[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CONNECTICUT STATE COLLEGE]

The Benzenesulfonyl Derivatives of *o*-Nitroaniline and *o*-Phenylenediamine

BY LAWRENCE H. AMUNDSEN

When attempts to prepare certain of the benzenesulfonyl derivatives of *o*-nitroaniline and *o*-phenylenediamine led to results somewhat different from those reported in the literature, the synthesis and characterization of all the N-substituted benzenesulfonyl derivatives of these two amines was undertaken. The monobenzenesulfonyl derivative of *o*-nitroaniline[1–3] and the monobenzenesulfonyl,[1,2] N,N′-dibenzenesulfonyl[4] and tetrabenzenesulfonyl[4] derivatives of *o*-phenylenediamine have been described in the literature. Our results indicate that the compound Hinsberg and Strupler described as the tetrabenzenesulfonyl derivative is the tribenzenesulfonyl derivative and our attempts to prepare the tetra derivative never have been successful.

The preparation of N-2-nitrophenylbenzenesulfonamide by the three published methods[1–3] failed to give as good yields as were obtained by boiling for ten hours *o*-nitroaniline with 0.5 molecular proportion of benzenesulfonyl chloride in dioxane solution (1 cc. of dioxane for each gram of *o*-nitroaniline) and isolating the product by evaporating the solution to dryness, washing the residue with water and crystallizing from 95% alcohol. The method of Morgan and Micklewait[2] led to low yields, at least partially due to the formation of some of the disubstituted derivative, N-2-nitrophenyldibenzenesulfonamide. Much better yields of N-2-nitrophenyldibenzenesulfonamide were obtained by boiling for forty-five minutes a dioxane solution of benzenesulfonyl chloride (4 cc. of dioxane for each gram of the chloride) and one molecular proportion of the sodium salt of N-2-nitrophenylbenzenesulfonamide. The compound was isolated by adding four volumes of water, filtering off the insoluble product and crystallizing from glacial acetic acid. The sodium salt of N-2-nitrophenylbenzenesulfonamide has been prepared by Opolski,[3] but was prepared by us by dissolving the sulfonamide in hot 20% sodium hydroxide and cooling. At room temperature the solution formed two layers, the lower one of which crystallized when the solution was placed in the refrigerator for a few hours. The crystals were filtered, washed with a little ice water, then with alcohol and dried at 110°.

N-2-Aminophenylbenzenesulfonamide was prepared by the method of Morgan and Micklewait.[2] Low yields of N,N′-(*o*-phenylene)-bis-benzenesulfonamide were obtained by the method of Hinsberg and Strupler,[4] but better results were obtained by adding slowly 41 g. of benzenesulfonyl chloride to a hot solution of 25 g. of *o*-phenylenediamine in 150 cc. of toluene and then heating for thirty minutes. After cooling and filtering the solid material was boiled with 400 cc. of water and again filtered. The residue was crystallized from glacial acetic acid. Addition of sodium carbonate to the water extract precipitated 9.4 g. of the mono derivative, N-2-aminophenylbenzenesulfonamide. When this compound was prepared by the method of Hinsberg and Strupler[4] and precipitated by acidifying the sodium hydroxide solution with hydrochloric acid, it was contaminated with the benzenesulfonic acid salt of N-2-aminophenylbenzenesulfonamide. More of the salt was obtained by concentrating and cooling the filtrate. This salt gave N-2-aminophenylbenzenesulfonamide when dissolved in ammonium hydroxide solution and carefully neutralized with hydrochloric acid. N-2-Aminophenyldibenzenesulfonamide was prepared by reducing the corresponding nitro compound in dioxane solution with hydrogen in the presence of platinum catalyst prepared by the Bruce[5] modification of the well-known procedure of Adams[6] and also by adding 14 g. of powdered iron slowly to a solution of 19.5 g. of the nitro compound in 65 cc. of glacial acetic acid heated to boiling. Heating was continued for one and one-half hours and the residue extracted several times with boiling acetic acid. The acetic acid solutions were decolorized by boiling with activated carbon and the compound was precipitated by adding water. This compound was also prepared by reducing a suspension of the nitro compound in dilute acetic acid with powdered iron, but preserving a uniform mixture

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[1] Lellmann, *Ber.*, **16**, 594 (1883); *Ann.*, **221**, 16 (1883).

[2] Morgan and Micklewait, *J. Chem. Soc.*, **87**, 73 (1905).

[3] Opolski, *Ber.*, **40**, 3530 (1907).

[4] Hinsberg and Strupler, *Ann.*, **287**, 223 (1895).

[5] Bruce, THIS JOURNAL, **58**, 687 (1936).

[6] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y. Coll. Vol. I, 1932, p. 452.

TABLE I

Solvents from which the compounds were crystallized: A, alcohol; B, glacial acetic acid; C, butanol; D, mixture of alcohol and dioxane; E, water.

No.	Compound	Yield, %	Cryst. from	M. p., °C.[a]	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
1	N-2-Nitrophenylbenzenesulfonamide	70	A	102.2–102.5[b]	$C_{12}H_{10}N_2O_4S$				
2	N-Sodium salt of 1	81		239–240[c]	$C_{12}H_9N_2NaO_4S$				
3	N-2-Nitrophenyldibenzenesulfonamide	72	B, C or D	189.8–190.5	$C_{18}H_{14}N_2O_6S_2$	6.70	6.54	15.31	15.16
4	N-2-Aminophenylbenzenesulfonamide	64	50% A	169.3–170.0[d]	$C_{12}H_{12}N_2O_2S$				
5	N,N′-(*o*-Phenylene)-bis-benzenesulfonamide	71	B	190.3–190.8[e]	$C_{18}H_{16}N_2O_4S_2$				
6	N-2-Aminophenyldibenzenesulfonamide	41–62	A	149.5–149.9	$C_{18}H_{16}N_2O_4S_2$	7.22	7.23	16.52	16.23
7	N-2-Benzenesulfonylaminophenyldibenzenesulfonamide	83	A or B	157.1–157.3[f]	$C_{24}H_{20}N_2O_6S_3$	5.30	5.30	18.20	18.02
8	Benzenesulfonic acid salt of 4	29[g]	A or E	204.9–205.4	$C_{18}H_{18}N_2O_5S_2$	6.90	6.70	15.76	15.46
9	N,N′-Disodium salt of 5	90		Not below 275	$C_{18}H_{14}N_2Na_2O_4S_2$	6.48	6.17	14.81	14.17

[a] All melting points were taken with completely immersed short stem thermometers calibrated by the National Bureau of Standards and have been corrected. [b] Lellmann[1] reported 104°; Morgan and Micklewait,[2] 104°; Opolski, 102–103.5°. [c] Opolski[3] reported 230° (our sample shrank a little at 230°). [d] Lellmann[1] reported 168°; Morgan and Micklewait,[2] 165–167°. [e] Hinsberg and Strupler[4] reported 186°. [f] This is believed by us to be the same compound that Hinsberg and Strupler[4] reported as the tetrabenzenesulfonyl derivative with a melting point of 150–151°. [g] As a by-product in the preparation of compound number 5 by the method of Hinsberg and Strupler.

was difficult even with mechanical stirring and the yield was often very low. N-2-Benzenesulfonylaminophenyldibenzenesulfonamide was prepared by heating on a water-bath for fifty hours a solution of 25 g. of the N,N′-disodium salt of N,N′-(*o*-phenylene)-bis-benzene-sulfonamide and 10.2 g. of benzenesulfonyl chloride in 250 cc. of dioxane. The compound was obtained by evaporating the solution to dryness, washing with water and crystallizing the residue from glacial acetic acid. The disodium salt of N,N′-(*o*-phenylene)-bis-benzenesulfonamide was prepared by dissolving the amide in a hot solution of sodium hydroxide (2 cc. of 10% sodium hydroxide for each gram of the amide). The product crystallized when the solution was cooled and was then filtered, washed with a very little ice cold water and then with alcohol. The compound was dried on porous tiles and then at 120° for one hour.

Data for these compounds are listed in the table. The author is indebted to Miss Victoria N. Bodrasky for some of the analytical data.

Summary

1. All but one of the N-substituted benzenesulfonyl derivatives of *o*-nitroaniline and *o*-phenylenediamine have been prepared. Improvements have been made in the methods of preparation of some of those previously reported.

2. The substance described in the literature as the tetrabenzenesulfonyl derivative of *o*-phenylenediamine[4] is probably the tribenzenesulfonyl derivative. Our attempts to prepare the tetra derivative have been unsuccessful.

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Studies in the Ketone Sugar Series. VIII. The Structure of *l*-Sorbose Pentaacetate

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It has been shown by Arragon[1] that a solution of zinc chloride in acetic anhydride acts upon *l*-sorbose to form, under varying conditions, a tetraacetate and a pentaacetate. Arragon later[2] reported that a much better yield of tetraacetate was obtained by the action of acetic anhydride and pyridine on sorbose.

Schlubach and Vorwerk[3] were able to prepare the pentaacetate, using zinc chloride as catalyst, in greatly improved yield by a modification of the conditions. These authors found pentaacetylsorbose to be strikingly indifferent to halogenating agents. As this behavior is characteristic of the pentaacetylfructose which Pacsu and Rich[4] have shown to have open chain structure, Schlubach and Vorwerk expressed the belief that they were dealing with pentaacetyl-keto-sorbose.

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(1) Arragon, *Compt. rend.*, **196**, 1733 (1933).

(2) Arragon, *ibid.*, **198**, 1508 (1934).

(3) Schlubach and Vorwerk, *Ber.*, **66**, 1251 (1933).

(4) Pacsu and Rich, THIS JOURNAL, **55**, 3018 (1933).