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Sulfonation of β-Bromostyrene

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Styrene[1] and its derivatives, α- and β-methylstyrene,[2] react with dioxane sulfotrioxide to yield unsaturated sulfonic acids. The electrophilic agent, sulfur trioxide, attaches itself to the β-carbon atom(s). It might be anticipated that the nature of the reaction would be modified by substituents on the β-carbon atom. For example, it was found that β-nitrostyrene is practically inert to this sulfonating agent, presumably because of the strong electron-attracting effect of the nitro group. This paper describes the results obtained with β-bromostyrene. A later paper will describe the results obtained with the stilbenes.

β-Bromostyrene was sulfonated slowly and incompletely by dioxane sulfotrioxide at 15–20°. The reaction mixture had to be neutralized carefully to avoid splitting off bromide and sulfite ions. An aqueous solution of the hydrolysis products yielded a large quantity of a crystalline barium sulfonate which proved to be barium 1-bromo-2-phenylethene-1-sulfonate. This compound did not react with bromine water but reduced a dilute solution of potassium permanganate with the formation of bromine and barium sulfate. The corresponding sulfonamide was prepared from the sodium sulfonate in poor yield. However, the barium sulfonate was reduced in good yield to barium 2-phenylethene-1-sulfonate which was converted directly to its sulfonamide, this being identical with authentic 2-phenylethene-1-sulfonamide.[1] The reduction was effected by zinc and hydrochloric acid following a procedure like that used by Kohler[3] to reduce α-bromoethylenesulfonic acid to ethylenesulfonic acid.

$$C_6H_5CH{=}CHBr \xrightarrow{OC_6H_4OSO_3} \xrightarrow[H_2O\ +\ Ba(OH)_2]{\text{then}} (C_6H_5CH{=}CBrSO_3)_2Ba$$

$$(C_6H_5CH{=}CBrSO_3)_2Ba + Na_2SO_4 \longrightarrow C_6H_5CH{=}CBrSO_3Na \xrightarrow[ClCH_2CH_2Cl]{PCl_5} \xrightarrow{NH_3} C_6H_5CH{=}CBrSO_2NH_2$$

$$(C_6H_5CH{=}CBrSO_3)_2Ba \xrightarrow[HCl]{Zn} \xrightarrow[ClCH_2CH_2Cl]{PCl_5} \xrightarrow{NH_3} C_6H_5CH{=}CHSO_2NH_2$$

Besides 1-bromo-2-phenylethene-1-sulfonic acid, a water-insoluble mixture was formed in the above sulfonation in about 10% yield. Two main fractions were isolated from this mixture by fractional crystallization. One had a definite crystalline nature and melting point. The compound did not yield a sulfonamide, the starting material being reisolated by the procedure used. The analysis agreed fairly well with that calculated for the formula, $(C_6H_5CHCHBrSO_2)_2$. The second fraction was an amorphous, difficultly-soluble solid with a somewhat variable decomposition point. It was converted in poor yield to 1-bromo-2-phenylethene-1-sulfonamide. Its analysis agreed well with that calculated for the formula, $(C_6H_5CHCBrSO_3)_x$. The hydrolysis of both materials was complicated by release of bromide and sulfite ions and, in the case of the first fraction, a small quantity of benzoic acid resulted.

Experimental

Sulfonation of β-Bromostyrene.—Two hundred and thirty-one grams (1.26 moles) of β-bromostyrene (Eastman Kodak Product, b. p. 104–108° (19 mm.), 119–123° (32 mm.)) was added slowly to a sludge of 175 g. (2.19 moles) of sulfur trioxide, 180 g. of dioxane, and 800 g. of ethylene chloride. The temperature of the reaction mixture was kept at 15–20°. Little heat was evolved. At the end of the addition, the mixture was stirred for two hours at 15–20°. The mixture was filtered; 68 g. (0.405 mole) of the dioxane–sulfotrioxide reagent remained as a residue. The filtrate was extracted with one liter of water. The ethylene chloride layer was dried and distilled, yielding 28 g. (0.153 mole) of β-bromostyrene (b. p. 92–93° (13 mm.)) and a large quantity of tar as a residue. The aqueous extract tested negatively for bromide ion but positively for sulfate ion. It was neutralized at 25–30° with an aqueous suspension of barium hydroxide. The resulting mixture was filtered. The dried residue weighed 249 g. The filtrate (about 1600 cc.) was evaporated to a volume of 500 cc. at a temperature of 48°. This solution was very slightly acidic and gave a very faint test for bromide ion. The mixture was chilled. A large quantity of white, crystalline material was deposited. This was filtered off and, after drying at 48° for eight days, weighed 130 g. The filtrate was evaporated to dryness. The residue (same as the above solid) was dried at 48° for five days and weighed 70 g. Some of this material was recrystallized from water and dried under reduced pressure.

Anal. Calcd. for $C_{16}H_{12}O_6Br_2S_2Ba$: Ba, 20.8. Found: Ba, 20.1.

A dilute aqueous solution of the barium sulfonate reduced a dilute solution of potassium permanganate slowly and with the formation of some bromine and sulfate ion. It had no apparent effect on bromine water.

The sodium salt was formed by metathesis with sodium sulfate. The resulting mixture was filtered and the filtrate was evaporated to dryness. The residue was crystallized from 95% ethyl alcohol. The material was dried under reduced pressure at 78° for two hours.

Anal. Calcd. for $C_8H_6O_3BrSNa$: Na, 8.01. Found: Na, 7.9.

No success was had in obtaining a crystalline S-*p*-chlorobenzylthiuronium salt.[4]

1-Bromo-2-phenylethene-1-sulfonamide.—A mixture of 10 g. of the sodium sulfonate, 22 g. of phosphorus pentachloride and 50 cc. of ethylene chloride was refluxed overnight. The mixture was filtered. The filtrate was washed

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[1] Bordwell, Suter, Holbert and Rondestvedt, THIS JOURNAL, **68**, 139 (1946).

[2] Suter and Truce, *ibid.*, **66**, 1105 (1944).

[3] Kohler, *Am. Chem. J.*, **21**, 349 (1899).

[4] Donleavy, THIS JOURNAL, **58**, 1004 (1936).

with two 50-cc. portions of cold water and then dried over anhydrous sodium sulfate. Liquid ammonia was added slowly to this filtrate. After the excess had evaporated, the mixture was heated to boiling and filtered. The filtrate was evaporated to a volume of 20 cc. and chilled. Long needles crystallized. These were filtered. They weighed 1.41 g. and after recrystallization from water melted at 132–133°.

Anal. Calcd. for $C_8H_8O_2BrNS$: Br, 30.5; N, 5.34. Found: Br, 30.9; N, 5.34.

A dilute aqueous solution of this amide reduced dilute potassium permanganate solution readily with the formation of sulfate ion.

Reduction of Barium 1-Bromo-2-phenylethene-1-sulfonate.—Fifteen grams of the barium sulfonate was dissolved in 75 cc. of hot water. Twenty-five grams of zinc powder was added. The mixture was stirred well and heated to 70–75°. Fifty milliliters of 6 *N* hydrochloric acid was added slowly. This mixture was stirred at 70–75° for one hour. Then a solution of hydrogen sulfide in dilute ammonium hydroxide was added until the mixture turned basic to litmus. The resulting mixture, containing precipitated zinc sulfide and zinc hydroxide, had to be filtered several times. Excess lead oxide was added to the filtrate to remove ammonium chloride and ammonium sulfide. This mixture was heated to boiling, cooled and filtered. The filtrate was evaporated to dryness on the steam-bath and the residue was dried at 100° under reduced pressure for three hours. This dried powder was mixed with 25 g. of phosphorus pentachloride and 50 cc. of ethylene chloride. The mixture was refluxed for fifteen hours and then filtered. The filtrate was washed with 50 cc. of cold water and dried over anhydrous sodium sulfate. Liquid ammonia was passed into the solution. After the excess ammonia had evaporated, the mixture was heated to boiling and filtered. Ligroin was added to this filtrate to the point of incipient turbidity at the boiling point. On chilling, no precipitate was obtained. The solution was evaporated to dryness, leaving a solid residue which melted at 130–135°. This was recrystallized three times from 25-cc. portions of water. This crystalline material melted at 140–142°, weighed 1.2 g. and contained sulfur and nitrogen but no halogen. 2-Phenylethylene-1-sulfonamide was prepared from sodium 2-phenylethylene-1-sulfonate which was obtained by sulfonating styrene with dioxane sulfotrioxide.[1] The melting point of this material was 140–142°. A mixed melting point with the sulfonamide prepared from the above reduction product was 140–142°.

Isolation and Investigation of Other Products.—A sludge of 84 g. (1.05 moles) of sulfur trioxide, 80 g. of dioxane, and 300 g. of ethylene chloride was added slowly to a solution of 185 g. (1.01 moles) of β-bromostyrene in 150 cc. of ethylene chloride. The temperature of the reaction mixture was kept at 15–20°. Sulfonation took place slowly as evidenced by the disappearance of solid dioxane sulfotrioxide and the formation of a light brown solution. No evolution of heat was observed. The mixture was kept in a refrigerator overnight. During the course of extracting the solution with 800 cc. of water, a white solid separated (as was also true in the previous and other sulfonations of β-bromostyrene). The two layers were filtered leaving 0.90 g. of residue. The ethylene chloride solution was evaporated to a sludge and filtered. The residue, after washing with ligroin, weighed 24.4 g. The filtrate, on chilling, deposited 3.0 g. of a white solid. The decomposition points of these products were 113–115°, 108–109° and 115–120°, respectively. These materials were subjected to several extractions and fractional crystallizations using chloroform, ethylene chloride and petroleum ether as solvents. Two fractions were obtained. Fraction A, a white crystalline solid which had been crystallized several times from chloroform melted at 117–119°. Fraction B, a white powder, decomposed at 109–110° and was but sparingly soluble in the above solvents. Both materials contained sulfur and bromine and dilute solutions in acetone had no effect on a cold, dilute, neutral potassium permanganate solution.

Anal. Calcd. for $C_{16}H_{14}O_4Br_2S_2$: C, 39.1; H, 2.86; Br, 32.34; S, 12.98; mol. wt., 494. Found for fraction A: C, 39.5; H, 3.06; Br, 32.3; S, 12.8; mol. wt. by benzene freezing-point depression, 405. Calcd. for $(C_8H_7O_3BrS)_x$: C, 36.5; H, 2.68; Br, 30.5; S, 11.91. Found for fraction B: C, 36.7; H, 2.97; Br, 30.5; S, 12.12. (Attempts to determine the molecular weight of fraction B were unsuccessful due to its poor solubility and its low decomposition point.)

A mixture of 0.33 g. of fraction A, 1.2 g. of phosphorus pentachloride and 10 cc. of ethylene chloride was refluxed for thirteen hours. The solution was diluted with 20 cc. of ethylene chloride, washed with water, dried over anhydrous magnesium sulfate, and filtered. Liquid ammonia was added to the filtrate. After the excess had evaporated, the mixture was heated to boiling and filtered. This filtrate was evaporated to a thick brown oil. A hot water extract yielded nothing. The oil was then crystallized from an ethyl alcohol–ligroin mixture. The crystalline material weighed 0.11 g. It did not depress the melting point of the starting material but it did depress the melting point of 1-bromo-2-phenylethene-1-sulfonamide.

A mixture of 3.0 g. of product B, 10 g. of phosphorus pentachloride and 50 cc. of ethylene chloride was refluxed for fifteen hours. The mixture was filtered. Liquid ammonia was added to the filtrate. After the excess had evaporated, the mixture was heated to boiling and filtered. The filtrate was evaporated to a thick brown oil which was extracted with 25 cc. of hot water. The extract, on cooling, deposited 0.13 g. of a fine, crystalline material, m. p. 129–131°. A mixed melting point with the sulfonamide (m. p. 132–133°) obtained from the water soluble sulfonate in the previous sulfonation was 130–132°.

Summary

1. β-Bromostyrene was sulfonated by dioxane sulfotrioxide primarily to 1-bromo-2-phenylethene-1-sulfonic acid. Two other sulfonation products were isolated in small yields.

2. 1-Bromo-2-phenylethene-1-sulfonamide was prepared from the barium sulfonate.

3. Barium 1-bromo-2-phenylethene-1-sulfonate was reduced with zinc and hydrochloric acid to barium 2-phenylethene-1-sulfonate.

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