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

THE ACTION OF CARBON TETRABROMIDE ON ORGANIC BASES.

BY WILLIAM M. DEHN AND ALBERT H. DEWEY.

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Molecules of certain compounds exhibit a tendency to unite with molecules of other compounds without the formation of by-products. The resulting molecular aggregates or "molecular compounds" are true chemical compounds because, being of constant composition, they conform to the laws of definit and multiple proportions. In organic chemistry almost every group furnishes examples of molecular compounds. This property, however, is best exemplified with compounds containing cyanogen and basic nitrogen. Thus when the amines or the alkaloids react with acids no water is eliminated, as is the case usually when inorganic bases are neutralized by acids; they simply unite, molecule for molecule, to form the salt. These salts unite further with other compounds, especially with the haloid salts of heavy metals, to form the so-called double salts.

In this contribution it will be shown that carbon tetrabromide reacts with organic bases in a similar manner and that the initial products are true molecular compounds. For instance, quinoline yields $C_9H_7N.CBr_4$, pyridine $C_5H_5N.(CBr_4)_2$, piperidine $C_5H_{11}N.(CBr_4)_2$, ethylamine $(C_2H_5NH_2)_4CBr_4$, etc. It will be observed that these compounds represent different proportions of carbon tetrabromide united with the respective organic bases. A number of typical bases have been studied and are herein described. Preliminary experiments on all types have been made and indicate reactions with all bases, either at ordinary or elevated temperatures, or under the influence of direct sunlight.

The reactions were invariably brought about in ether solution; usually an ether solution of the base was added to an ether solution of the carbon tetrabromide and the mixture was permitted to stand a number of hours or days. The best results were obtained when absolute ether was employed and all contact with moist air was avoided. Sometimes an immediate precipitation of crystals occurred; most often several hours or days were necessary to yield the crystals. Since both the organic bases and the carbon tetrabromide are soluble in ether, the formation of any crystals was an indication of a reaction, and its progress could be estimated by the rate of such precipitation. When the precipitation had progressed sufficiently, the ether was decanted and the precipitates were washed with anhydrous ether. They were then either analyzed directly or after recrystallizing from chloroform or other solvents.

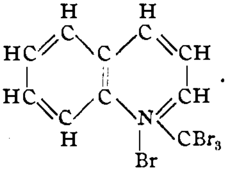
Since, as will be shown below, hydrobromides of the respective bases are the end-products of many of the reactions, or they were invariably obtained from the reaction products by treatment with water, the formation of these salts was an indication of the progress of the reaction, even when no precipitates were obtained from the ether solutions or when these precipitates represented mixtures difficult to separate.

A rational explanation of the mechanism of formation of the initial molecular aggregates and the salts of the bases is attended with great difficulty if a hypothesis of vaguely described "molecular valencies" is employed, or if the usually accepted ionic or kinetic hypotheses are resorted to.

Briefly, it may be stated that an hypothesis of "valencies of compounds" is so at variance with the conceptions of structure of organic compounds that it can and must be dispensed with. Therefore we are concerned most largely with the adequateness of the ionic and kinetic hypotheses.

Let us consider, by way of illustration, the formation of *quinoline carbon tetrabromide* and assume its structure to be

(1)



The *ionic* and also the *kinetic* hypotheses would require a *preliminary dissociation* of the carbon tetrabromide as indicated in the equation,

$$CBr_4 \longrightarrow CBr_3 + Br, \quad (2)$$

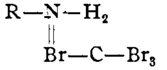
and a subsequent addition of these parts to the trivalent nitrogen atom, yielding the structure shown above.

However, (1) since the reactions are brought about in anhydrous ether, itself a non-electrolyzing medium, (2) since the evident rates of reaction are different, and (3) since sunlight is an accelerating agent, the conclusion is inevitable that preliminary ionic or kinetic dissociation of the carbon tetrabromide is not the *sine qua non* of the reaction. If the reactions were dependent upon this dissociation of carbon tetrabromide, then not only would reactions with all organic bases result but the *rates* of reaction would be equal and, by analogy with known ionic reactions, these rates would be practically instantaneous. However, easily followed differences of reactions are observable, and the rates often are extended over weeks of time. Therefore the reactions are not dependent upon a state of *constant dissociation of the carbon tetrabromide.*

Let us then look to the bases themselves for an explanation of the reactions. Except in cases of the quaternary compounds, the nitrogen organic bases are weak; in fact they differ but little from ammonia itself in basic properties, hence wide variations of reaction would not be expected if relative basic properties were the cause of variation. However, wide variations of reactions are observed and therefore degrees of ionization of the bases, or relative kinetic dissociation of the same, are not to be assigned as the cause of these variations of reactions.

We must then turn to other possibilities of the case. It must be remembered that most organic bases contain atoms of nitrogen in the trivalent condition. These atoms are potentially pentavalent, and therefore all of these compounds are potentially reactive; in other words, the two "latent," "residual," or "partial" valencies present the possibilities of reaction, and reactions will result if other causes do not supervene. Bromine likewise has residual valencies and if a molecule of carbon tetrabromide is brought within the sphere of reaction of a molecule of an organic base it may be assumed that there is first a *coalescence*,[1] due to the residual valencies of the nitrogen and the bromine, which may be represented as follows:

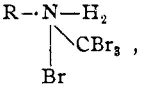
(3)



$$\begin{array}{c}R—N—H_2\\ \|\\ Br—C—Br_3\end{array}$$

It may be assumed that this compound either is reversibly dissociated or is progressively transformed. For the reason that in the above formula trivalent bromine represents an unstable state, we can easily conceive of a shifting of bonds. This shifted state of the valencies may be represented by the formula

(4)



$$\begin{array}{l}R—N—H_2\\ \quad|\diagdown CBr_3\,,\\ \quad Br\end{array}$$

a compound analogous in composition and stability to the salts of the base.

In consideration of the two molar aggregates, (3) and (4), there can be little doubt but that the latter correctly represents the structure of the stable end-product, for we arrive at this same structure if we proceed on a kinetic, an ionic, or the above-described coalescent basis. Only the initial coalescent molecule (3) requires proof.

The fact that the kinetic and the ionic hypotheses are themselves inadequate to account for the end-product is sufficient to justify some other hypothesis. The above-described *coalescent hypothesis*, employing as it does only the usually accepted assumptions of the science, is offered as an explanation. However, some evidence apparently confirming the assumption is gathered. Sunlight is necessary for the starting, progress, and completion of some of these reactions. Cases of no reaction, when the ether solutions have been preserved for days in darkness,[2] have given an immediate precipitate when brought into direct sunlight. This ac-

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[1] See *Am. Chem. J.*, 40, 93.

[2] See Pyridine, p. 1594.

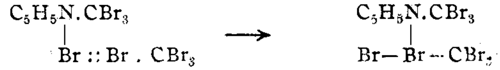
celerating effect of sunlight may be accounted for in two ways: either the actinic rays produce a kinetic dissociation as represented by equation (2) above, or these rays *promote the shifting of bonds* as represented by the transformation of (3) to (4). That the latter is more probable is indicated by the fact that *heat*, the specific agent in kinetic dissociations, does not promote some of these reactions, whereas sunlight does. The transverse ether vibrations of light evidently produce effects different from those produced by heat vibrations.

With pyridine and piperidine, one molecule of the base unites with two molecules of carbon tetrabromide. That these two molecules of carbon tetrabromide are held by the base with different degrees of tenacity and that they are differently united in the molar aggregate is evidenced by two different lines of observations. First, vapor pressure curves indicate a dissociation of one molecule of carbon tetrabromide below 100° and of the second molecule between 100° and 210°. Second, when decomposed by water the complex compound yields products in accordance with the equation

(5) $C_5H_7N.(CBr_4)_2 + 2H_2O \longrightarrow CBr_4 + CO_2 + 3HBr + C_5H_7N.HBr.$

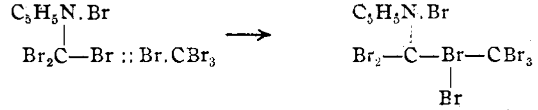
Here one molecule of carbon tetrabromide is liberated as such and the other molecule is decomposed into carbon dioxide, water, and hydrobromic acid. By analogy with (3) and (4) above we may, therefore, assume the following structures for *pyridine dicarbontetrabromide*:

(6)



$$\begin{array}{l} C_5H_5N.CBr_3 \\ \;| \\ Br :: Br . CBr_3 \end{array} \longrightarrow \begin{array}{l} C_5H_5N.CBr_3 \\ \;| \\ Br—Br—CBr_3 \end{array}$$

(7)

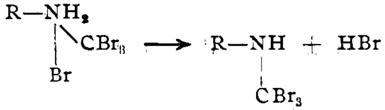


$$\begin{array}{l} C_5H_5N.Br \\ \;| \\ Br_2C—Br :: Br.CBr_3 \end{array} \longrightarrow \begin{array}{l} C_5H_5N.Br \\ \;\vdots \\ Br_2—C—Br—CBr_3 \\ \quad\;\;| \\ \quad\;\;Br \end{array}$$

If either (6) or (7) is the correct formula it is impossible at present to indicate the more probable one. In one case the trivalent bromine atom is assumed to be united to *nitrogen*; in the other case, to the *methane carbon* atom.

From equation (5) above it is evident that a hydrobromide salt of the base is formed when those compounds containing "carbon tetrabromide of crystallization" are treated with water. It was found that these salts were always produced when moist ether was employed, also sometimes even when anhydrous conditions were observed; that is, primary and secondary amines yield salts in the absence of water in accordance with the following equations:

(8)



$$\begin{array}{l} R—NH_2 \\ \;|\diagdown CBr_3 \\ Br \end{array} \longrightarrow \begin{array}{l} R—NH + HBr \\ \quad\;\;| \\ \quad\;\;CBr_3 \end{array}$$

(9) $R—NH_2 + HBr \longrightarrow R—NH_2HBr$.

Tertiary bases, containing, as they do, no N-hydrogen, do not yield salts except in presence of water. In cases of primary and secondary amines these salts are more often the only crystallin products. This ether solution method is, in many cases, the best method of preparation of pure hydrobromides of organic bases, hence a number of new hydrobromides have been contributed. For the purpose of identification, a number of bromoaurates also are contributed.

The mechanism of reaction of water on the carbon tetrabromides may be indicated as follows:

(10) $R—NH_2=(CBr_3)Br=OH_2 \longrightarrow R—NH_2 : (CBr_3)Br : H(OH) \longrightarrow$
$R—NH_2HBr + CBr_3OH$.

The hypothetical substance *tribromocarbinol* may be decomposed as follows:

(11) $CBr_3OH + H_2O \longrightarrow 3HBr + CO_2$.

Since four molecules of hydrobromic acid were formed, the resulting aqueous solutions were usually *acid*. Sometimes, however, the solutions were *neutral* or *alkaline*, thus indicating an incomplete reaction according to (10). In fact, since carbon tetrabromide was obtained in the aqueous solution, the effect of hot water was largely in accordance with the equation

(12) $R—NH_2CBr_3Br \longrightarrow R—NH_2 + CBr_4$.

Preparation of the Sodium Hypobromite.—To prepare a sodium hypobromite solution of maximum concentration, the method previously described by one of us[1] was employed.

Methods of Preparation of Carbon Tetrabromide.—(*a*) The method previously suggested by one of us[2] was found to be easy and economical. Bromoform was placed in stout bottles with an excess of sodium hypobromite solution and shaken either occasionally by hand or constantly by some convenient shaking device. When the liquid bromoform was transformed to a solid mass of crystals of carbon tetrabromide, most of the clear supernatant hypobromite solution was removed by decantation and the remaining mixture was subjected to steam distillation. Pure carbon tetrabromide passed over and was separated from the water and dried on filter paper or clay plates, or better the mass of wet crystals was melted and resolidified, when the supernatant water could easily be poured off and the carbon tetrabromide dried by filter paper used as a blotter.

(*b*) In a convenient sized flask, bleaching powder is treated with an excess of a solution of sodium bromide. The spent sodium hypobromite

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[1] This Journal, 31, 526.

[2] *Ibid.* 31, 1227; cf. *Ann.*, 167, 174; *Ibid.*, 275, 149; *Soc.*, 65, 264.

solution used above, containing as it does most of the bromine in the form of sodium bromide, is conveniently and economically employed. When the bleaching powder and the sodium bromide are brought into contact a yellow solution of hypobromite is formed. This is then treated with acetone in quantities not quite sufficient to discharge the yellow color. This mixture is permitted to stand until the next day, being shaken occasionally if convenient. Finally the mixture is subjected to steam distillation. From 20 g. of acetone 62 g. of CBr_4, or 53 per cent., were obtained.

Preparation of Solutions.—In the earlier experiments ordinary ether was used, but mixtures of varied composition were formed. It was found that these mixtures resulted from the action of water on the carbon tetrabromide compounds of the bases, which were first formed. When absolute ether was employed, no such difficulties were encountered. If necessary, the ether solution of carbon tetrabromide was dried with calcium chloride before adding to the ether solution of the base. The action of moist air was avoided in the removal of the crystals and in the subsequent treatment of the solutions.

Piperidine.—When equimolecular quantities of piperidine and carbon tetrabromide in dry ether solutions were mixed, an immediate, white, flaky precipitate was formed. This precipitate increased steadily on standing and finally yielded beautiful prismatic needles melting at 148°. Coarse needles were easily obtained by heating the ether solutions in a sealed tube.

Calculated for $C_5H_{11}N.(CBr_4)_2$: Br, 85.42; C, 11.23; H, 1.48; N, 1.87.
Found: Br, 85.33; C, 11.13; H, 1.26; N, 2.17.

Piperidine dicarbontetrabromide is decomposed by heat alone in accordance with the equations:

$$(13) \qquad C_5H_{11}N.(CBr_4)_2 \longrightarrow C_5H_{11}N.CBr_4 + CBr_4$$

$$(14) \qquad C_5H_{11}N.(CBr_4)_2 \longrightarrow C_5H_{11}N + 2CBr_4.$$

When water is present the above decompositions and the following one take place:

$$(15) \quad C_5H_{11}N.(CBr)_2 + 2H_2O \longrightarrow C_5H_{11}N.HBr + CBr_4 + 3HBr + CO_2.$$

Equation (14) yields an alkaline end reaction toward litmus; equation (15), an acid end reaction; a proper combination of (14) and (15), a neutral end reaction. In different decompositions by cold and hot water these various conditions of end reaction were observed; however, usually an alkaline end reaction was observed, showing that there is a preponderance of reaction (14). The carbon tetrabromide was identified by its melting point and other properties; the hydrobromic acid, by the acidity of the aqueous solution; the carbon dioxide, by passing the aqueous decomposition product into lime water; the hydrobromide of piperidine, by evaporating the solution and recrystallizing the residue from absolute alcohol, when it was found to darken and melt at 238°–239°.[1]

Calculated for $C_5H_{11}N.HBr$: C, 36.14; H, 7.29; Br, 48.14.
Found: C, 36.55; H, 8.03; Br, 48.21.

Bromoaurate, dark, red-brown needles melting at 242°.

Calculated for $C_5H_{11}N.HBr.AuBr_3$: Au, 32.73.
Found: Au, 32.61.

Pyridine.—When equimolecular quantities of pyridine and carbon tetrabromide were brought together in dry ether solution, they yielded a voluminous crop of iridescent crystals which were easily recrystallized from chloroform. A solution of the two reacting substances could be preserved for hours or days in the dark without precipitating; in the direct sunlight the precipitation was immediate. The crystals darken at 155° and melt at 218–220°. By the pycnometer method with benzene, the specific gravity was found to be 2.70 at 21°.

Calculated for $C_5H_5N.(CBr_4)_2$: C, 11.31; H, 0.68; N, 1.89; Br, 86.12.
Found: C, 11.30; H, 1.04; N, 2.01; Br, 85.89.

Pyridine dicarbontetrabromide is decomposed by heat alone, yielding the first molecule of carbon tetrabromide below 100° and the second molecule near its melting point. The reaction is at best difficultly reversible, for after heating the vapor pressure at ordinary temperature is much greater than the original pressure at ordinary temperature.

VAPOR PRESSURES[2] OF PYRIDINE DICARBONTETRABROMIDE.

Temperature.	1st sample.	2nd sample.	Temperature.	1st sample.	2nd sample.
26	..	11	107	87	...
28	..	14	111	...	242
32	..	21	113	101	...
36	..	24	115	...	255
42	..	31	116	115	...
46	..	39	120	...	281
47	..	61	126	146	...
52	..	65	131	167	...
55	8	..	135	...	344
60	..	87	136	187	...
62	..	99	141	193	...
65	..	104	150	...	410
66	12	...	155	216	...
72	..	128	160	...	465
76	..	140	164	252	...
79	35	...	170	...	520
81	..	149	175	334	...
82	..	156	190	434	...
91	..	203	198	650	...
92	58	...	208	981	...
97	..	215	212	1381	...
106	78	...			

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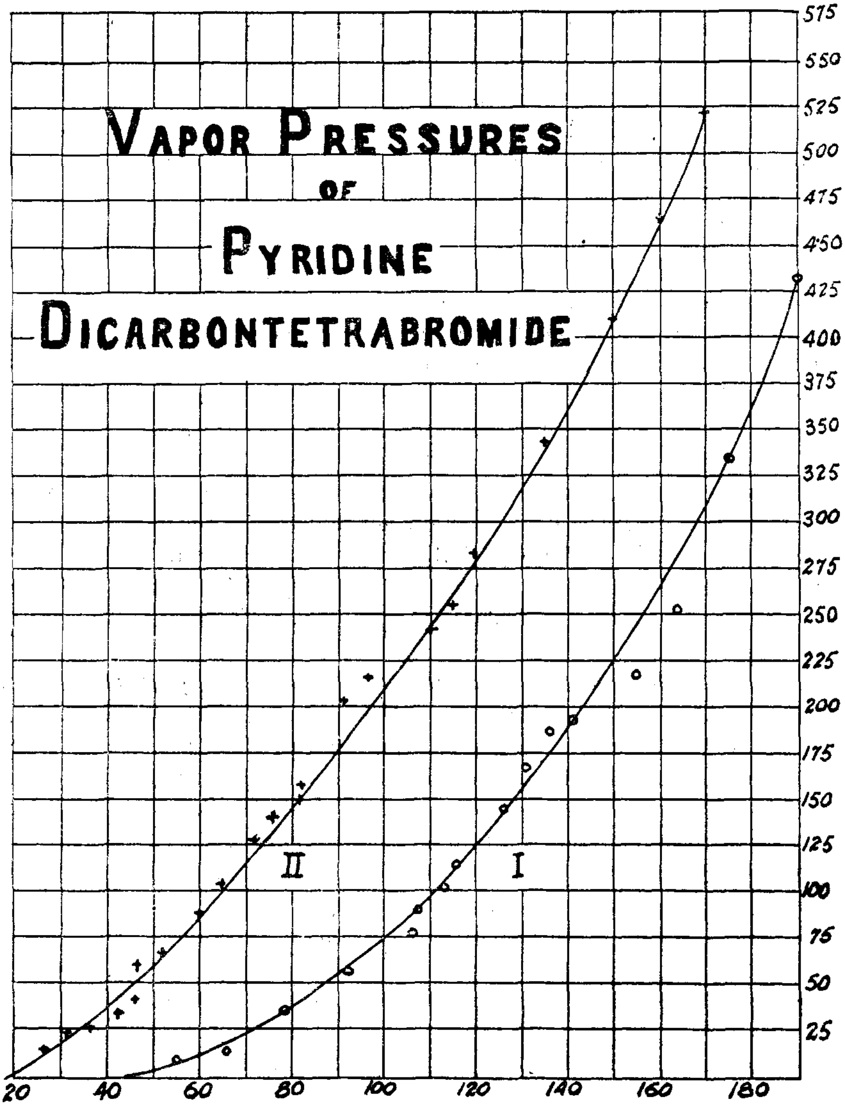
[1] Bischoff gives melting point at 235°, *Ber.*, 31, 2841; Fock, *Ber.*, **32**, 1409.

[2] For method used see THIS JOURNAL, **29**, 1052–65.



Sample (1) was dried at ordinary temperature for a number of days in a desiccator and sample (2) was used as soon as freed from solvent. With water it decomposes in a manner analogous to piperidine dicarbontetrabromide, yielding, however, an acid end reaction; hence the main reaction is

(16) $C_5H_5N.(CBr_4)_2 + 2H_2O \longrightarrow C_5H_5N.HBr + 3HBr + CO_2 + CBr_4$.

The cold aqueous solution yielded bubbles of carbon dioxide and, by evaporation, the hydrobromide of pyridine which softens at 200° and melts at 213°.[1] Calculated for: Br, 49.95. Found: Br, 49.57.

Bromoaurate, fine, brown, prismatic needles melting at 319°. Calculated for $C_5H_5N.HBr.AuBr_3$: Au, 33.03. Found: Au, 33.15.

With boiling absolute alcohol, no ethyl bromide, carbon dioxide, carbon tetrabromide or pyridine hydrobromide could be detected in accordance with the following reaction:

$$(17)\quad C_5H_5N.(CBr_4)_2 + 2C_2H_5OH \longrightarrow 2C_2H_5Br + CO_2 + CBr_4 + C_5H_5N.HBr;$$

therefore, the compound is stable toward absolute alcohol.

Quinoline.—When brought together, an immediate turbidity resulted; after a number of hours, small white prismatic needles separated. After recrystallizing from chloroform, they soften at 110° and melt at 142°.

Calculated for $C_9H_7N.CBr_4$: H, 1.55; N, 3.04; Br, 69.38.
Found: H, 1.74; N, 3.20; Br, 69.23.

An aqueous solution of *quinoline carbon tetrabromide* is neutral and yields by evaporation *quinoline hydrobromide*, white, hygroscopic needles, melting at 62–65°. Calculated for $C_9H_7N.HBr$: Br, 38.06. Found: Br, 38.06.

Bromoaurate, small, dark brown needles, difficultly soluble in water and melting at 209°. Calculated for $C_9H_7N.HBr.AuBr_3$: Au, 30.49. Found: Au, 30.48.

Picoline.—α-Picoline and carbon tetrabromide in dry ether solution yielded an immediate precipitate. After recrystallizing from chloroform, large needles softening at 190° and melting at 214° were obtained. Calculated for $C_6H_7N(CBr_4)_2$: Br, 84.52. Found: Br, 84.78.

Picoline dicarbontetrabromide, with water, yields picoline hydrobromide,[2] and this, with an aqueous solution of auric bromide, yields *picoline bromoaurate*, short, red-brown prisms melting at 209°. Calculated for $C_6H_7N.HBr.AuBr_3$: Au, 32.29. Found: Au, 32.25.

Lutidine.—When α,α-lutidine and carbon tetrabromide were mixed in dry ether solution clusters of short needles formed slowly. Evidently sunlight promoted the precipitation. The crystals melted at 106°.

Calculated for $C_5H_3(CH_3)_2N.(CBr_4)_2$: Br, 82.98.
Calculated for $C_5H_3(CH_3)_2N.(CBr_4)$: Br, 72.86.
Calculated for $C_6H_3(CH_3)_2N.HBr$ Br, 42.51.
Found: Br, 69.40.

Evidently *lutidine carbon tetrabromide*, or a mixture of dicarbontetrabromide with *lutidine hydrobromide* was formed. The latter was obtained from the aqueous solution as white hygroscopic needles melting, not sharply, at 114°. Found: Br, 42.64.

Its *bromoaurate* consisted of dark brown needles melting at 180° and

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[1] Trowbridge gives the melting point at 200°, THIS JOURNAL, **21**, 67.

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

easily soluble in water and alcohol. Calculated for $C_5H_3(CH_3)_2N.HBr.AuBr_3$: Au, 31.55. Found: Au, 31.70.

Phenylhydrazine.—Equimolecular quantities of phenylhydrazine and carbon tetrabromide in dry ether gave an immediate precipitate of mother-of-pearl leaflets and an evolution of nitrogen. The ether solution, distilled first directly and then with steam, yielded bromoform, carbon tetrabromide, and a yellow residue. The leaflets melted sharply at 210°. Calculated for $C_6H_5N_2H_3.HBr$: N, 14.83; Br, 42.29. Found: N, 14.74; Br, 42.48.

The substance was phenylhydrazine hydrobromide[1] and the main reaction evidently was as follows:

$$(18)\ C_6H_5NHNH_2 + CBr_4 \longrightarrow C_6H_5NHNH_2.HBr + CHBr_3 + N_2.$$

This reaction will be investigated further.

Benzylamine.—Equimolecular quantities of benzylamine and carbon tetrabromide gave an immediate and voluminous precipitate of benzylamine hydrobromide, appearing as beautiful, white, glistening leaflets, melting at 204°.[2] When heated with water, some undissolved carbon tetrabromide appeared, indicating its somewhat impure form.

Calculated for $C_6H_5CH_2NH_2.HBr$: N, 7.45; Br, 42.51.
Calculated for $(C_6H_5CH_2NH_2)_4.CBr_4$: N, 7.37; Br, 42.06.
Found: N, 8.17; Br, 40.70.

The *bromoaurate* consists of long, fan-like, brownish red flakes, melting at 178°. Calculated for $C_6H_5CH_2NH_2.HBr.AuBr_3$: Au, 31.35. Found: Au, 31.43.

Diisoamylamine.—Equimolecular quantities of the two substances yielded immediately beautiful feathery crystals. After a few days a solid mass of crystals, so compact that the ether would not flow off, was formed.

Calculated for $(C_5H_{11})_2NH.HBr$: C, 50.39; H, 10.15; N, 5.89; Br, 33.56.
Calculated for $[(C_5H_{11})_2NH.]_4CBr_4$: C, 51.22; H, 9.65; N, 5.83; Br, 33.28.
Found: C, 49.69; H, 9.74; N, 6.45; Br, 33.61.

Dipropylamine.—Needles melting at 144.5° were formed immediately. Analyses indicated that the crystals were a mixture of the hydrobromide and the carbon tetrabromide derivative.

Ethylamine.—An immediate precipitate of beautiful, white, feathery crystals resulted. These needles were found to be a mixture of two compounds. One, easily soluble in water and insoluble in chloroform, melted

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[1] Two hydrobromides are described: $C_6H_5N_2H_3.HBr$ (Balbiano, *Gazz. chim. ital.*, **16**, 138), needles, m. p. 204° (Broche, *J. prakt. Chem.*, **50**, 113); $(C_6H_5N_2H_3)_2.HBr$ (Allain le Cann, *Compt. rend.*, **129**, 105) decomposing and melting at 195°. The latter is prepared by a method somewhat analogous to the above; le Cann treated phenylhydrazine with ethyl bromide in ether solution. Broche's preparation, melting at 204°, is evidently less pure than the above, melting at 210°.

[2] Bischoff gives m. p. at 206°, *Ber.*, **30**, 3170.

at 157°. It proved to be *ethylamine hydrobromide*. Calculated for $C_2H_5NH_2.HBr$: Br, 62.59. Found: Br, 62.43.

Bromoaurate, coarse, red-brown prisms melting at 190°. Calculated for $C_2H_5NH_2.HBr.AuBr_3$: Au, 35.03. Found: Au, 34.98.

The second compound referred to is easily soluble in chloroform; on treating with water, insoluble carbon tetrabromide was formed. From boiling chloroform beautiful prismatic needles melting at 150° were obtained. Calculated for $(C_2H_5NH_2)_4CBr_4$: Br, 62.44. Found: Br, 62.39.

These compounds will be more closely investigated.

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

THE ACTION OF DIIODOACETYLENE ON ORGANIC BASES.

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Diiodoacetylene was first prepared by Berend[1] from silver acetylide and iodine in ether solution. Biltz[2] prepared it from calcium carbide and iodine in potassium iodide solution. Nef[3] prepared it from tetraiodoethylene and acetylene diiodide[4] by treatment with alkali alcoholates.

New Method of Preparation.—The following excels the above methods not only in the ease of preparation but also in the quality and quantity of the yields. Water is admitted from a dropping funnel to a flask containing calcium carbide, at such a rate that a steady stream of gas is generated. The acetylene is conducted into a flask containing a solution of potassium iodide and carrying a dropping funnel and an exit tube.[5] A solution of sodium hypochlorite[6] or sodium hypobromite,[7] preferably the former,[8] is admitted a drop at a time. By reaction with potassium iodide, the hypohalite yields a yellow or brown-red colored solution and this, with the acetylene, immediately forms a beautiful flocculent precipitate of the diiodoacetylene. The precipitate increases in volume until the potassium iodide is exhausted and finally forms, during the pas-

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[1] *Ann.*, **135**, 256; cf. Baeyer, *Ber.*, **18**, 2274; also Nef, *Ann.*, **298**, 343.

[2] *Ber.*, **30**, 1202; cf. G. de Chalmot, *Am. Chem. J.*, **19**, 877.

[3] *Ann.*, **298**, 341.

[4] *Ibid.*, **298**, 342.

[5] The unchanged excess of acetylene may be passed into a gas reservoir and later passed again through the solution.

[6] This is best prepared by dropping concentrated hydrochloric acid into a flask containing potassium permanganate and passing the chlorine into a moderately concentrated solution of sodium hydroxide.

[7] For the best method of preparing sodium hypobromite, see THIS JOURNAL, **33**, 526.

[8] With sodium hypochlorite, acetylene does not precipitate at all; with sodium hypobromite it precipitates "an oil." G. de Chalmot, *Am. Chem. J.*, **19**, 878.