

NOTE

A Modified Pirani Gage for Use in Corrosive Systems.—In studying reactions in gaseous systems at low pressures, frequent use has been made of the Pirani gage or some modification of it. If one of the gases involved is corrosive or if there is possibility of the reaction rate being affected by catalysis at a metal surface, the ordinary type of gage using a metal wire is unsatisfactory. In this Laboratory these difficulties have been eliminated by using a thin-walled glass capillary filled with mercury as the hot filament. The capillaries are drawn from ordinary 6-mm. Pyrex glass tubing and are usually made about 20 cm. long. These are then ring-sealed into a tube of about 1 cm. internal diameter. The resistance of such a gage varies from about 10 to 30 ohms depending on the size of the capillary.

The most satisfactory way to use this type of gage is to measure the current necessary to keep the temperature of the mercury thread constant. At low pressures the relation between the pressure and the heating current is linear, but at higher pressures the rate of increase of the current with increasing pressure falls off rapidly. These gages have been used with hydrogen and carbon monoxide and found to be quite satisfactory. The response to changes in pressure is so rapid that it does not cause any delay in taking readings. The maximum pressure readable with these gages varies with the accuracy of the current measurement. Using a milliammeter the practical upper limit is about 2 mm. of mercury, but by using a potentiometer this can be increased to several millimeters.

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SOME MERCURY DERIVATIVES OF HALOGEN COMPOUNDS OF RESORCINSULFONEPHTHALEIN

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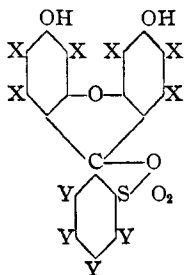
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For several years this Laboratory has been interested in the preparation of mercury derivatives of pht haleins and sulfonepht haleins and a study of their properties as therapeutic agents. In the course of this research we have had occasion to produce mercury derivatives of halogenated resorcinsulfonepht haleins. As many of the parent resorcinsulfonepht haleins, particularly those with halogen atoms present in the *o*-sulfobenzoic acid residue of the molecule, are unknown, we thought it advisable to make a brief report on the preparation of these compounds.

Results

The compounds which have been prepared may be represented in a general way by the following structural formula



Where X = H, Cl, Br, I, or HgOH and no more than two are halogen or mercury.
Y = H, Cl, Br, I; all four being similar in individual compounds.

The following new halogenated resorcinsulfonephthaleins have been prepared: dichlororesorcinsulfonephthalein, resorcintetrachlorosulfonephthalein, resorcintetrabromosulfonephthalein and resorcintetra-iodosulfonephthalein. The mono- and dihydroxymercuri derivatives of all of these compounds have been prepared. In addition, the mono- and dihydroxymercuri derivatives of resorcinsulfonephthalein, dibromoresorcinsulfonephthalein and di-iodoresorcinsulfonephthalein have likewise been prepared.

These sulfonephthaleins show two color changes corresponding to the first formation of the mono- and then the disodium salts. They cannot be used as indicators, however, as they exhibit to a marked degree the phenomenon of dichromatism.

The preparation of resorcinsulfonephthalein has been described in the literature by Remsen and others.¹

We have made use of the methods described by many of these investigators and with a modification in technique have been able to produce resorcinsulfonephthalein by condensing resorcinol with *o*-sulfobenzoic acid, *o*-sulfobenzoic anhydride, the acid ammonium salt of *o*-sulfobenzoic acid and saccharin. It was discovered that unless the condensation proceeded rapidly, a large amount of a by-product, probably a condensed polymer of resorcinol was formed. This may be separated from the resorcinsulfonephthalein by extraction with alcohol. Very pure resorcinsulfonephthalein can be obtained by any of these methods and, although no attempt was made to crystallize, the material obtained analyzed exactly as predicted by theory.

¹ Remsen, *Am. Chem. J.*, **6**, 180 (1884-1885); Remsen and Hayes, *ibid.*, **9**, 372 (1887); Remsen and Linn, *ibid.*, **11**, 73 (1889); Blackshear, *ibid.*, **14**, 472 (1892); White, *ibid.*, **17**, 545 (1895); Remsen and McKee, *ibid.*, **18**, 802 (1896); Sohon, *ibid.*, **20**, 257 (1898); Fahlberg and Barge, *Ber.*, **22**, 754 (1889); Sisley, *Bull. soc. chim.*, [3] **17**, 822 (1897); Orndorff and Vose, *THIS JOURNAL*, **46**, 1896 (1924).

Preparation of Halogenated Resorcinsulfonephthaleins

Dichlororesorcinsulfonephthalein.—Fifty grams of resorcinsulfonephthalein was dissolved in 270 cc. of normal sodium hydroxide, forming the disodium salt, and 200 cc. of water was added. Fifteen grams of sodium chloride and 150 g. of Chloramine T (sodium salt of *p*-toluene chlorosulfonamide) were dissolved in water and added to the first solution. Concentrated hydrochloric acid (approximately 10 cc.) was added to start the reaction. The solution was allowed to stand overnight and a salmon-colored precipitate consisting mainly of *p*-toluene sulfonamide settled out. This mixture was made alkaline with sodium carbonate, to insure the solution of the dye. *p*-Toluene sulfonamide is only slightly soluble in sodium carbonate in the cold; therefore, the solution was cooled to 5–10° for several hours before filtering. The filtrate was acidified with hydrochloric acid and this precipitate was collected on a Büchner funnel. As the precipitate at this point is contaminated with the by-product, it was dissolved in sodium bicarbonate and reprecipitated with hydrochloric acid. This procedure was repeated several times. The final precipitate was collected on a Büchner funnel, washed with a small amount of cold water and then dried at 110°. No attempt was made to crystallize this compound. As obtained it is light red-brown in color, slightly soluble in water, alcohol, acetone and acetic acid. It dissolves readily in dilute sodium hydroxide, forming either a mono- or disodium salt. The solution of the sodium salt exhibits a marked fluorescence; yield, 65%.

Anal. Calcd. for $C_{19}H_{10}O_6Cl_2S$: Cl, 16.23; S, 7.33. Found: Cl, 16.28; S, 7.29.

Dibromoresorcinsulfonephthalein and di-iodoresorcinsulfonephthalein were prepared by the method of Orndorff.²

Preparation of Resorcin Halogenated Sulfonephthaleins.—Tetra-chloro-, tetrabromo- and tetra-iodo-*o*-sulfobenzoic anhydrides were prepared by Dr. D. Twiss, of this Laboratory. These anhydrides were condensed with resorcinol to form the corresponding phthaleins.

The general method found to be satisfactory for preparing these compounds is as follows. The tetra-halogenated *o*-sulfobenzoic anhydride was mixed thoroughly with resorcinol, in the molecular proportion of 1:2. This mixture was heated in a flask in an oil-bath to 110–120° until the mass became very dark and solid. The temperature must be kept low as otherwise the yields will be poor. This melt was dissolved in 10% sodium hydroxide, the solution filtered and the filtrate precipitated with hydrochloric acid. It is necessary to use concentrated hydrochloric acid to precipitate both resorcintetrachlorosulfonephthalein and resorcintetrabromosulfonephthalein; the precipitates are tarry. These were dried, powdered, washed with hydrochloric acid and then dried. Both compounds are dark brown in color, strong dibasic acids in solution, soluble in water and dilute alkali and moderately soluble in alcohol and acetone. Resorcintetra-iodosulfonephthalein is not a very strong acid and may be precipitated with dilute hydrochloric acid. It is dark brown in color, slightly soluble in water, alcohol and acetone and readily soluble in dilute alkali. The yields were poor with resorcintetrachloro- and tetrabromosulfonephthalein. Resorcintetra-iodosulfonephthalein gave a yield of 80%.

Anal. Calcd. for $C_{19}H_8O_6Cl_4S$: Cl, 28.03; S, 6.34. Found: Cl, 28.24; S, 6.40. Calcd. for $C_{19}H_8O_6Br_4S$: Br, 46.75; S, 4.70. Found: Br, 46.18; S, 4.80. Calcd. for $C_{19}O_8I_4S$: I, 58.23; S, 3.69. Found: I, 58.35; S, 3.70.

Preparation of Mercury Derivatives.—The mono- and di-mercury

² Orndorff and Vose, *THIS JOURNAL*, 46, 1910 (1924).

derivatives of these halogenated resorcinsulfonephthaleins can be prepared by several of the known methods of mercuration.

A solution of molecular proportions of the disodium salt of a sulfonephthalein and of mercuric acetate will react readily on heating. No precipitate is formed by this reaction. The solution is filtered and then precipitated by dilute hydrochloric acid at 60°, with rapid stirring. This will avoid decomposition by loss of mercury. An alternate method is to boil an aqueous solution of the sodium salt of a sulfonephthalein with mercuric oxide in molecular proportions. This solution is filtered and can be taken to dryness on a water-bath or in vacuum and the sodium salt of the mercury derivative obtained immediately in very pure form.

The mercury compounds prepared were all insoluble in water and organic solvents. Both mono- and disodium salts can be readily formed. The solutions of these sodium salts show only a slight fluorescence, as compared with the parent phthalein.

TABLE I
COMPOUNDS AND ANALYSES

| Sulfonephthalein | Formula | Mercury, % | |
|---|----------------------------|------------|-------|
| | | Calcd. | Found |
| Monohydroxymercurioresorcin- | $C_{19}H_{12}O_7SHg$ | 34.3 | 34.0 |
| Dihydroxymercurioresorcin- | $C_{19}H_{12}O_8SHg_2$ | 50.1 | 50.4 |
| Monohydroxymercuridibromoresorcin- | $C_{19}H_{10}O_7Br_2SHg$ | 27.0 | 26.3 |
| Dihydroxymercuridibromoresorcin- | $C_{19}H_{10}O_8Br_2SHg_2$ | 41.8 | 41.0 |
| Monohydroxymercuridichlororesorcin- | $C_{19}H_{10}O_7Cl_2SHg$ | 30.7 | 30.1 |
| Dihydroxymercuridichlororesorcin- | $C_{19}H_{10}O_8Cl_2SHg_2$ | 46.1 | 45.8 |
| Monohydroxymercuridi-iodoresorcin- | $C_{19}H_{10}O_7I_2SHg$ | 23.9 | 23.8 |
| Dihydroxymercuridi-iodoresorcin- | $C_{19}H_{10}O_8I_2SHg_2$ | 38.1 | 37.5 |
| Monohydroxymercurioresorcintetra-iodo- | $C_{19}H_8O_7I_4SHg$ | 18. | 18.0 |
| Dihydroxymercurioresorcintetra-iodo- | $C_{19}H_8O_8I_4SHg_2$ | 30.7 | 31.8 |
| Monohydroxymercurioresorcintetrachloro- | $C_{19}H_8O_7Cl_4SHg$ | 27.8 | 27.3 |
| Dihydroxymercurioresorcintetrachloro- | $C_{19}H_8O_8Cl_4SHg_2$ | 42.7 | 42.3 |
| Monohydroxymercurioresorcintetrabromo- | $C_{19}H_8O_7Br_4SHg$ | 22.3 | 21.5 |
| Dihydroxymercurioresorcintetrabromo- | $C_{19}H_8O_8Br_4SHg_2$ | 35.9 | 34.7 |

Analytical

Sulfur and the halogens were determined by the Parr bomb oxidation method. Mercury was determined by the ordinary method of decomposing with sulfuric acid and potassium permanganate, reducing manganese dioxide formed with oxalic acid and precipitating the mercury with hydrogen sulfide. However, when both iodine and mercury are present in the compound this method cannot be used to determine the latter, due to the formation of mercury iodide. The method used was devised by Mr. A. E. Stickels of this Laboratory and is as follows.

To a 0.3- to 0.5-g. sample in a Kjeldahl flask is added 25 cc. of concentrated sulfuric acid and the flask is heated until the material is dissolved. Powdered potassium permanganate is slowly added until the compound is entirely decomposed, taking care not to heat too high in order to prevent any mercury from volatilizing. The mixture is cooled, diluted with about 50 cc. of water and decolorized with oxalic acid or ammonium oxalate. It is diluted to about 400 cc. with water and if a precipitate forms it is heated

until the precipitate is dissolved. The solution is cooled, 5 g. of potassium nitrite added and it is heated to boiling. About 2 g. of potassium bromide is added, the solution heated again to boiling, cooled and transferred to a separatory funnel. It is shaken out two or three times with chloroform in order to remove the free bromine. About 1 cc. of phenol is added and the shaking out continued with chloroform or carbon tetrachloride until all of the iodine is removed, which is evident when the chloroform has no color. From time to time more phenol may be required. The aqueous solution is filtered, heated to about 80° and the mercury precipitated with hydrogen sulfide. The precipitate is collected on a tared Gooch crucible, washed with alcohol, then carbon disulfide, again with alcohol and dried in an oven for an hour at 110°. The precipitate is weighed as mercuric sulfide.

This method has been used on known organic mercury compounds to which analyzed potassium iodide has been added with excellent results. Different experimenters have checked analyses with less than 0.3% error.

Summary

1. Several new halogen derivatives of resorcinsulfonephthalein have been made.
2. Mercury derivatives of a number of halogen compounds of resorcinsulfonephthalein have been prepared.
3. A satisfactory method for analysis for mercury in the presence of iodine is included.
4. Work in this field is being continued.

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POLARIZED LIGHT AND COCAINE DECOMPOSITION

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Introduction

Macht and Anderson² report that polarized light has a selective action on the decomposition of cocaine, digitalis and quinine as measured by their pharmacological effects. Other chemical effects attributed to polarized light have been reported.³ Semmens and Baly and Semmens⁴ have found that polarized light accelerates the hydrolysis of starch by diastase. Macht announced a substantiation of this work.⁵ These reports have been ques-

¹ A portion of a thesis submitted to the Faculty of Northwestern University Dental School in partial fulfilment of the requirements for the degree of Master of Science in Dentistry.

² Macht and Anderson, *THIS JOURNAL*, **49**, 2017 (1927).

³ S. S. Bhatnagar, *Science*, **64**, 359 (1927).

⁴ Semmens, *Nature*, **cxi**, 49 (1923); *J. Soc. Chem. Ind.*, **xl**, 716 (1923); Baly and Semmens, *Proc. Roy. Soc. London*, **97**, 250 (1924).

⁵ Macht, *Proc. Soc. Exptl. Biol. Med.*, **22**, 473 (1924).