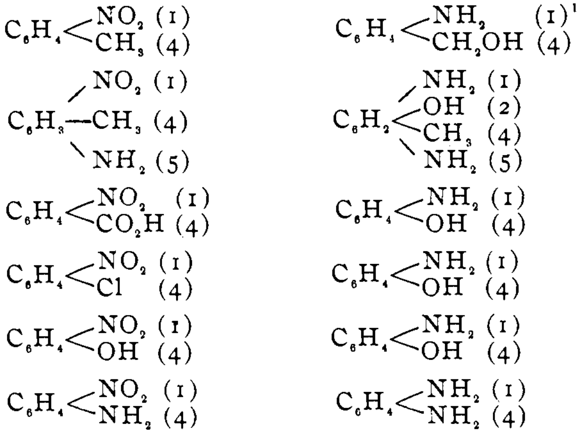

$$C_6H_4\left\langle\begin{matrix}NO_2\ (1)\\ CH_3\ (4)\end{matrix}\right. \qquad C_6H_4\left\langle\begin{matrix}NH_2\ (1)\\ CH_2OH\ (4)\end{matrix}\right.$$[1]

$$C_6H_3\left\langle\begin{matrix}NO_2\ (1)\\ CH_3\ (4)\\ NH_2\ (5)\end{matrix}\right. \qquad C_6H_2\left\langle\begin{matrix}NH_2\ (1)\\ OH\ (2)\\ CH_3\ (4)\\ NH_2\ (5)\end{matrix}\right.$$

$$C_6H_4\left\langle\begin{matrix}NO_2\ (1)\\ CO_2H\ (4)\end{matrix}\right. \qquad C_6H_4\left\langle\begin{matrix}NH_2\ (1)\\ OH\ (4)\end{matrix}\right.$$

$$C_6H_4\left\langle\begin{matrix}NO_2\ (1)\\ Cl\ (4)\end{matrix}\right. \qquad C_6H_4\left\langle\begin{matrix}NH_2\ (1)\\ OH\ (4)\end{matrix}\right.$$

$$C_6H_4\left\langle\begin{matrix}NO_2\ (1)\\ OH\ (4)\end{matrix}\right. \qquad C_6H_4\left\langle\begin{matrix}NH_2\ (1)\\ OH\ (4)\end{matrix}\right.$$

$$C_6H_4\left\langle\begin{matrix}NO_2\ (1)\\ NH_2\ (4)\end{matrix}\right. \qquad C_6H_4\left\langle\begin{matrix}NH_2\ (1)\\ NH_2\ (4)\end{matrix}\right.$$

The most striking of the results are those obtained with the paranitrobenzoic acid and with the parachlornitrobenzene, the group para to the nitro group being driven out in each case. It seems not improbable that this behavior is a general characteristic of nitro compounds with negative para groups, but an investigation of others would be needed in order to establish it as a fact.

It is also worthy of note that, contrary to what might be expected, in only one of the six cases, that of the nitrotoluidine, does the oxygen atom display any tendency to migrate to any other than the para position.

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PERIODIDES OF PYRIDINE.[2]

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Received September 20, 1895.

PYRIDINE ALKYL PERIODIDES.

1. *Pyridine Methyl Pentiodide.*—This was obtained in the manner given in detail below, very satisfactorily in preparation I, and with slight impurity in two other preparations, II and III, by different ways, through separation from other periodides.

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[1] The substance isolated was a condensation-product of this with a second molecule of nitrotoluene; but this is undoubtedty the primary reduction-product.

[2] Read at the Springfield meeting of the American Association for the Advancement of Science, September 2, 1895.

Preparation I is in greenish-black long needles of very dark green luster, some of the crystals being nearly two inches in length. The melting-point is 47.5° C.[1]

Preparation II is of small quantity, in greenish-black crystals, very hard and compact, melting at 47° C.

Preparation III is in crystals exactly like I, melting at 47° C., by recrystallization in alcohol from a greenish-black crystalline powder, the latter being stable and melting at 43° C. The analysis of III was obtained only from this powder, before the final crystallization. These three preparations are, alike, so far stable that after keeping eight months in glass-stoppered bottles, most of the time in the dark, the glass is but just perceptibly stained with iodine liberated from decomposition.

The analyses of the methyl pentiodide, by methods detailed further on, gave results as follows:

	Calculated for $C_5H_5N.CH_3I.I_4$.	Found.		
		I.	II.	III.
Iodine total	87.06	86.74	....	86.69
Iodine by titration	69.65	68.87	69.83	69.55

2. *Pyridine Methyl Diiodide.* — Obtained through different ways, as stated later, in two preparations. I is in reddish-brown crystals, thick plates, compact in clusters. Some crystals are an inch long and a fourth of an inch wide. Melting-point, 91.5° C. The crystals are very stable. On eight months' standing there are no perceptible results of decomposition. II is in red interlaced fine needles of good length, the last previous crystallization having been in dark-red sheaf-form clusters of great beauty. Melting-point, 91.0° C. In stability II is equal to I.

The analyses, with duplicates as specified later, gave the following:

	Calculated for $C_5H_5N.CH_3I.I$.	Found.	
		I.	II.
Iodine total	72.91	72.88	72.33
Iodine by titration	36.55	36.97	36.40

3. *Pyridine Methyl Triiodide.*—Obtained in three preparations, each from a separate recrystallization out of a common mother-

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[1] Measurements of the crystals, and various optical determinations, as well as work by other physical methods, especially such as bear upon molecular weight and constitution, are reserved together for a continued investigation of these bodies.

liquor, that of II of the methyl diiodide. Again it is obtained in the first crystallization by another method, that for IV. I is in dark-red fine needles, quite perfect in outline and partly clustered in certain sheaves characteristic of the earlier crystallizations of this triiodide. Melting-point, 50° C. Perfectly stable.

II shows dark-red needles, the previous crystallization having been merely a loose crystalline mass. Obtained perfectly stable, with melting-point of 50° C.

III is dark-red needle clusters of a certain exact sheaf-form appearing illusively in several earlier crystallizations. But a small quantity was obtained, with a melting-point of 49°–50° C.

IV, perhaps the most perfect, is in very dark red or reddish-black plates with needles, perfectly stable, and melting at 48° C.

The results in analysis have been these :

	Calculated for $C_5H_5N.CH_3I.I_2$.	Found. I.	II.	III.	IV.
Iodine total	80.14	79.32	79.22	....	78.70
Iodine by titration	53.43	53.08	51.52	52.75	53.15

4. A product was obtained of seeming distinct character, in composition and melting-point nearly approaching the pentiodide, but with the elemental figures of a tetrapentaiodide, that is, dipyridinedimethylenneaiodide. It is reserved for further work. It is in greenish-black, lustrous, long needles, well defined, of a melting-point of 44° C. The total iodine in three successive determinations was found to be, respectively, 85.83, 85.88, and 85.83 per cent. ; calculation for $(C_5H_5N.CH_3I)_2I_7$ giving 85.68 per cent., and for $C_5H_5N.CH_3I.I_4$, 87.06 per cent. The iodine by titration was found to be 67.52, 67.08, 67.02, and 66.69 ; calculation giving for these formulas, respectively, 66.45 and 69.65 per cent.

5. *Pyridine Methyl Octaiodide.*—This product is named provisionally, one fairly satisfactory preparation of it being obtained, a second preparation having the requisite composition but (possibly from its more compact crystallization) having a higher melting-point, and a third preparation, while agreeing in melting-point with the first, falling too low in percentages of iodine. The preparation, detailed below, was instituted in the hope of obtaining the enneaiodide. I, by recrystallization from alcohol below

0° C., is greenish-black, in both plates and needles, melts at about 26° C., and is fairly stable when kept at about 15° C. or below. II is in crystals of the same color as those of I, but more slowly formed and more compact, consisting of flat needles, some of them an inch long, with melting-point of about 41° C.. III was imperfectly crystallized, rather solidified in a crystalline mass, of the color of I, and melting at 25° C. We do not include III among the determinate preparations. It gave of total iodine, 90.36 per cent., and of iodine by titration 78.41 per cent., both figures being low for the octaiodide and much too high for the heptaiodide.

	Calculated for $C_5H_5N.CH_3I.I_7$.	Found. I.	Found. II.
Total iodine	91.51	90.79	90.99
Iodine by titration	80.07	79.82	80.13

6. *Pyridine Ethyl Triiodide.*—Obtained, as specified under the account of preparations, from liquid secondary products corresponding to those which gave the three samples of the pyridine methyl triiodide, in lustrous greenish-black needles, well defined, stable through exposure to the air, and melting at 49° C. In the analysis, two determinations by silver iodide gave for iodine 78.389 and 78.388. Three titrations with the thiosulphate gave for iodine 52.784, 52.612 and 52.616. Inasmuch as the mother liquids have been found to contain higher periodides, it is evident that these crystals are not wholly freed from mother liquid.

	Calculated for $C_5H_5N.C_2H_5I.I_2$.	Found.
Iodine total	77.85	78.39
Iodine by titration	51.90	52.67

7. Higher ethyl periodides of pyridine, in nearly black crystals melting below 10° C., were indicated from treatment of the primary oil-like product, though not yet obtained in purity, as stated under the preparation of the triiodide.

Methods of Preparation.—The methyl periodides of pyridine are best obtained, first, by adding the methyl normal iodide of pyridine to dissolved iodine. We have also obtained several pyridine methyl periodides; second, by adding pyridine to a solution of methyl iodide and iodine. We have found, however, as stated further on, that in the latter way there is formed some proportion of a pyridine periodide destitute of methyl, though the avidity of pyridine for methyl iodide ensures a considerable proportion of methyl periodides. For pyridine ethyl periodides the second way would not promise formative results at all owing to the tardy addition of ethyl iodide to pyridine. The normal pyridine alkyl iodides used were prepared for the purpose, and had the properties specified in another paper by one of us (P), in which, also, is a statement of the constants of the pyridine used in these preparations. In adding the pyridine alkyl normal iodide to iodine, the latter was taken in the proportion to make the particular periodide desired, but other periodides would appear as subordinate products. As to just how much effect the relative quantity of iodine added exerts upon the extent of iodine combination, further investigation is now in progress.

The preparation of pyridine methyl pentiodide was done as follows: Eighteen grams of pyridine methyl iodide dissolved in a little alcohol were added to fifty grams of iodine previously dissolved in 200 cc. of alcohol, the solutions being taken at low temperature. A dark green oil-like liquid, thick and cohesive, at once separated in abundance at the bottom. The thin alcoholic liquid above was decanted off and the oil set aside at temperature several degrees below 0° C., when it shortly solidified in crystals, not melting at 25° C. These were dissolved in warm alcohol, and the solution set aside at about —5° C., when crystals of preparation I appeared. They were dried over sulphuric acid to a constant weight, for analysis and determination of the melting-point. This periodide was undoubtedly obtained in its amorphous oil-like state by O. Lange in 1885[1] while engaged in obtaining decomposition products of pyridine methyl iodide by Ladenburg's process. He reported obtaining the heavy dark-green oil, which would not solidify on standing for a day, and which he apparently did not analyse.[2] III of the methyl pentiodide was obtained by treating a part of the first crystalline form of the methyl octaiodide before described, with ether, which

[1] On Picolines, *Ber. d. Chem. Ges.* **18**, 3436.

[2] It was in following Lange that this preparation I of the methyl pentiodide was first undertaken, and the "oil" obtained. After fruitless attempts to crystallize it from various solvents, it was abandoned for six weeks, when, on one very cold day, in moving things it was set in the window next the glass, and presently it became a mass of crystals. These did not melt when returned to the warmer air of the laboratory. A new preparation was at once commenced as above.

dissolves a small portion of the crystals, leaving the remainder as this preparation III of the pentiodide. Preparation II of the methyl pentiodide was obtained from the mother liquor of the methyl octaiodide by evaporation and redissolving the crystals in alcohol.

The preparations of the pyridine methyl diiodide in I and II were from solutions quite different from each other from the beginning, but in both cases they were from later crops of crystals following the addition of free pyridine to solution of the other two materials. The final crystals of I were washed in a very little cold alcohol, and then dried over sulphuric acid for ten days. The crystals of II were obtained fine by rapid formation in alcohol surrounded by a freezing mixture.

The preparations of pyridine methyl triiodide in I, II and III were crystallized from the mother liquids of II of the corresponding diiodide. II of the triiodide was itself recrystallized several times. I and III were in more compact crystals of slower formation. But IV was the result of a different method throughout, following the addition of iodine solution to the methyl normal iodide, using proportions intended for the diiodide. The final crystals were by a single recrystallization of the first crop. It was dried between filter papers over sulphuric acid.

The preparations of pyridine methyl octaiodide (provisionally so termed) were instituted by adding eleven grams of the normal iodide dissolved in a little alcohol, to fifty-five grams of iodine in as little alcohol as possible, both solutions being hot. The greenish black oil-like mass separated at once. The decanted solution was cooled, and other portions of the oil obtained. Below 0° C. the oil crystallized well. I was crystallized from solution in alcohol at low temperature. II was crystallized from alcohol by spontaneous evaporation out of doors in cool weather. The final crystals of each were dried between filter papers, and kept in the vault at about 12° C.

Pyridine ethyl triiodide was obtained following the addition of alcoholic solution of the normal iodide to alcoholic solution of iodine. The first product, chiefly higher iodides, appeared in an oil-like precipitate, and this, after decanting the alcoholic liquid, was dissolved in hot alcohol, and the solution kept for six hours at —4° C. without obtaining crystallization. Afterward crystals were obtained but without success in drying them. Moist with the oil they gave figures a little too low for the tetraiodide. Repeating the entire operation, but not decanting the oil, the entire mixture was exposed to low temperature as before, and the oil solidified in a mass of fine crystals better than before, but these melted below 10° C., and the attempt to obtain a pure high periodide had to be deferred. That the oil, which is stable when dried and has no odor of iodine, contains high iodine additive combination was shown by its analysis, giving figures midway between hexiodide and heptiodide. Now the alcoholic liquid decanted from the oil in the first operation, on cooling below 0° C., gave an excellent crop of crystals. These, dried for several days over sulphuric acid, at about 21° C., constitute the preparation described under the name pyridine ethyl triiodide.

PERIODIDES OF THE AMINE AND OF THE TERTIARY AMMONIUM BASE.

1. *Pyridine Tetraiodide*, $C_5H_5N.I_4$.—Adding to pyridine an alcoholic solution of iodine until the precipitate ceased to form, thereby leaving a slight excess of iodine, there was obtained a bulky crystalline precipitate of a green color, not of a red color as reported by Dafert.[1] This precipitate was filtered out, drained, washed with alcohol, and drained dry, all under the filter pump, then dried between filters over sulphuric acid for several days. It was found soluble in alcohol, ether, chloroform, and less readily in benzene. It was recrystallized from benzene in I, from chloroform in II, and from alcohol in III. In each result the crystals were dark lustrous green. Those of III were in button-like aggregations of fine needles, the whole about half an inch in diameter. From each solution the crystals showed the same melting-point, 85° C. The alcoholic mother-liquor on evaporation gave a crop of very small dark-green crystals IV of the same melting-point. All these crystals gave off perceptible traces of iodine on standing in a glass-stoppered bottle, being very perceptibly less stable than the crystal preparations of the various pyridine *quaternary* base periodides already described. This instability may be the cause of the slight deficiency of iodine found in analysis, the resulting figures being as follows:

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[1] *1883*, Monatsh. Chem., 4, 509.

	Calculated for $C_5H_5NI_4$	Found I.	II.	III.	IV.
Iodine total, by silver iodide	86.49	85.72	85.94	85.63	85.48
Iodine by titration with thiosulphate		85.05	84.79	85.73	85.63

This periodide, therefore, contains no iodine firmly bound as in all normal iodides, none that is not promptly taken up by thiosulphate. In this constitutional feature it is a periodide sharply unlike all the pyridine alkyl periodides known, and unlike the pyridine hydrogen pentiodide found by Dafert,[1] and further described below as examined by us. A superbromide of pyridine was obtained, in 1882, by Grimaux,[2] who writes for it the formula, $(C_5H_5NBr_2)HBr$. He found it not very stable ; in analysis he made but one estimation of bromine, that by silver bromide ; and he found the compound reduced by hydrogen sulphide to pyridine hydrobromide and hydrobromic acid. The triethylphosphine tetraiodide, $P(C_2H_5)_3I_4$, *inferred* by Masson and Kirkland in 1889,[3] is of the same type as our pyridine tetraiodide. Treated with hydrogen sulphide half its iodine entered into phosphonium normal iodide, and half into hydriodic acid.

Several months before the preparation of pyridine tetraiodide as above given, a product was obtained in another way which puzzled us at the time, but which we now recognize as this last-formed pyridine tetraiodide. It was obtained in the first crystalline precipitate after adding free pyridine to the solution of methyl iodide and iodine, in the second way for making the methyl periodides. The mother-liquor of the precipitate gave us the methyl diiodide, preparation I of that product. The precipitate itself crystallized from a chloroform solution, gave very dark green short needles, melting at 84.5° C., and soluble in ether and in benzene. The total iodine was found as 86.32 per cent (the average of four results, lowest 86.22, highest 86.50). At that time a satisfactory titration for iodine was not obtained

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[1] F. W. Dafert, *1883*, Monatsh. Chem., 4, 508. Dafert says, p. 509, "In alkoholischer und in wässeriger Lösung des Pyridins erzeugt Iod in Alkohol, respective in Iodjodkaliumlösung ebenfals unter gewissen umständen eine Fällung. Eben so bei Anweudung von Schwefelkohlenstoff. Das dabei erhältene Präparat ist roth gefärbt und jedenfalls mit dem obigen Superiodid *nicht* identisch. Eine weitere Untersuchung wird wohl näheres ergeben." We have not been able to find a further publication by Dafert upon this compound.

[2] E. Grimaux. *Compt. rend.*, **95**, 87 ; Bull. Soc. Chim., **38**, 127.

[3] *J. Chem. Soc.*, 55, 139.

on account of the solvent, but without any solvent one slow titration resulted in 85.82 per cent., indicating the absence of normal iodine, when the preparation was put aside for later inquiry. It appears, therefore, that when free pyridine is added to methyl iodide and iodine, in alcoholic solution of each, some periodide of pyridine without methyl is formed in the first precipitate, notwithstanding the extreme avidity with which pyridine unites directly with methyl iodide.

2. *The Pyridine Hydrogen Pentiodide of Dafert.*[1]—This was obtained, following the plan given by that author, in crystals such as described by him, melting at about 85° C. (Dafert 89° C.) In analysis it gave 88.03 per cent. of total iodine, and 70.20 per cent. of iodine by titration (calculation for $C_5H_5N.HI.I_4$, total iodine 88.77 per cent., and superiodine 71.02 per cent.). For the titration the periodide was dissolved in alcohol, the end reaction was sharp, and the result conclusive as to the fundamental difference between the two compounds, one of which we believe to be a periodide of C_5H_5NH, and the other of C_5H_5N.

A hydrogen periodide of pyridine, therefore, like alkyl ammonium periodides in general, includes for each atom of nitrogen (in the molecule whatever its magnitude) just one atom of iodine which is left united to the nitrogen after the action of reducing agents of sufficient strength. On the contrary the periodides of pyridine not having ammonium hydrogen or alkyl contain no iodine left by such reducing agents in union with the base, as we say, no iodine firmly bound. Various forms of these two types may be represented as follows:

(1) $R_4NI.I_n$, quarternary alkyl ammonium periodides.
$(R'''N)RI.I_n$, quarternary pyridine periodides.
$(R'''N)HI.I_n$, pyridine hydrogen periodide.
(2) $(R'''N).I_n$, pyridine (amine) periodide.
$(R'''N)Br_2HBr$, a superhalide (Grimaux).
$R_3PI_n.I_n$, inferred by Masson and Kirkland.

ESTIMATIONS OF THE IODINE OF PERIODIDES.

1. The total iodine is obtained by precipitation as silver iodide, weighing this on filters to be described later.

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[1] *1883*: Monatsh. Chem., 4, 508.

The sample is weighed, from a weighing bottle, by difference into a No. 2 beaker. About twenty cc. of a saturated solution of sulphurous acid is added, then a slight excess of silver nitrate solution (used of known strength). The mixture is heated on the water-bath for about an hour, breaking the crystals of periodide if necessary with a flat end of a glass rod, then acidulated strongly, using twenty to thirty cc. of nitric acid, (sp. gr. 1.20), and heated one to two hours or until the precipitate is of a uniform light straw color and the liquid perfectly clear. The precipitate is then put upon the prepared funnel of ascertained weight and washed, first with five per cent. nitric acid and then with hot water, using the pump throughout. The funnels are small sized "carbon tubes," the bottom loosely fitted with a glass plug or shoulder, on which is a layer of cracked glass, twelve to twenty mm. thick, made from beakers and sieved to pass a ten-mesh but not a twenty-mesh. After this is washed level, under pressure of the filter-pump, a layer of acid-washed asbestos is floated over it, and the whole dried at 130° to 150° C. for about two hours or for constant weight. Weighing is done with duplicate funnels, suspending them with an aluminum loop.

The washed silver iodide in the funnel is dried, with its duplicate (also wetted), for two hours at 130° to 150° C., or until weight is constant. A set of about thirty of the funnels have been in hand, and when all have been used, the asbestos layer and precipitate are carefully removed, and a fresh asbestos layer floated on, all which can be done for the set in about two hours.

Two to four parallel estimations have been made, and the average taken. The agreement of the estimations is fairly shown in these figures, quoted from the results: 86.69, 86.79, 86.84, 86.66; 72.45, 72.08, 72.45 ; 86.65, 86.29.

2. The iodine in excess of that for a normal iodide, that is, the iodine responding to reducing agents, has been estimated volumetrically by thiosulphate, using a solution of which one cc. equals 0.010 of iodine. To make this solution, "C. P. sodium thiosulphate" is recrystallized small by stirring while the solution cools. The volumetric solution is standardized by standard solution of potassium dichromate, which in turn is checked with one standardized with "chemically pure" iron wire. The dichro-

mate is purified by fusing a chemically pure article and pouring upon a tile. The factor of the thiosulphate solution is taken every two or three days. The periodide analyzed is weighed by difference, from a weighing bottle into a No. 3 beaker, taking 0.150 to 0.600 gram. Of alcohol from ten to fifteen cc. are added. All the periodides so far obtained are soluble in cold alcohol, but with much difference in the readiness and abundance of this solubility, and this property governs the speed of the estimation. The crystals can be broken under a flat end of a rod, and if not readily soluble, the titration is commenced before solution is completed, keeping down the excess of the iodine-like color. At the end starch can be used as an indicator, but after practice this is not necessary, as the extinction of the iodine-like color can be read to within one drop of the thiosulphate. The burettes had been calibrated and were used with a table of corrections. Other solvents have been tried but alcohol proves far the best for the crystals in titration. Two to four titrations have been made and the average given in each estimation. The agreement of the titrations is represented by a few quotations: of the pyridine methyl diiodide, 37.01, 37.24, 36.48, 37.17; pyridine methyl triiodide, 78.55, 78.84.

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ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND ARSENIC.[1]

BY LAUNCELOT ANDREWS.

Received September 9, 1895.

THE experiments described in the present paper were carried out under my direction during the last winter by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch,[2] and of Jannasch and Schmitt[3] on the same subject. All experiments referred to here, relate to the analysis of an alloy containing in round numbers eighty per cent. lead, thirteen per cent. antimony, seven per cent. tin. The exact composition of this metal will be given later.

[1] Read at the Springfield meeting.

[2] *Ber. d. chem. Ges.* 27, 3335.

[3] *Ztschr. anal. Chem.*, 9, 274.