which apparently holds for other readily reversible electromotively active organic oxidation–reduction systems. Preliminary experiments with certain other substituted thioindigo sulfonates indicate that these also exhibit semiquinone formation.

The formulation by Remick for the thioindigo disulfonate–leuco thioindigo disulfonate system was developed by considering that the reduction of two molecules of oxidant involving two electrons, one for each molecule, resulted in the formation of one molecule of reductant. This interpretation cannot be applied to the data presented for the tetrasulfonate, which show that one molecule of oxidant requires two reducing equivalents for conversion into one molecule of reductant. The introduction of the additional two sulfonic acid groups probably would not change the fundamental character of the reduction process of the thioindigo nucleus. The oxidation–reduction process for the several homologous indigo sulfonates has been found to be of the same type.

A comparison of the constants of indigo tetrasulfonate (E_0 = 0.365 volt and pK_{R1} = 6.9) and thioindigo tetrasulfonate (E_0 = 0.409 volt and pK_{R1} = 4.5) reveals that the substitution of S for N into the two heterocyclic organic nuclei would increase the E_0 value and the acidic dissociation of the reductant.

The instability of the oxidant or its reduction products and the semiquinone formation make thioindigo tetrasulfonate unsuitable for use as an oxidation–reduction potential indicator, except in acid *p*H regions below about *p*H 2.5.

Summary

The tetrapotassium salt of thioindigo tetrasulfonate has been prepared after direct sulfonation of thioindigo with fuming sulfuric acid. The oxidation–reduction potentials of the system thioindigo tetrasulfonate–leuco thioindigo tetrasulfonate have been determined for the *p*H range 0.0 to 11.5. The orange-red oxidant is converted into the yellow reductant by a reaction involving two reduction equivalents per molecule. The constants of the system established are E_0 = 0.409 volt and the first *pK* of the reductant is 4.5. Formation of a deeper red semiquinone was noted in the *p*H region from 8.5 to 11.5. Except in acid solution of *p*H less than 2.5, the material is not particularly suitable as an oxidation–reduction indicator.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SCHOOL OF PHARMACY OF THE UNIVERSITY OF MARYLAND]

The Preparation of Some Organic Mercurials from Diazonium Borofluorides

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Of the many methods of making aromatic mercury compounds, only two have made use of the diazonium salts. McClure and Lowy[2] noticed that on reducing electrolytically a diazonium solution using mercury electrodes, a small amount of mercurial was formed. They were also successful in preparing the corresponding mercury derivatives by stirring the diazonium solution with finely divided mercury produced mechanically. Nesmejanow[3] has succeeded in preparing the mercury derivatives of nuclei containing no group or groups such as alkyl, halogen, hydroxyl, etc., by treating the diazonium chloride–mercuric chloride double salt with precipitated copper powder; but when the nuclei contained groups such as carboxyl, nitro, sulfonic acid, etc.,[4] temperatures ranging from −10 to −70° were necessary.

Using more stable diazonium compounds such as the diazonium borofluorides of Balz and Schiemann,[5] and by producing very finely divided mercury by reduction with stannous chloride directly in the reaction mixture, it was found that some aromatic mercurials could be prepared in better yields. The replacement of the diazonium group with mercury was carried out at room temperature. In the course of the preparation of the necessary diazonium borofluorides, better yields were obtained by diazotizing in borofluoric acid.

The probable equations are illustrated by the following

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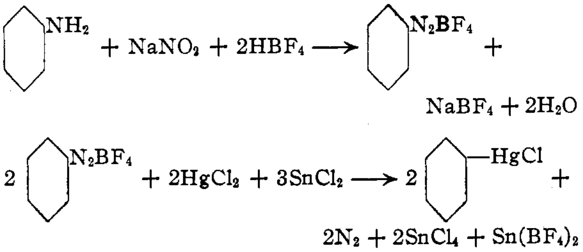
(1) Abstracted in part from a thesis submitted by Melvin F. W. Dunker to the Graduate School of the University of Maryland for the degree of Master of Science.

(2) McClure and Lowy, THIS JOURNAL, **53**, 319 (1931).

(3) Nesmejanow, *Ber.*, **62**, 1010 (1929).

(4) Nesmejanow and co-workers, *ibid.*, **67**, 130 (1934).

(5) Balz and Schiemann, *ibid.*, **60**, 1186 (1927).



Experimental

Diazonium Borofluorides.—The preparation of phenyl diazonium borofluoride illustrates the improved method referred to above.

To a mixture of 21.6 g. of aniline in 115 cc. of 50% fluoboric acid cooled in an ice-bath and stirred vigorously was added slowly a solution of 18 g. of sodium nitrite in 36 cc. of water. The diazonium compound was collected on a Büchner funnel, washed once with fluoboric acid, twice with alcohol and then thoroughly with ether. The yield was 90 to 97% of the theoretical amount as compared to 63% reported by Balz and Schiemann.[5] The yields of the other diazonium borofluorides are given in the table.

Phenylmercuric Chloride.—To a rapidly stirred suspension of 12.7 g. of $SnCl_2 \cdot 2H_2O$ and 7.0 g. of mercuric chloride in 50 cc. of acetone and 25 cc. of water was slowly added a solution of 5.0 g. of $C_6H_5N_2BF_4$ and 10.5 g. of mercuric chloride in 200 cc. of acetone. When the effervescence had ceased, the mixture was refluxed for about ten minutes and filtered hot, washing the residue with small portions of hot acetone. On standing, 5.25 g. of phenylmercuric chloride crystallized out, representing 60% of the theoretical based on aniline as compared to 51% obtained by Nesmejanow[3] and 70% obtained by the same author[4] at −70°. When the above reaction was carried out at 0 to 5°, a yield of 16% was obtained.

***p*-Chloromercuri-benzenesulfonic Acid, *o*-Chloromercuri-benzoic Acid, *p*-Chloromercuri-benzoic Acid.**—These compounds were prepared in the same manner, except that the diazonium borofluorides and mercuric chloride were added as a suspension rather than a solution, the volume of the solvent being reduced from about 300 to 100 cc. or less. The mercurial was extracted from the mixture with ammonium hydroxide and then converted to the free acid.

5-Chloromercuri-salicylic Acid.—In this case no appreciable yield was obtained using stannous chloride. To a suspension of 0.04 mole of precipitated copper powder and 0.016 mole of mercuric chloride in 150 cc. of water was added a dry mixture of 0.016 mole of the diazonium compound and 0.016 mole of mercuric chloride. The solid was filtered out and extracted with 10% sodium hydroxide. The sodium hydroxide solution was decolorized with charcoal and precipitated with hydrochloric acid. The mercurial was crystallized from acetone and then from alcohol.

In an attempt to prepare 2-chloromercuri-*p*-phenolsulfonic acid by the above method, the product obtained as indicated by analysis seemed to be 2,6-dichloromercuri-*p*-phenolsulfonic acid. Rupp and Herrmann[6] reported the mono-mercury compound to be unstable, changing to the di-mercury compound on crystallization from water.

***p*-Chloromercuri-diphenyl.**—Five grams of *p*-diphenyldiazonium borofluoride and 5 g. of mercuric chloride were mixed with 50 cc. of glacial acetic acid and added slowly to 5 g. of mercuric chloride and 8 g. of $SnCl_2 \cdot 2H_2O$ in 50 cc. of acetone. The mixture was stirred for two hours and filtered. On standing in a refrigerator, the filtrate deposited shiny white plates. The mercurial was crystallized from acetone. The crystals melted at 329° with decomposition. When copper powder was used, no mercurial was obtained. If the reaction mixture was cooled strongly, the decomposition was very slow. It is believed that this is the first report of the preparation of this compound.

Further applications of this method of synthesis of mercurials are being studied.

TABLE I

Aryl radical	Yield of diazonium compd., %	Chloromercuri compds. % yield based on amine	% Hg Calcd.	% Hg[a] Found
Phenyl	90–97	60	64.1	64.5
p-Sulfophenyl	99	46	50.6	49.9
			(as Na salt)	
o-Carboxyphenyl	46	34	56.2	55.1
p-Carboxyphenyl	76	Not detd.	56.2	55.8
p-Phenylphenyl	94	Small	51.6	51.8
3-Carboxy-4-hydroxyphenyl	75–85	26	53.7	53.4
2-Hydroxy-5-sulfophenyl	(In soln.)	Not detd.	62.3	60.0

[a] The mercury analyses were made by the method of Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

Summary

1. Several aryl mercurials have been prepared by replacing the diazonium borofluoride group using freshly reduced mercury.

2. A new compound, *p*-chloromercuri-diphenyl has been prepared.

3. An improved method for the preparation of diazonium borofluorides is reported.

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[6] Rupp and Herrmann, *Arch. Pharm.*, **254**, 500 (1916).