Dimethylethylstannyl hydroxide was also prepared from dimethylethylstannyl bromide by treating the bromide with 30% sodium hydroxide solution. The reaction mass was extracted with ether, the ether solution dried over anhydrous calcium chloride and the ether removed by boiling under reduced pressure at room temperature. There remained a mass of white crystals which, too, were hygroscopic.

Anal. Subs., 0.2492: SnO_2, 0.1926. Calcd. for $(CH_3)_2C_2H_5SnOH$: Sn, 60.96. Found: Sn, 60.88.

The authors wish to acknowledge their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of the present investigation.

Summary

1. Trimethylethylstannane has been prepared in yields of 80% by treating sodium trimethyl stannide with ethyl bromide.

2. On brominating trimethylethylstannane a methyl group is removed and dimethylethylstannyl bromide is formed.

3. Dimethylethylstannane has been prepared by treating sodium dimethyl ethyl stannide in liquid ammonia with ammonium bromide.

4. On slow atmospheric oxidation of dimethylethylstannane there is formed dimethylethylstannyl hydroxide.

Geneva, New York

[Contribution from the Chemical Laboratory of the College of Liberal Arts of Northwestern University]

THE ACTION OF BASES ON CERTAIN MERCURATED ANILINES

By Frank C. Whitmore, E. R. Hanson and F. L. Carnahan[1]

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A reaction which has received considerable study in this Laboratory is the conversion of mercury compounds of the type RHgX into the so-called "mercuri-*bis*" compounds of the type R_2Hg, in which both valences of the mercury are attached to carbon.

$$2\ RHgX \rightleftharpoons R_2Hg + HgX_2$$

This reaction readily goes to the left without any special precautions. It can be made to go to the right by a great variety of reagents, such as iodides, sulfides, thiosulfates, cyanides, sodium stannite and metals such as copper and sodium. For some time the working hypothesis in this Laboratory was that the formation of the mercuri-*bis* compounds could be brought about by "any reagent which removes mercuric ions more completely than does sodium hydroxide." This hypothesis proved useful but

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[1] This work was carried on during the years 1923–1927 under grants from the Public Health Institute of Chicago.

was apparently contradicted by an observation of Pesci[2] that 3-acetoxymercuridimethyl-*p*-toluidine on standing with aqueous ammonia gives the corresponding mercuri-*bis* compound. After unsuccessful attempts to repeat this work, it was decided to use a more drastic treatment with potassium hydroxide. Indications early were found that certain mercurated dialkylanilines when treated with aqueous alcoholic potassium hydroxide gave traces of the mercuri-*bis* compounds. Great difficulty was found in applying this generally, however, even in this series. By the use of more concentrated solutions it has been possible to show that the reaction is general for the *p*-mercurated dialkylanilines. The *p*-acetoxymercuri compounds of dimethylaniline, diethylaniline, di-*n*-propylaniline, di-*n*-butylaniline, methylethylaniline and benzylethylaniline on refluxing with concentrated aqueous alcoholic solutions of potassium hydroxide give the corresponding mercuri-*bis* compounds.

The general method used in forming the mercuri-*bis* compound was to reflux for thirty minutes one mole of the mercurated aniline with 32 moles of potassium hydroxide in a solution of 100 moles of alcohol and 100 moles of water. In the case of *p*-acetoxymercuridiethylaniline only a trace of the mercuri-*bis* compound was obtained under these conditions. The use of 64 moles of potassium hydroxide gave the desired substance in small quantities.

The yields of the mercuri-*bis* compounds were small under the conditions of the experiments. Quantities large enough for separation and identification were all that were desired. It is no doubt possible to increase the yield greatly by proper variation of the conditions and concentrations.

The chief products accompanying the mercuri-*bis* compounds were organomercuri oxides and hydroxides. The inorganic mercury produced as a result of the formation of mercuri-*bis* compounds appeared largely as mercurous and mercuric oxides. In the case of *p*-acetoxymercuridimethylaniline the formation of metallic mercury took place. The amount of insoluble material removed by hot filtration of the various reaction mixtures is consistent with the quantity of mercuri-*bis* compound formed. The formation of ethane-hexamercarbide is also possible under the conditions. Mercuric oxide reacts with alcoholic alkali to form this substance. In the case of the action of *p*-acetoxymercuridimethylaniline with 32 moles of potassium hydroxide, the formation of a small amount of the mercarbide was proved.

The formation of the mercuri-*bis* compounds by means of aqueous alcoholic potassium hydroxide in the case of mercury compounds containing the $-NR_2$ group is probably very complex in mechanism. Undoubtedly the result is due chiefly to the existence of an alkaline reducing environment due both to the alkylated amines and the potassium ethylate present.

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[2] Pesci, *Gazz. chim. ital.*, **28**, II, 106 (1898).

The various steps in the reactions may be indicated as follows

$$RHgOCOCH_3 \longrightarrow RHgOH \rightleftharpoons (RHg)_2O \rightleftharpoons R_2Hg + HgO$$

The mercuric oxide is partly reduced to mercurous oxide or mercury and partly converted to the very insoluble ethane-hexamercarbide.

Experimental Part

Crystalline *p*-Bromomercuri-aniline, $BrHgC_6H_4NH_2$.—Five g. of *p*-acetoxymercuri-aniline was refluxed with a solution of 2 g. of sodium bromide in 1500 cc. of water for three hours. A small amount of undissolved material was removed by filtration. On cooling the filtrate deposited colorless, lustrous plates. When dried in air these became slightly greenish; yield, 1.8 g.; m. p. 181°.

Anal. Subs., 0.2112, 0.2206: Hg, 0.1147, 0.1202. Calcd. for C_6H_6NBrHg: Hg, 53.9. Found: Hg, 54.3, 54.4.

Crystalline *p*-Iodomercuri-aniline, $IHgC_6H_4NH_2$.—This substance was prepared similarly to the bromomercuri compound. The fine, flat plates which separated from the hot filtrate were crystallized from 250 cc. of hot alcohol. On drying the crystals assumed a slightly golden tint; yield, 1.2 g.; m. p. 165°.

Anal. Subs., 0.2023: Hg, 0.0971. Calcd. for C_6H_6NIHg: Hg, 47.8. Found: Hg, 47.9.

Treatment of *p*-Acetoxymercuri-aniline with Potassium Hydroxide.—To a solution of 44.8 g. of potassium hydroxide in 35 cc. of water and 153 cc. of 95% alcohol was added 8.79 g. of *p*-acetoxymercuri-aniline (mercury compound 1 mole, potassium hydroxide 32 moles, alcohol 100 moles, water 100 moles). The mixture was refluxed for thirty minutes. A yellow precipitate was formed during the reaction. This was filtered off, washed with cold water and air dried. Its insolubility in alcohol, ether, chloroform, benzene and acetone, together with the fact that it decomposed on heating, proved that it was not the mercuri-*bis* compound. This is probably the usual compound formed by the action of concentrated alkalies on *p*-acetoxymercuri-aniline. Its true formula apparently is not known.

_p_-Acetoxymercuri-di-alkyl-anilines, $R_2NC_6H_4HgOCOCH_3$.—These substances were prepared by mercurating the N-di-substituted anilines with mercuric acetate in a mixture of water, 95% ethyl alcohol and acetic acid. With the last two the reaction mixtures gave no crystals until most of the acid had been neutralized by sodium hydroxide.

TABLE I

ANALYTICAL AND OTHER DATA

R_2	M. p., °C.	Yield, %	Hg, calcd.	Hg, found[a]
Dimethyl	165	82	..	..
Diethyl	105	51	..	..
Di-*n*-propyl	99	90	46.1	45.9
Di-*n*-butyl	89–90	91	43.3	43.4
Methylethyl	92–93	85	51.0	51.0
Benzylethyl	92–94	72	42.7	42.8

[a] Mercury analyses were made by the "gold crucible" method.

_p_-Halogenmercuri Compounds.—The ClHg- and BrHg-compounds were made by refluxing alcoholic solutions of the acetoxymercuri compound with calcium chloride and sodium bromide, respectively. The IHg-compounds were made by means of exactly equivalent amounts of sodium iodide in *cold* acetone.

TABLE II

ANALYSES

R	ClHg-compounds M. p., °C.	Mercury, % Calcd.	Found	BrHg-compounds M. p., °C.	Mercury, % Calcd.	Found	IHg-compounds M. p., °C.	Mercury, % Calcd.	Found
Diethyl	.....	..	..	158	46.8	46.1[a]	120–121	42.2	41.9[a]
Di-*n*-propyl	170–172	48.7	48.7	165–167	43.9	43.8	150	39.8	39.7[a]
Di-*n*-butyl	162–163	45.5	45.0[a]	164–165	41.4	41.1[a]	151	37.7	37.3[a]
Methylethyl	162–166	54.2	53.2[a]	154–155	48.4	48.2	137–138	43.5	43.3
Benzylethyl	150–151	45.0	44.7	155	40.9	41.2	132–134	37.3	37.3

[a] Average of two or more analyses.

Action of the Acetoxymercuri Compounds with Alcoholic Potassium Hydroxide.—In each case the acetoxymercuri compound was boiled for thirty minutes with the indicated molecular proportions of potassium hydroxide, 100 moles of ethyl alcohol and 100 moles of water.

TABLE III

ANALYTICAL AND OTHER DATA

R	Hg cpd. g.	Mole ratio Hg cpd.	KOH	Product	M. p., °C.	Mercury, % Calcd.	Found
Dimethyl	9.5	1	1	$(CH_3)_2NC_6H_4HgOH$[a]	152–156	59.4	59.3[b]
	9.5	1	1	$((CH_3)_2NC_6H_4Hg)_2O$[c] and	180	61.1	61.2[b]
				hydroxide	153–156	59.4	59.3[b]
	9.5	1	2	Oxide	180	61.1	60.8[b]
	9.5	1	4	Oxide	180	61.1	61.1[b]
	9.5	1	8	$((CH_3)_2NC_6H_4)_2Hg$[d]	168	45.3	45.4[b]
				and oxide	180	61.1	60.7
	9.5	1	16	Hg-*bis* compound	168	45.3	45.6
				and oxide	180	61.1	60.7
	9.5	1	32	Hg metal and oxides, Hg-*bis*	168	45.3	45.5
				compound and oxide	180	61.1	61.0[b]
Diethyl	10.2	1	32	$((C_2H_5)_2NC_6H_4)_2Hg$ (trace)			
				and $((C_2H_5)_2NC_6H_4Hg)_2O$	210–219	56.2	56.4
	10.1	1	64[d]	Oxide and Hg-*bis* compound[e]	161	40.4	40.4
Di-*n*-propyl	10.9	1	32	$((C_3H_7)_2NC_6H_4)_2Hg$[f]	86	36.3	36.5
				$((C_3H_7)_2NC_6H_4Hg)_2O$	184–185	52.2	52.3[b]
Di-*n*-butyl	11.6	1	32	$((C_4H_9)_2NC_6H_4)_2Hg$[g]	79– 80	33.0	33.2
				$((C_4H_9)_2NC_6H_4Hg)_2O$	170	48.6	48.7[b]
Methylethyl	9.8	1	32	$(CH_3)(C_2H_5)NC_6H_4)_2Hg$[h]	139–142	42.8	42.0
				$(CH_3)(C_2H_5)NC_6H_4HgOH$	192–199	57.0	56.4[b]
Benzylethyl	11.7	1	32	$((C_6H_5CH_2)(C_2H_5)NC_6H_4)_2Hg$[i]	128	32.3	32.5
				$(C_6H_5CH_2)(C_2H_5)NC_6H_4Hg$-OH	158–167	46.9	46.6[b]

[a] Boiled for only ten minutes.

[b] Average of two or more analyses.

[c] Boiled for twenty minutes.

[d] The fact that this product was *p*-mercuri-*bis*-dimethylaniline was confirmed by

refluxing it with mercuric chloride in alcohol. The theoretical yield of *p*-chloromercuridimethylaniline was obtained; m. p., 225°; Hg calcd., 56.3; found, 56.2. Sodium hydroxide under similar conditions gave the same products.

[e] Treatment with mercuric chloride gave the chloromercuri compound; m. p., 164°; Hg calcd., 52.2; found, 51.8.

[f] Mercuric chloride gave the ClHg-compound; m. p., 171°; Hg calcd., 48.7; found, 48.5.

[g] The ClHg-compound was prepared as usual; m. p., 162–163°; Hg calcd., 45.6; found, 45.8.

[h] ClHg-compound, m. p., 165°; Hg calcd., 54.2; found, 53.0.

[i] ClHg-compound, m. p., 150–151°; Hg calcd., 45.0; found, 44.0.

Action of Sodium Ethylate on *p*-Acetoxymercuridiethylaniline.—(a) Four g. of sodium was dissolved in 54 g. of absolute alcohol. To the solution of sodium ethylate thus formed was added a solution of 2 g. of *p*-acetoxymercuridiethylaniline in 8 g. of absolute alcohol. The mixture was refluxed for twenty minutes. Metallic mercury separated from the reaction mixture. No mercuri-*bis* compound was obtained.

(b) Eight g. of sodium was dissolved in 94 g. of absolute alcohol and to the solution of sodium ethylate thus formed was added a solution of 2 g. of *p*-acetoxymercuridiethylaniline in 8 g. of absolute alcohol. The mixture was refluxed for twenty minutes. No mercuri-*bis* compound was detected in the reaction products.

(c) More vigorous treatment with sodium ethylate gave completely unmanageable products.

Preparation of Mercuri-*bis* Compounds from Acetoxymercuri Compounds and Sodium Iodide.—The reactions were carried out in cold acetone solution using an excess of the iodide.

TABLE IV

ANALYTICAL AND OTHER DATA

R	Hg-*bis* compound Yield, %	M. p., °C.	Mercury, % Calcd.	Found	
Dimethyl	40	168–169[a]	..	..	..
Diethyl	31	160–161[a]	..	..	..
Di-*n*-propyl	39	86[a,b]	36.3	36.5	36.4
Di-*n*-butyl	50	80– 81	..	..	..
Methylethyl	..	133–135[c]	42.8	42.3	42.5
Benzylethyl	..	125–126[d]	32.2	32.6	32.6

[a] The melting point was not lowered by mixing with the Hg-*bis* compound obtained by means of alcoholic potassium hydroxide.

[b] The Hg-*bis* compound was further identified by conversion to the ClHg-compound, m. p. 170°.

[c] It was converted to the ClHg-compound, m. p. 161–165°. A 1:1 mixture of the Hg-*bis* and IHg-compounds melted at 100–122°.

[d] The ClHg-compound was obtained from it, m. p. 149–150°. A mixture of the Hg-*bis* and IHg-compounds melted at 110–120°.

Conversion of the Acetoxymercuri Compounds to the Mercuri-*bis* Compounds by Sodium Thiosulfate in cold concentrated aqueous solution.

TABLE V

MERCURI-*bis* COMPOUNDS

	Hg-*bis* compound		Mercury, %		
R	Yield, %	M. p., °C.	Calcd.	Found	
Di-*n*-propyl	38	86	..	..	..
Di-*n*-butyl	..	80– 81	33.0	31.8	32.3
Methylethyl[a]	..	132–133[b]	..	..	..
Benzylethyl[a]	28	125[b]	..	..	..

[a] The Hg-*bis* compound could not be obtained from the acetoxymercuri compound but was produced in small amount by treating an alcohol suspension of the hydroxymercuri compound with concd. aqueous sodium thiosulfate.

[b] The m. p. was not lowered by addition of known Hg-*bis* compound.

Formation of Ethane-hexamercarbide.—(a) A mixture of 7.96 g. of mercuric acetate, 44.8 g. of potassium hydroxide, 35 cc. of water and 153 cc. of alcohol (mercuric acetate 1 mole, potassium hydroxide 32 moles, water 100 moles, alcohol 100 moles) was refluxed for thirty minutes. The residue on hot filtration was washed with water and dilute alkali. It was then digested with 20% nitric acid until it became white. The solid was filtered off, washed with water and digested with potassium hydroxide solution. The residue was filtered, washed with water and air dried. The product was yellowish; yield, 0.64 g. It exploded violently at 230°.

(b) *p*-Acetoxymercuridimethylaniline was treated with 32 moles of potassium hydroxide as above using four times the quantities listed. The residue from hot filtration was treated like that obtained in (a). Ethane-hexamercarbide was separated in a yield of 0.25 g. It exploded violently at 230°.

The formation of ethane-hexamercarbide is no doubt a secondary reaction. Mercuric oxide is set free by the formation of the mercuri-*bis* compound. This reacts with alcohol in the presence of alkali to form ethane-hexamercarbide. No attempt to isolate the substance from other reactions in which mercuri-*bis* compounds were formed was made. The conditions necessary for its formation, however, were satisfied in all cases.

Summary

1. Mercuri-*bis* compounds of the type R_2Hg have been obtained from six mercurated dialkylanilines by reaction with alcoholic potassium hydroxide, a new reagent for producing this change.

2. Crystalline *p*-bromomercuri- and *p*-iodomercuri-aniline have been prepared for the first time.

3. Earlier work on mercury derivatives of diethylaniline has been confirmed and extended.

4. Series of mercury derivatives have been prepared from di-*n*-propyl-, di-*n*-butyl-, methylethyl- and benzylethylanilines.
5. The conversion RHgX ⟶ R_2Hg has also been accomplished in all these cases by means of sodium iodide.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 594]

A STUDY OF SOME OF THE REACTIONS OF 3-HYDROXY-6-AMINOTOLUENE AND OF CERTAIN OF ITS DERIVATIVES[1,2]

BY MARSTON TAYLOR BOGERT AND GEORGE HERBERT CONNITT

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Since this *o*-amino-*m*-cresol is an industrial by-product, it seemed desirable to investigate it somewhat more fully as a possible source of useful intermediate or final products.

Because of its *p*-aminophenol structure, the first line of attack consisted in the synthesis of derivatives analogous to various well-known synthetic drugs, but none of these products have been subjected as yet to pharmacological examination. It is hoped that, since *m*-cresol is a somewhat stronger antiseptic than phenol, and the toluidines are less toxic than aniline, there may be some advantages in these new products, although Heubner[3] and Rhode[4] have pointed out that the analogous derivatives of *o*,*o*-dimethyl-*p*-phenetidine are all inferior therapeutically to those of *p*-phenetidine itself.

The simple phenacetin homolog, 3-ethoxy-6-acetylaminotoluene, is somewhat more soluble in water than phenacetin. The most soluble derivative of this type prepared in the course of the work was the 3-hydroxyethoxy-6-acetylaminotoluene, which structurally resembles "Pertonal," a drug stated by Cow[5] to be far less toxic than phenacetin, and as antipyretic to possess a much feebler but longer continued action. Like salicylyl-*p*-phenetidide, the corresponding salicylylaminocresol derivative was too resistant to hydrolysis to hold out much promise as a medicament. "Malakin" is the trade name under which salicylal-*p*-phenetidine has been marketed. It is stated to be a good analgesic, but too difficultly soluble in water. We synthesized the aminocresol analog and the corre-

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[1] Presented in abstract before the Organic Division, at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] This investigation was made possible through the generous assistance of the Verona Chemical Co., North Newark, N. J., who, through their Chief Chemist, Dr. Jacob Ehrlich, supplied us with the necessary raw material. We take this opportunity of expressing our thanks to both of them.—M. T. B.

[3] Heubner, *Biochem. Z.*, **93**, 395 (1919).

[4] Rhode, *Ber. deut. pharm. Ges.*, **31**, 271 (1921).

[5] Cow, *J. Pharmacol.*, **12**, 343 (1919).