principle of counter-currents.[1] The essential feature of this condenser is the spiral cooling tube. The condensate between it and the outside-jacket forms a seal, compelling the vapor to travel a spiral distance of 4 feet up through the condenser.[2] To avoid heating the incoming cooling water by the outgoing warm water the outlet tube is insulated by an air-jacket. This jacket is enlarged so as to make the cooling water also take a spiral course exactly against the vapor.

This apparatus is manufactured by Greiner & Friedrichs, G. m. b. H, Stützerbach, Germany.

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THE ACTION OF TETRABROMETHANE ON ORGANIC BASES.

BY WILLIAM M. DEHN.

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Tetrabromethane (acetylene tetrabromide) reacts with organic bases[3] with the greatest ease, yielding products in accordance with the equations:

$$
\begin{aligned}
&RNH_2 + C_2H_2Br_4 \longrightarrow RNH_2.HBr + C_2HBr_3\\
&R_2NH + C_2H_2Br_4 \longrightarrow R_2NH.HBr + C_2HBr_3\\
&R_3N + C_2H_2Br_4 \longrightarrow R_3N.HBr + C_2HBr_3
\end{aligned}
$$

The reactions were brought about in anhydrous ether, the salts of the respective bases being precipitated and the tribromethylene remaining in the ether solution. It was easily observed that the precipitations of the salts were accelerated by direct sunlight.[4] Solutions which remained clear in the dark were immediately precipitated by direct sunlight. These reactions were easy and quantitative and afford a convenient method of preparation not only of crystallized salts of the bases but also tribromethylene.[5]

In general aliphatic amines were more easily acted upon by tetrabromethane than the aromatic bases; primary amines were more easily acted upon than the secondary and the tertiary amines. Piperidine was almost instantaneously and quantitatively precipitated as the hydrobromide when treated with tetrabromethane, hence it is the most useful of all the bases to prepare tribromethylene from tetrabromethane.

Preparation of Tribromethylene.—A solution of tetrabromethane in dry ether is treated with piperidine as long as a precipitate forms. The

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[1] *Chem. Z.*, 35, 1125 (1911).

[2] *Z. angew. Chem.*, 23, 2425–26. *C. A.*, 5, 1347 (1911).

[3] Ells and Neuman studied the effect of ammonia, aniline and dimethyl aniline on tetrabromethane in alcoholic solution. They also obtained tribromethylane as the end-product. Ells, Neuman, *J. prakt. Chem.*, [2] 58, 250.

[4] Compare Dehn and Dewey, THIS JOURNAL, 33, 1588.

[5] See page 287. Also compare Lennox, *Ann.*, 122, 125. Sabanejeu, *Ann.*, 178, 122. Demole *Biol.*, 29, 207. Dworkowitsch, *Ann.*, 216, 280.

filtered ether solution, if alkaline in reaction, is neutralized with dilute hydrochloric acid; the ether solution then is dried with calcium chloride and fractionated. Tribromethylene, boiling at 163–164°, is obtained in nearly quantitative yields. Since the piperidine is easily recovered from its hydrobromide salt, the method is inexpensive.

In the following experiments nearly quantitative yields of the pure hydrobromides of the bases were obtained. When prepared from the free bases by treatment with aqueous hydrobromic acid, many of these salts are more or less colored and are imperfectly crystallized. The former of these defects results from hydrolysis and decomposition of the salts in accordance with the equations:

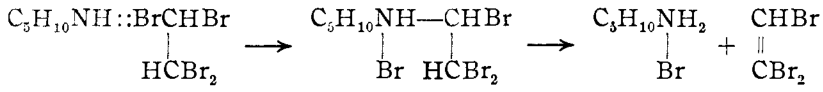
$$\begin{aligned} RNH_2.HBr &\longrightarrow RNH_2 + HBr \\ 2HBr &\longrightarrow H_2 + Br_2 \\ RNH_2.HBr + Br_2 &\longrightarrow RNH_2.HBr.Br_2, \end{aligned}$$

mixtures of the salts with *perbromides* of the salts being formed. Furthermore, imperfectly crystallized forms of the salts are usually obtained, when their aqueous solutions are evaporated, because of the too ready solubility of the salts in water.

Since convenient quantities of pure hydrobromides were obtained in the treatment of the organic bases with tetrabromethane, their *mercuric bromides* and *bromaurates* were prepared. These latter compounds, derivatives of convenient form to identify the bases, were found invariably to be composed of one molecule of the salt and one molecule of the mercuric bromide or the auric bromide. The mercuric bromides were formed by dissolving equimolecular quantities of the respective salts and mercuric bromide in water and concentrating on the water bath until crystals began to form. If the solutions tended to lose free base by hydrolysis and volatilization, a little aqueous hydrobromic acid was added before evaporating; if too much hydrobromic acid was added, oily precipitates were formed.

The bromaurates were formed by adding to an aqueous solution of the salts a solution of the auric bromide, as long as a precipitate formed. The precipitates were filtered out and recrystallized from water.

The mechanism of the reaction of organic bases with tetrabromethane is very simple as indicated below:



$$C_5H_{10}NH::\begin{array}[t]{l}BrCHBr\\ \;|\\ HCBr_2\end{array} \longrightarrow \begin{array}[t]{l}C_5H_{10}NH\text{—}CHBr\\ \qquad\;\; |\qquad\;\; |\\ \qquad\; Br\;\; HCBr_2\end{array} \longrightarrow \begin{array}[t]{c}C_5H_{10}NH_2\\ |\\ Br\end{array} + \begin{array}[t]{c}CHBr\\ \|\\ CBr_2\end{array}$$

Ammonia.—When an anhydrous ether solution of tetrabromethane was treated with anhydrous ammonia,[1] a slow-forming white precipitate, promoted by direct sunlight, was formed. The precipitate was dried and analyzed. Calculated for NH_4Br; Br: 81.59; found, 81.59. The ether

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[1] Ells and Neuman, *J. prakt. Chem.*, [2] 58, 250.

solution yielded by distillation tribromethylene, therefore, the following reaction took place:

$$NH_3 + C_2H_2Br_4 \longrightarrow NH_4Br + C_2HBr_3.$$

Ethylamine.—When equimolecular quantities of ethylamine and tetrabromethane were brought together in anhydrous ether, an immediate and voluminous white precipitate was formed; the solution warmed almost to the point of boiling. The ether solution yielded by distillation an oil boiling between 163–165°. Calculated for C_2HBr_3: Br, 90.55: found, 90.66. The precipitate proved to be ethylamine hydrobromide.[1] Calculated for $C_2H_5NH_2.HBr$: Br, 62.59; found, 62.72. *Mercuric bromide,* crystals easily soluble in alcohol and water, but insoluble in ether. Melts at 91°. Calculated for $C_2H_5NH_2:HBr.HgBr_2$: Br, 49.55; found, 49.22.

Diethylamine.—Equimolecular quantities of the two substances gave a quantitative yield of tribromethylene and white crystalline *diethylamine hydrobromide,* melting sharply at 205°. Calculated for $(C_2H_5)_2NH.HBr$: Br, 51.88; found, 51.96. *Bromaurate,* small red needles, quite soluble in water and melting at 162°. Calculated for $(C_2H_5)_2NH.HBr.AuBr_3$: Au, 33.37; found, 33.25. *Mercuric bromide,* needles, melting at 120°. Calculated for $(C_2H_5)_2NH.HBr.HgBr_2$: Br, 46.65; found, 46.50.

Triethylamine.—When equimolecular quantities of the two substances were brought together in anhydrous ether the solution remained clear for some time. Later, especially in direct sunlight, flaky crystals of the hydrobromide[2] separated. Calculated for $(C_2H_5)_3N.HBr$: Br, 43.84; found, 43.63. *Bromaurate,* red flaky crystals, melting at 140°. Calculated for $(C_2H_5)_3N.HBr.AuBr_3$: Au, 31.85; found, 32.01. *Mercuric bromide,* beautiful tufts of long white needles, melting at 109°. Calculated for $(C_2H_5)_3N.HBr.HgBr_2$: Br, 44.24; found, 44.18.

Dipropylamine.—An immediate and voluminous precipitate was formed; after two days, beautiful mother-of-pearl leaflets of *dipropylaminehydrobromide,* melting at 271°, were obtained. Calculated for $(C_3H_7)_2NH.HBr$: Br, 43.89; found, 43.95. *Bromaurate,* fan-like clusters of red needles, melting at 119°. Calculated for $(C_3H_7)_2NH.HBr.AuBr_3$: Au, 31.86; found, 31.75. *Mercuric bromide,* long, white needles, melting at 109°. Calculated for $(C_3H_7)_2NH.HBr.HgBr_2$: Br, 44.24; found, 44.21.

Tripropylamine.—The solution remained clear in diffused sunlight, and in direct sunlight slowly precipitated *dipropylaminehydrobromide,*

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[1] THIS JOURNAL, 33, 1598.

[2] Garzine gives the melting point at 238–240°, *Jahrb.,* 1889, 1327. The above crystals melted at 236°. Since most of the salts given in this contribution melt with decomposition, the melting points were determined by rapidly heating the substances in sealed capillary tubes.

small white needles, melting at 180°. Calculated for $(C_3H_7)_3N.HBr$: Br, 35.66; found, 35.52. *Bromaurate*, small prismatic needles, difficultly soluble in water and melting at 149°. Calculated for $(C_3H_7)_3.N.HBr.AuBr_3$: Au, 29.83; found, 29.75. *Mercuric bromide*, white glistening needles, melting at 104°. Calculated for $(C_3H_7)_3N.HBr.HgBr_2$: Br, 41.05; found, 41.15.

Isobutylamine.—The solution remained clear at first but after a few hours a heavy oily precipitate, which finally became solid, was obtained. *Isobutylaminehydrobromide*, small white flakes, melting at 138°. Calculated for $C_4H_9NH_2.HBr$: Br, 51.82; found, 51.68. *Bromaurate*, needles, easily soluble in water and melting at 154°. Calculated for $C_4H_9NH_2.HBr.AuBr_3$: Au, 33.36; found, 33.41. *Mercuric bromide*, long transparent rectangular plates, melting at 164°. Calculated for $C_4H_9NH_2.HBr.HgBr_2$: Br, 46.63; found, 46.73.

Diisobutylamine.—Precipitates slowly in direct sunlight the *hydrobromide*, pearly flakes, melting at 313°. Calculated for $(C_4H_9)_2NH.HBr$: Br, 38.04; found, 37.96. *Bromaurate*, rectangular plates, melting at 245°. Calculated for $(C_4H_9)_2NH.HBr.AuBr_3$: Au, 30.48; found, 30.35. *Mercuric bromide*, pearly white flakes, melting at 60°. Calculated for $(C_4H_9)_2NH.HBr.HgBr_2$: Br, 42.06; found, 41.87.

Amylamine.—An immediate precipitation of the *hydrobromide*, mother-of-pearl scales, melting at 243°. Calculated for $C_5H_{11}NH_2.HBr$: Br, 47.55; found, 47.43. *Bromaurate*, needles, very soluble in water and melting at 105°. Calculated for $C_5H_{11}NH_2.HBr.AuBr_3$: Au, 32.59; found, 32.40. *Mercuric bromide*, a feathery mass of glistening white plates, melting at 213°. Calculated for $C_5H_{11}NH_2.HBr.HgBr_2$: Br, 45.42; found, 45.19.

Diisoamylamine.—Beautiful mother-of-pearl leaflets of the *hydrobromide*, melting about 315°. Calculated for $(C_5H_{11})_2NH.HBr$: Br, 33.56; found, 33.67. *Bromaurate*, long feathery needles, melting at 220°. Calculated for $(C_5H_{11})_2NH.HBr.AuBr_3$: Au, 29.21; found, 29.16. *Mercuric bromide*, transparent leaflets, melting at 97°. Calculated for $(C_5H_{11})_2NH.HBr.HgBr_2$: Br, 40.10; found, 40.19.

Allylamine.—An immediate though not heavy precipitate; a liquid at first, then a solid. The *hydrobromide*, hygroscopic needles melting at 91°. Calculated for $C_3H_5NH_2.HBr$: Br, 57.97; found, 57.74. *Mercuric bromide*, white flakes, melting at 115°. Calculated for $C_3H_5NH_2.HBr.HgBr_2$: Br, 48.16; found, 48.01.

Benzylamine.—Clear at first, then pearly leaflets of the hydrobromide.[1] *Mercuric bromide*, transparent rhombic plates of a soapy feel and melting at 211°. Calculated for $C_7H_7NH_2.HBr.HgBr_2$: Br, 42.51; found, 42.65.

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[1] Bischoff, *Ber.*, **30**, 3170.

Dibenzylamine.—Mother-of-pearl leaflets of the hydrobromide.[1] *Bromaurate,* orange powder, insoluble in water and melting at 165°. Calculated for $(C_7H_7)_2NH.HBr.AuBr_3$: Au, 27.58; found, 27.41. *Mercuric bromide,* pearly white flakes, melting at 145°. Calculated for $(C_7H_7)_2NH.HBr.HgBr_2$: Br, 37.58; found, 37.41.

Pyridine.—Clear at first; opaque in direct sunlight. The precipitate consisted of red-yellow crystals and a dark colored oil. Crystals, soluble in water, melting[2] at 212° and forming a bromaurate,[3] proved the presence of the hydrobromide. *Mercuric bromide,* rectangular plates and prisms, melting at 152°. Calculated for $C_5H_5N.HBr.HgBr_2$: Br, 46.12; found, 46.17.

Picoline.—At first a clear solution, then a dark colored oil, finally a solid, proving to be the hydrobromide.[4] *Mercuric bromide,* coarse white needles, melting at 88°. Calculated for $C_6H_7N.HBr.HgBr_2$: Br, 44.91; found, 44.89.

Piperidine.[5]—An immediate and voluminous precipitate of the hydrobromide.[6] *Mercuric bromide,* transparent hexagonal plates or long needles, melting at 143°. Calculated for $C_5H_{11}N.HBr.HgBr_2$: Br, 45.68; found, 45.71.

Phenylhydrazine.—Glistening white rhombic plates or needles, melting at 188°, the hydrobromide,[7] $(C_6H_5N_2H_3)_2.HBr$.

The action of tetrachlorethane, tetraiodoethylene, chloropicrin, bromopicrin, tribromophenol, perchlorobenzene, iodoform and other polyhalogenated compounds on organic bases is being investigated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF TETRAIODOETHYLENE ON ORGANIC BASES.

BY WILLIAM M. DEHN.

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It was previously shown that carbontetrabromide[8] and diiodoacetylene[9] react with organic bases in ether solution to form "carbontetrabromides of crystallization" and "diiodoacetylenes of crystallization," respectively. It is shown herein that tetraiodoethylene unites with organic bases in a similar manner, yielding *tetraiodoethylenes of crystallization.* Usually

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[1] Limpricht, *Ann.*, 144, 313.

[2] Trowbridge, THIS JOURNAL, 21, 67. Dehn and Dewey, *Ibid.*, 33, 1596.

[3] *Ibid.*, 33, 1596.

[4] Murrill, THIS JOURNAL, 21, 842; *Phil. Mag.*, [5] 2, 271.

[5] See page 286.

[6] Bischoff, *Ber.*, 31, 2841. Fock, *Ibid.*, 32, 1409.

[7] *Ibid.*, 33, 1597.

[8] THIS JOURNAL, 33, 1588.

[9] *Ibid.*, 33, 1598.