate melted at 234–235° dec. and gave no depression of melting point.

1-Phenyl-1-propene-2-sulfonamide.—A mixture of 8.0 g. of the sodium salt, 20 g. of phosphorus pentachloride and 50 ml. of carbon tetrachloride gave an immediate and vigorous reaction. The mixture was refluxed for eighteen hours. It was cooled and filtered and the filtrate was washed with water. After drying and refiltering, liquid ammonia was added to the solution. On adding ligroin and a little ethylene chloride to the solution and then chilling, 3.6 g. of a white solid was obtained. This was recrystallized from ethylene chloride–ligroin mixtures and melted at 138–139°.

Anal. Calcd. for $C_9H_{11}O_2NS$: S, 16.26. Found: S, 16.42, 16.55.

Proof of Structure of 1-Phenylpropene-2-sulfonic Acid.—Mixtures of the halohydrin and the dihalide were obtained by treating propenylbenzene with bromine water¹³ or with an aqueous solution of hypochlorous acid. Therefore, 1-phenyl-1-hydroxy-2-bromopropane was prepared according to the method of Stevens, Allenby and Dubois,⁹ in yields of 60% of the theoretical based on the amount of α -bromopropiophenone. Thirty-nine grams (0.181 mole) of this material, 23 g. (0.182 mole) of anhydrous sodium sulfite and 100 ml. of water were mixed, heated and stirred on the steam-bath for thirty-six hours. The mixture was cooled and extracted with ether. This extract yielded 8.7 g. of a viscous oil. The aqueous solution was evaporated to 70 cc. This was extracted with 500 ml. of hot 95% alcohol. The extract was evaporated to dryness leaving 29.4 g. of a white solid which was recrystallized from 95% alcohol. The material did not reduce bromine water or dilute potassium permanganate solution, and it tested negatively for bromide and sulfate ions. It decomposed above 250°.

Anal. Calcd. for $C_9H_{11}O_4SNa$: Na, 9.65. Found: Na, 9.65, 9.67.

A portion of the sodium salt was used to prepare the sulfonamide according to the method described earlier. This material melted at 138–139° and gave a mixed melting point with the sulfonamide from the sulfonation product of propenylbenzene of 138–139°.

The *S-p*-chlorobenzylthiuronium salt of the sodium salt was formed. After several crystallizations from water–alcohol mixtures this material melted at 184–185°.

Summary

1. α -Methylstyrene when sulfonated gave 2-phenylpropene-1,3-disulfonic acid as the principal

(12) Read and Ried, *J. Chem. Soc.*, 1487 (1928).

product. By moderating the conditions, an appreciable amount of monosulfonation took place.

2. In the sulfonation of propenylbenzene the sole product was 1-phenylpropene-2-sulfonic acid.

3. Allylbenzene gave about a 50% yield of 3-

phenyl-2-hydroxypropane-1-sulfonic acid, isolated as the barium salt from the hydrolyzed reaction mixture. An appreciable quantity of 3-phenyl-2-propene-1-sulfonic acid also was formed.

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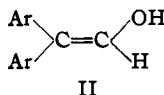
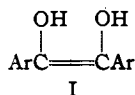
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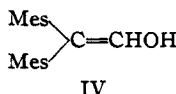
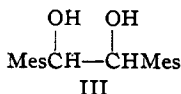
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It has been demonstrated⁴ that in stilbenediols (I) the tendency of a hydroxyl group to undergo ketonization is dependent on the radical in the 2 position to a greater extent than on that in the adjacent 1 position. It was conceivable that



crowding at the 1 carbon atom might be dispensed with altogether. This postulates the existence of a stable enol of type II. Reports have been made, in fact, of the isolation of certain diaryl-acetaldehydes in the corresponding enol forms. These claims, however, have not been substantiated.

In the search for such a vinyl alcohol it was assumed that its stability would increase with the size and complexity of the aryl radicals and attention was turned to the mesityl radical. As was reported earlier,⁵ dehydration of hydromesitoin (III), isohydromesitoin⁶ or a mixture of the two was found experimentally to yield the enol form (IV) of the normal rearrangement product, dimesitylacetaldehyde. The dehydration was accomplished with 55% sulfuric acid, a mixture of glacial acetic acid and hydrochloric acid or phosphorus pentoxide. In fact, the vinyl alcohol could be produced from isohydromesitoin simply by heating. The highest yields (80%) were obtained by the sulfuric acid method. Two high-melting by-products, apparently a dimer and a trimer of the vinyl alcohol, were isolated in small amounts.



2,2-Dimesitylvinylic alcohol (IV) yielded an acetate which proved to be unlike either of the

(1) For the preceding communication in this series see Fuson, Armstrong and Shenk, *THIS JOURNAL*, **66**, 964 (1944).

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(4) Fuson and Soper, *THIS JOURNAL*, **65**, 915 (1943).

(5) Fuson and Rowland, *ibid.*, **65**, 992 (1943).

(6) Fuson, Horning, Ward and Marsh, *ibid.*, **64**, 36 (1942).

two 1,2-dimesitylvinylic acetates. 2,2-Dimesitylvinylic benzoate was also synthesized. It, likewise, was found to be different from the 1,2-dimesitylvinylic benzoates. These results confirm the conclusion that in the stable vinyl alcohol the two mesityl radicals are attached to the 2 carbon atom.

The new vinyl alcohol (IV) behaved in general as an alcohol rather than as an enol. For example, it was not acidic and gave no color with ferric chloride. Its stability was remarkable, as the methods of preparation attest. In contrast to typical enols, it was unaffected by oxygen even on long contact. Catalytic hydrogenation converted the vinyl alcohol to the corresponding saturated alcohol, 2,2-dimesitylethanol; m. p. 118-119°. The isomeric 1,2-dimesitylethanol melts at 128-129°.⁷

Attempts to bring about ketonization of the vinyl alcohol by heating with solutions of hydrogen chloride in methanol or ethanol produced solid derivatives which were identified as the corresponding methyl and ethyl ethers, respectively. In methanol under similar conditions isohydromesitoin also yielded the methyl ether. The aldehyde, 2,2-dimesitylacetaldehyde, which was to be expected is not known. There is, in particular, no evidence of the presence of the aldehyde in solutions of the enol.

Oxidation of the vinyl alcohol as well as of the corresponding saturated alcohol, 1,1-dimesitylethanol, generally produced abnormal changes. There was observed a pronounced tendency for rearrangement to a 1,2-dimesityl derivative. Thus when the vinyl alcohol was oxidized with ozone the product was mesitoin; chromic anhydride or selenium dioxide produced mesitil.

Oxidation with permanganate or hypochlorite produced a dimeric derivative, which had properties reminiscent of those of hexaarylethanes. Its solutions developed a red or purple color when heated. Cooling of the mixture discharged the color. The compound could be recovered unchanged. It contained one active hydrogen atom. No satisfactory formula has been written for this compound. Oxidation with chromic acid converted it to mesitil. There was evidence that

(7) Fuson, Denton and Best, *J. Org. Chem.*, **8**, 64 (1943).