[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF AROMATIC SULFONIC ACIDS[1]

Preliminary Paper

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RECEIVED NOVEMBER 30, 1925 PUBLISHED MARCH 5, 1926

In the mercuration of nitrobenzene[3] and of benzoic acid,[4] the mercury group enters the nucleus in the position *ortho* to the orienting group instead of *meta*. It might thus be expected that groups which ordinarily orient to the *meta* position would cause mercuration in the *ortho* position. Of such compounds, one of the most important classes is that of the aromatic sulfonic acids. The mercuration of these substances was undertaken because the literature contains no satisfactory data on the subject.[5]

The general method of mercuration was to reflux a water solution of the free sulfonic acid or its sodium salt with the molecular proportion of mercuric acetate and enough acetic acid to prevent the formation of mercuric oxide by hydrolysis. The mercuration was regarded as complete when a sample, diluted with an equal amount of water and treated with sodium hydroxide, gave a clear solution. In most cases the mercuration of the free acids was complete in less than one hour. In the case of the sodium salts the process usually required several hours.

The following have been mercurated: benzene sulfonic acid, sodium benzenesulfonate, sodium *p*-chlorobenzenesulfonate, sodium *p*-bromobenzenesulfonate, *p*-iodobenzenesulfonic acid, 2,5-dichlorobenzenesulfonic acid, *m*-nitrobenzenesulfonic acid, *o*-toluenesulfonic acid, sodium *o*-toluenesulfonate, *p*-toluenesulfonic acid, sodium *p*-toluenesulfonate, 2-chlorotoluene-5-sulfonic acid.

The products were white, amorphous, insoluble substances, soluble in alkalies but not reprecipitated by acids. Analyses indicated that they were mixtures. The only case in which pure products have thus far been isolated is that of *p*-toluenesulfonic acid which mercurates in the 2 position

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[1] This paper was presented in part at the 63rd Meeting of the American Chemical Society at Birmingham, April, 1922, and at the 69th Meeting at Baltimore, April, 1925.

[2] This research was carried out in part under a grant from the Public Health Institute of Chicago. Some of the mercurated products are being studied pharmacologically at the University of Wisconsin by Dr. A. S. Loevenhart under a similar grant.

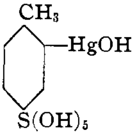
[3] Dimroth, *Ber.*, **35**, 2036 (1902).

[4] Pesci, *Atti accad. Lincei*, [5] **101**, 362 (1901); *Chem. Zentr.*, **1901**, II, 108.

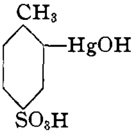
[5] Rother [*Dissertation*, Berlin, **1911**, p. 8] states briefly and without experimental details that the product of the action of benzenesulfonic acid solution with mercuric oxide reacts with bromine to give *m*-bromobenzenesulfonic acid. Brieger and Schulemann [*J. prakt. Chem.*, [2] **89**, 154 (1914)] obtained substances by heating the sodium salts of α- and β-naphthalenesulfonic acids with mercuric acetate, but failed to purify or study them.

(*ortho* to the methyl group and *meta* to the sulfonic acid group). The position of the mercury was established by replacement with iodine to form 2-iodotoluene-4-sulfonic acid which was identified by conversion to the acid chloride and the amide which were compared with known samples prepared from 2-aminotoluene-4-sulfonic acid.

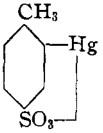
Three mercurated substances were obtained in crystalline form pure enough for analysis,



I



II



III

The *o*-sulfonic acid or dihydrate (I) was obtained from the crude reaction mixture. Dehydration to constant weight over calcium chloride gave II, and drying in a vacuum over phosphorus pentoxide gave the inner salt III.

The question as to whether the mercuration of sulfonic acids follows the ordinary rules of substitution still remains open, as the result in the case of the *p*-toluenesulfonic acid may be due to the directing influence of the methyl group. The study of the problem of the mercuration of sulfonic acids is being continued.

Experimental Part

Mercuration of *p*-Toluenesulfonic Acid.—One hundred and ninety g. (1.1 moles) of *p*-toluenesulfonic acid was dissolved in 750 cc. of water and 35 cc. of acetic acid, and the solution was boiled and filtered from a little undissolved material. Three hundred and twenty g. of mercuric acetate (1.01 moles) was dissolved in 750 cc. of water and 35 cc. of acetic acid, heated to boiling and filtered from a small amount of suspended solid. The two solutions were mixed boiling hot and refluxed. After an hour a sample treated with sodium hydroxide gave a yellow precipitate, but when the material was previously diluted with an equal volume of water it gave a clear solution.

Eighty-one g. of an insoluble white solid (A) was filtered off. On cooling 135 g. of a solid (B) crystallized and was filtered off.

No satisfactory product was obtained from (A). The precipitate (B) was extracted with water in a Soxhlet extractor and gave a beautiful crystalline solid soluble in warm water, alkali and salt solutions. Part of the crystals were dried in a vacuum over phosphorus pentoxide.

Anal. Subs., 0.1101, 0.1048, 0.1015, 0.2232: Hg, 0.0551, 0.0573, 0.0552, 0.1305. Calcd. for $C_7H_6O_3SHg$: Hg, 54.1. Found: 54.4, 54.6, 54.4, 54.0.

A second part was air-dried.

Anal. Subs., 0.1573, 0.1264: Hg, 0.0751, 0.0609. Calcd. for $C_7H_8O_4SHg.2H_2O$: Hg, 47.3. Found: 47.7, 47.3.

A third portion was dried over calcium chloride.

Anal. Subs., 0.1184: Hg, 0.0640. Calcd. for $C_7H_8O_4SHg$: Hg, 52.0. Found: 52.5.

A solution of 3.7 g. of the air-dried material in 50 cc. of water containing 0.7 g. of sodium chloride was warmed and shaken until complete solution took place. The warm solution was treated with 2.54 g. of iodine and shaken for half an hour. Mercuric iodide precipitated. The mixture was allowed to stand overnight and then refluxed for 15 minutes, treated with 0.5 g. of iodine in excess and refluxed for 15 minutes longer. The suspension was filtered from the mercuric iodide and excess of iodine. The filtrate was boiled to remove the color due to the dissolved iodine, concentrated to 30 cc. and cooled. On cooling, a pinkish crystalline precipitate formed; this was separated and dried at 100°. It became white. On concentrating the filtrate further a second precipitate of white crystals formed. The filtrate from these was evaporated to dryness. The residue weighed 2.5 g. and was ground with phosphorus pentachloride to form the acid chloride. The amide was prepared from the chloride and ammonium carbonate. The melting points of the amide and chloride were 185° and 68.9°, respectively.

Samples of the known compounds were prepared from 2-aminotoluene-4-sulfonic acid by diazotizing, replacing with iodine and preparing the acid chloride and amide in the usual way. The melting points of the amide and chloride prepared in this way were 68.2° and 184.5°, respectively.

Mixed melting points of the amide obtained from the mercury compound and the amide of the known 2-iodotoluene-4-sulfonic acid were obtained as follows: 184.5–185° for a ratio of known to unknown of 1:2, and 184–184.5° for a ratio of 2:1.

Summary

1. The mercuration of aromatic sulfonic acids takes place with extreme ease and rapidity.
2. The mercuration of sodium aromatic sulfonates is a much slower process.
3. *p*-Toluenesulfonic acid is mercurated in the position *meta* to the sulfonic acid group to form 2-hydroxymercuri-toluene-4-sulfonic acid.

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[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN AND FINK, INCORPORATED]

THE PREPARATION OF 2,4-DIHYDROXYDIPHENYLMETHANE AND OF 2,4-DIHYDROXYDIPHENYLETHANE

BY EMIL KLARMANN

RECEIVED DECEMBER 8, 1925 PUBLISHED MARCH 5, 1926

Alkyl derivatives of resorcinol achieved a prominent interest recently, because it was shown that it is possible to increase the germicidal properties of resorcinol considerably by the introduction of certain alkyl groups into its nucleus. In the course of our investigations on the influence of the nature of the substituent on the germicidal action we studied the introduction of aromatic groups into phenols.

The method of introduction of substituents which was applied by us differs from that used by Johnson[1] and co-workers and by V. Leonard.[2] These authors first allowed a fatty acid to act on resorcinol in the presence of zinc chloride and reduced the keto compound thus obtained. We

[1] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

[2] Leonard, *J. Am. Med. Assoc.*, **83**, 2005(1924).