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.

SEATTLE, WASH.

[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.

one molecule of the base unites with one or two molecules of tetraiodoethylene to form the molecular compound.

Though the bases unite with one or two molecules of tetraiodoethylene, the resulting "molecular compounds" cannot be considered "loosely combined compounds," or compounds closely related to hydrated salts. This conclusion is reached first for the reason that here, as with the carbontetrabromides and the diiodoacetylenes, sunlight is usually necessary to promote the reactions, when the substances are brought together in anhydrous ether. Secondly, the molecular compounds, when decomposed by water, do not smoothly yield the original compounds. For instance, with the diethylamine compound and water, though the main reaction is in accordance with the equation,

$$(C_2H_5)_2NH.C_2I_4 \longrightarrow (C_2H_5)_2NH + C_2I_4, \qquad (1)$$

the compound also dissociates largely in the following complicated manner:

$$3(C_2H_5)_2NH.C_2I_4 + 3H_2O \longrightarrow 3(C_2H_5)_2NH.HI + 3C_2I_2 + 2HI + HIO_3. \quad (2)$$

Though the normal course of reaction of the organic bases on tetraiodoethylene is as indicated above, secondary reactions give rise to deep-colored solutions possessing the odor of diiodoacetylene. These facts are accounted for by the following equations,

$$3Et_2NH + 2C_2I_4 \longrightarrow 2Et_2NH.HI + 2C_2I_2 + Et_2NH.I_2, \quad (3)$$

$$3Et_2NH + 3C_2I_4 \longrightarrow Et_2NH.HI + Et_2NH.I_2 + Et_2NH.HI.I_2 + 3C_2I_2, \quad (4)$$

periodides being formed and giving rise to the deep-colored solutions. For this and the following described reasons the mass of crystals precipitated from the ether solution is usually a mixture of two or more substances. For instance, with diethylamine, there may be present in the mass $Et_2NH.HI$, $Et_2NH.C_2I_4$, $Et_2NH(C_2I_4)_2$, $Et_2N(C_2I_4)(C_2I_2)$, C_2I_4, the periodides indicated above, C_2I_2 and its derivatives with organic bases.[1] The mixtures thus formed often presented great difficulties in separation. The periodides, tetraiodoethylene and diiodoacetylene are soluble in ether; the two types of compounds of the base with tetraiodoacetylene are insoluble in ether but soluble in chloroform; the salts of the base are insoluble in ether and chloroform but are soluble in alcohol or water; the compounds represented by the type $Et_2NH.(C_2I_4)(C_2I_2)$ are usually insoluble in these organic solvents and with water yield tetraiodoethylene and diiodoacetylene.

The crystals, therefore, are washed with ether and extracted first with chloroform, to separate the tetraiodoacetylenes of the bases; then with absolute alcohol to remove the hydroiodides; the residue is usually a compound of the type $Et_2NH.(C_2I_4)(C_2I_2)$.

The tetraiodoethylene used in these experiments was prepared from

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[1] THIS JOURNAL, 33, 1598.

diiodoacetylene[1] by treatment in petroleum ether with iodine in slight excess.[2] The tetraiodoethylene precipitated as golden scales and after filtering and drying was dissolved in anhydrous ether. A saturated solution of tetraiodoethylene in anhydrous ether at 19° contains 47 g. to the liter. Such an ether solution was used as the basis for the calculation of the quantities used.

The *mercuric iodides* were prepared by adding to the aqueous solutions of the hydroiodides an excess of mercuric iodide and heating to boiling. The solutions were filtered and permitted to stand or spontaneously evaporate until crystals of the double compound separated.

The melting points were made by rapidly heating the substances in sealed capillary tubes.

Ethylamine.—When equimolecular quantities of ethylamine and tetraiodoethylene were mixed in anhydrous ether, small glistening light yellow crystals were formed very slowly in diffused sunlight and very rapidly in direct sunlight. The crystalline mass proved to be a mixture of two substances: The first, easily soluble in chloroform and crystallizing in long, white needles, shrinks at 122° and melts at 133°. Calculated for $C_2H_5NH_2(C_2I_4)_2$: I, 91.60; found, 91.96. The other, insoluble in chloroform and absolute alcohol and crystallizing in transparent rectangular leaflets, melts at 155°. Calculated for $C_2H_5NH_2C_2I_4$: I, 88.03; found, 87.87. Evidently the latter is *ethylaminetetraiodoethylene;* the former, *ethylamine-di-tetraiodoethylene.* These two substances in moist air give off the odor of diiodoacetylene and with water yield a precipitate of tetraiodoethylene and an aqueous solution of *ethylaminehydroiodide,* mother-of-pearl leaflets, easily soluble in alcohol, insoluble in ether and melting at 167°. Calculated for $C_2H_5NH_2.HI$: I, 73.36; found, 73.61. *Mercuric iodide,* coarse glistening light yellow prismatic needles, melting at 136°. Calculated for $C_2H_5NH_2.HI.HgI$: I, 60.74; found, 60.65.

Diethylamine.—When equimolecular quantities of diethylamine and tetraiodoethylene were brought together in ether solution, a slow-forming, buff-colored precipitate was obtained. Sunlight greatly promoted the reaction. After four or five days the substance was separated and washed by decantation and recrystallized from chloroform. Beautiful, transparent, rectangular tablets, darkening at 146° and melting at 158°, were obtained. Calculated for $(C_2H_5)_2NH.C_2I_4$: I, 83.94; found, 83.50. With water *diethylaminetetraiodoethylene* yields a variety of products, as shown in equations (1) and (2) above. When 1.4 g. were subjected to steam distillation for two hours, a residue of 0.88 g. or 63% of tetraiodoethylene was obtained. This indicates that reaction (1) is the more

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[1] THIS JOURNAL, 33, 1598.

[2] Homolka and Stolz, *Ber.*, 18, 2283. Moissan, *Bull. soc. chim.*, [3] 7, 746. Biltz, *Ber.*, 30, 1204; 29, 1411.

abundant. The distillate contained 0.12 g. of diiodoacetylene; the aqueous solution, about 0.10 g. of iodic acid and 0.40 g. of *diethylaminehydroiodide*, plates or needles, easily soluble in chloroform and melting, not sharply, at 165°. Calculated for $(C_2H_5)_2NH.HI$: I, 63.13; found, 63.09. *Mercuric iodide*, long transparent needles melting at 115°. Calculated for $(C_2H_5)_4NH.HI.HgI$: I, 57.14; found, 58.02.

Triethylamine.—The substances reacted slowly in the dark and quickly in direct sunlight. The solid product yielded by recrystallization from chloroform or glacial acetic acid transparent prismatic needles which darken at 120° and melt not sharply at 132°.

Calculated for $(C_2H_5)_3N(C_2I_4)_2$: C, 10.31; H, 1.29; N, 1.20; I, 87.18.
Found: C, 10.70; H, 1.56; N, 1.44; I, 87.29.

Triethylamine-di-tetraiodoethylene is decomposed by water yielding tetraiodoethylene and *triethylaminehydroiodide*, short prismatic needles shrinking at 150° and melting with decomposition at 173°. Calculated for $(C_2H_5)_3N.HI$: I, 55.41; found, 55.25. *Mercuric iodide*, light yellow flakes, melting at 84°. Calculated for $(C_2H_5)_3N.HI.HgI_2$: I, 55.75; found, 55.61.

Isopropylamine.—The mixture yielded in direct sunlight a mass of crystals that clung to the glass with great tenacity. After recrystallizing from chloroform, short transparent prisms were obtained. They became opaque in moist air, and melted sharply at 160°.

Calculated for $C_3H_7NH_2(C_2I_4)(C_2I_4)$: I, 87.67; found, 87.48, 87.70. When distilled with steam, diiodoacetylene was carried over, a precipitate of tetraiodoethylene and an alkaline solution of isopropylaminehydroiodide[1] were obtained.

Dipropylamine.—An immediate white precipitate was obtained in direct sunlight. After a number of days the somewhat yellowish precipitate was separated and recrystallized from chloroform. Glistening white prismatic needles or flakes, softening at 116° and melting at 130°, were obtained.

Calculated for $(C_3H_7)_2NH(C_2I_4)_2$: C, 10.31; H, 1.29; I, 87.19.
Found: C, 10.36; H, 1.55; I, 86.88.

With water, *dipropylamine-di-tetraiodoethylene* yields iodic acid, diiodoacetylene, tetraiodoethylene and *dipropylaminehydroiodide*, pearly white flakes, easily soluble in alcohol, insoluble in ether, softening at 220° and melting with decomposition at 229°. Calculated for $(C_3H_7)_2NH.HI$: I, 55.41; found, 55.12. *Mercuric iodide*, colorless leaflets, melting at 81°. Calculated for $(C_3H_7)_2NH.HI.HgI_2$: I, 55.75; found, 55.63.

Diisoamylamine.—Flakes formed almost immediately in direct sunlight. After recrystallizing from chloroform, needles or plates, darkening at 137° and melting at 150°, were obtained.

Calculated for $(C_5H_{11})_2NH.C_2I_4$: C, 20.90; H, 3.37; N, 2.15.
Found: C, 20.85; H, 3.45; N, 2.03.

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[1] Malbot, *Bull. soc. chim.*, [3] 4, 69.

With water *diisoamylaminetetraiodoethylene* forms diisoamylaminehydroiodide.[1] *Mercuric iodide*, colorless rhombic or six-sided plates or light yellow flakes, melting at 110°. Calculated for $(C_5H_{11})_2NH.HI.HgI_2$: I, 51.52; found, 50.89.

Benzylamine.—A slow-forming precipitate, accelerated by direct sunlight, was obtained; after recrystallizing from chloroform, long silky needles melting at 115°. Calculated for $C_6H_5CH_2NH_2.C_2I_4$: I, 79.47; found, 79.48. Boiled with water, *benzylaminetetraiodoethylene* yielded *benzylaminehydroiodide*, pearly flakes darkening at 150° and melting at 162°. Calculated for $C_6H_5CH_2NH_2.HI$: I, 54.00; found, 55.96. *Mercuric iodide*, small light yellow, glistening needles or prisms, melting at 134°. Calculated for $C_6H_5CH_2NH_2.HI.HgI_2$: I, 55.28; found, 55.35.

ω-Phenylethylamine.—In direct sunlight transparent prisms were slowly precipitated; they melted not sharply at 160°. The crystalline mass was extracted first with chloroform, then with absolute alcohol and yielded a crystalline residue melting with decomposition at 138°. Calculated for $C_6H_5.C_2H_4NH_2(C_2I_4)(C_2I_2)$: I, 81.83; found, 82.14. The portion soluble in alcohol yielded by concentrating, tetraiodoethylene, and by treating with ether, pearly flakes of *ω-phenylethylaminehydroiodide* darkening at 245° and melting at 267°. Calculated for $C_8H_9NH_2.HI$: I, 50.97; found, 50.91. *Mercuric iodide*, small yellow compact six-sided prismatic needles, softening at 120° and melting at 131°. Calculated for $C_8H_9NH_2.HI.HgI_2$: I, 54.17; found, 54.02.

Piperidine.—In diffused sunlight only a few crystals formed in five days; in direct sunlight, an immediate and voluminous precipitate was obtained. A number of careful analyses were made of this crystalline mass:

Calculated for $C_5H_{11}N.HI$:	C, 28.17;	H, 5.68;	N, 6.59;	I, 59.59.
Calculated for $C_5H_{11}C_2I_4$:	C, 13.63;	H, 1.80;	N, 2.27;	I, 82.27.
Calculated for $C_5H_{11}N(C_2I_4)_2$:	C, 9.40;	H, 0.96;	N, 1.22;	I, 88.41.
Found:	C, 15.57, 15.58;	H, 3.49, 3.30;	N, 2.58, 2.84;	I, 77.83.

Evidently the crystalline mass was a mixture of piperidine hydroiodide with the mono- or the di-tetraiodoethylene of piperidine. After recrystallization from chloroform alone or from chloroform by addition of anhydrous ether, white needles melting at 147° were obtained. Calculated for $C_5H_{11}N(C_2I_4)_2$: I, 88.41; found, 88.02. When treated with water and distilled, this *piperidine-di-tetraiodoethylene* yielded an alkaline distillate and *piperidinehydroiodide*, white needles softening at 172°. Calculated for $C_5H_{11}N.HI$: I, 59.59; found, 59.51. *Mercuric iodide*, small glistening white or light yellow needles, melting at 104°. Calculated for $C_5H_{11}N.HI.HgI_2$: I, 57.09; found, 56.56.

Quinoline.—A dark granular precipitate was formed very slowly in

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[1] Malbot, *Ann. chim phys.*, [6] 13, 504.

direct sunlight. The crystalline mass gave, by recrystallization from chloroform or from absolute alcohol, needles melting at 132°. Calculated for $C_9H_7N.C_2I_4$: I, 76.84; found, 76.79. With water *quinolinetetraiodoethylene* yields tetraiodoethylene and quinolinehydroiodide.[1]

Other Bases.—Pyridine gave a slow-forming, dark-colored precipitate difficultly soluble in chloroform; triphenylphosphine, a white granular sticky precipitate melting at 115°; triethylstibine, white crystals; paraphenylenediamine, a blue-black precipitate; collidine, an immediate precipitate; picoline, coarse dark crystals. The following substances gave no recognizable reaction-products: PCl_3, $AsCl_3$, $SbCl_3$, AsI_3, CH_3AsH_2.

Acetamide.—Golden rhombic flakes, melting at 175°. Calculated for $CH_3CONH_2.C_2I_4$: I, 85.94; found 85.63. This and otner products formed by the action of tetraiodoethylene on organic bases will be investigated.

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

THE FORMATION OF METATHIAZINES FROM THIOUREA.[2]

BY WILLIAM J. HALE AND HARVEY C. BRILL.

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In a recent publication[3] the condensation of urea with nitromalonic aldehyde was shown to give a nitrohydroxypyrimidine as a final product. A comparison of this reaction with condensations where an amino-imino grouping about a central carbon atom could be brought into reaction with this same aldehyde led to the conclusion that this latter grouping was far more reactive in the formation of pyrimidines than the β-diamino grouping in urea.

When thiourea is substituted for urea in this connection, we naturally were led to expect a pyrimidine containing a mercapto group as a substituent in place of the hydroxyl group of that product obtained from urea. The condensation, however, has been found to proceed in a totally different manner.

It is well known that thiourea may exist in two isomeric forms, the normal and the pseudo. Granting that the presence of the two amino groups in the normal form ($S : C : (NH_2)_2$) does not offer the favorable configuration which the amino-imino grouping of the pseudo form ($HS.C(:NH)NH_2$) has been found to give for pyrimidine formation, it would follow that we should have from this pseudo form a direct and

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[1] Trowbridge, THIS JOURNAL, 21, 67.

[2] The work described in this article formed part of a thesis presented to the Faculty of the Department of Literature, Science and the Arts of the University of Michigan for the degree of Doctor of Philosophy, by Harvey C. Brill.

[3] THIS JOURNAL, 34, 82 (1912).