

wash bottle. Cover the residue in the dish with the half-saturated solution of ammonium chloride prescribed in the official method for the determination of potash, and stir thoroughly. Decant through the Gooch crucible and treat with five or more portions of sal-ammoniac solution, decanting through the crucible each time. Finally wash into the crucible with eighty per cent. alcohol. When the transfer is complete, rinse the sides of the crucible thoroughly and finally fill it twice with alcohol, of course, constantly filtering with a vacuum. Dry for an hour at 100° and weigh.

Pour about 150 cc. of boiling water through the weighed Gooch crucible. If the platinum potassium chloride is not wholly dissolved, again bring the filtrate to a boil and pour through once more. Store this filtrate finally in a large flask, containing aluminum clippings, to reduce the platinum. Bring a fresh portion of water (150 cc.) to a boil and pour through the Gooch crucible. Remove the crucible from the vacuum apparatus, wipe, and dry in an air-bath, with good ventilation, for two hours, at 110° . Weigh once more. The loss in weight is the double chloride. The second portion of hot water is used to dissolve the double salt in the next crucible operated upon, after being once more brought to a boil.

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

PERIODIDES OF PYRIDINE.¹

BY P. F. TROWBRIDGE.

Received February 1, 1897.

Pyridine Methyl Pentiodide, $C_5H_5N.CH_3.I_5$.—This preparation has been reported,² but the present method of preparation is of interest. It was obtained in two experiments, when pyridine was added to an alcoholic solution of iodine containing methyl iodide. The precipitate of the pyridine tetriodide² was filtered off and the liquor set aside for partial evaporation. The crystals obtained were purified by recrystallizations from alcohol. Melting-point 44.5° C.

	Calculated for $C_5H_5N.CH_3.I_5$.	Found.	
		1.	2.
Total iodine ³	87.06	86.24	87.19
Titrated iodine.....	69.65	69.64	69.21

¹ Continuation of paper by Prescott and Trowbridge. This Journal, 17, 859.

² This Journal, 17, 859.

³ This Journal, 17, 867, for methods of analysis.

Pyridine Methyl Heptiodide, $C_5H_5N.CH_3I.I_6$.—A provisionally named octaiodide was reported,¹ but it is very probable that it was a mixture of the heptiodide with some free iodine. In the present experiment, the iodine was taken in great excess to the pyridine methyl iodide; *i.e.*, sufficient for twelve atoms of additive iodine. The pyridine methyl iodide and the iodine were mixed when in the form of hot saturated alcoholic solutions. The mixture was kept hot for fifteen minutes. A heavy dark-green oil formed, which was rapidly separated. This became a crystalline solid at about 20° C. and melted when warmed above 30° C. Insoluble in water, but soluble in dilute alcohol, from which it crystallizes in fine green needles, which are fairly stable. Melting-point 26° C.

	Calculated for	Found.	
	$C_5H_5N.CH_3I.I_6$.	1.	2.
Total iodine	90.40	90.36	90.23
Titrated iodine.....	77.48	77.31	78.21

The liquor from the above was found to contain the pentiodide not entirely pure.

At the present writing we have not succeeded in preparing a higher periodide of pyridine methyl iodide. When pyridine methyl iodide is heated in sealed tubes to 125° C. with an alcoholic solution of iodine, the pentiodide is formed. When the same mixture is heated to 175° C. ethyl iodide is formed and no definite periodide could be isolated. When pyridine methyl iodide and iodine are heated in tubes to 200° C. without the addition of alcohol, the heptiodide is formed. This product was purified by recrystallization from alcohol. Melting-point 26.5° C. Reported as 2 above.

When pyridine and iodine are heated to 175° C. the tetriodide is formed.

Pyridine Ethyl Pentiodide, $C_5H_5N.C_2H_5I.I_5(?)$.—When pyridine, iodine, and alcohol are heated in tubes to 175° C., a pasty mass is formed having a carbonaceous odor. Definite black crystals were obtained by treatment with alcohol. Melting-point 83° C.

	Calculated for	Found.
	$C_5H_5N.C_2H_5I.I_5$.	
Total iodine	85.41	86.32
Titrated iodine	68.33	68.59

The corresponding methyl compound melts at about 44° C.¹

¹ This Journal, 17, 859.

This ethyl compound should melt below 44°C ., as the normal ethyl iodide melts at a much lower temperature than the methyl compound.¹ It is quite possible that ethyl iodide is first formed, which combines with the pyridine; and then, under the pressure and heat, the Ladenburg reaction takes place and ethyl pyridine hydriodide tetriodide, $\text{C}_5\text{H}_4(\text{C}_2\text{H}_5)\text{N.HI.I}_4$, is formed. Pyridine ethyl triiodide (described later in this paper) also melts at 51°C . Pyridine ethyl pentiodide must melt at a lower temperature. Further investigation will be made of this preparation.

To find, if possible, the limit of iodine addition to pyridine methyl iodide, the following series of experiments was made. A definite amount of carefully purified pyridine methyl iodide, $\text{C}_5\text{H}_5\text{N.CH}_3\text{I}$, was dissolved in a small amount of alcohol, and to this a cold saturated alcoholic solution of iodine was added. The amount was taken so that in (1) there was just sufficient iodine for one atom of additive iodine; in (2) just enough for two atoms of additive iodine; etc. In this series of experiments the solutions were not warmed. All were treated at the temperature of ordinary summer weather.

1. No crystals formed in twenty-four hours. On cooling in salt and ice an abundance of red needle-like crystals was obtained. These were purified from alcohol. Melting-point 49°C .

	Calculated ² for $\text{C}_5\text{H}_5\text{N.CH}_3\text{I.I}$.	Calculated for $\text{C}_5\text{H}_5\text{N.CH}_3\text{I.I}_2$.	Found.
Total iodine.....	72.91	80.14	79.26
Titrated iodine.....	36.46	53.43	52.11

2 and 3. Crystals formed at once, and upon purification gave handsome, overlapping, reddish-brown plates. Melting-point 50°C .

	Calculated for $\text{C}_5\text{H}_5\text{N.CH}_3\text{I.I}_2$.	Found. ²	
		2.	3.
Total iodine.....	80.14	79.46	79.59
Titrated iodine.....	53.43	53.09	53.08

4. A heavy green oil formed at once, which became a semi-solid green mass upon standing. This was purified from alcohol. Short greenish needles were obtained. Melting-point 44°C . From the liquor, after removal of the oil, crystals were

¹ This Journal, 18, 91.

² This Journal, 17, 860.

obtained, which, upon purification, gave the reddish-brown plates. Melting-point 50° C.

	Calculated for		Found.	
	$C_5H_5N.CH_3I.I_2$.	$C_5H_5N.CH_3I.I_4$.	Oil.	Liquor.
Total iodine.....	80.14	87.06	86.12	79.40
Titrated iodine..	53.43	69.65	66.47	53.13

5. A dark-green oil formed at once, forming crystals upon purification. Analysis gave 85.73 per cent. of total iodine and 66.76 per cent. of titrated iodine. From the liquor more oil was obtained, which also gave crystals upon purification. Analysis gave 80.17 per cent. of total and 63.80 per cent. of titrated iodine. In both the above cases the crystals were not sharply defined, nor were they of definite melting-points. Theory as $C_5H_5N.CH_3I.I_3$ gives 84.33 per cent. of total and 63.25 per cent. of titrated iodine.

6. Results very similar to those in (5) were obtained, except no crystals whatever could be secured from the first oil. Green needles were obtained from the liquor. Iodine found, 86.30 per cent. total and 70.08 per cent. titrated.

7. The green oil which formed at once gave the dark-green needles upon crystallization from alcohol. Melting-point 44° C. Found 86.50 and 68.56. From the liquor dark-green crystals were obtained. Melting-point 45° C. Found 85.92 and 70.08.

8. A dark-green oil formed at once. This was purified. Found 86.31 and 69.51. In the liquor long dark-green needles formed on standing over night. These were analyzed without further purification. Melting-point 44.5° C. Found 86.57 and 68.24.

9. As in 8. Melting-point 44.5° C. Found from oil 86.88 and 69.17; from liquor 86.81 and 68.99.

10. The dark-green oil would not crystallize from alcohol. The liquor gave very long (three inches) dark-green needles. These were analyzed without further purification. Melting-point 44° C. Found 86.26 and 68.87.

The following table gives a brief summary of the results in the series above described :

	Melting-point.	Total iodine.		Titrated iodine.		Calculated for
		Found.	Theory.	Found.	Theory.	
1	49	79.26	80.14	52.11	53.43	$C_5H_5N.CH_3I.I_2$
2	50	79.46	80.14	53.09	53.43	$C_5H_5N.CH_3I.I_2$
3	..	79.59	80.14	53.08	53.43	$C_5H_5N.CH_3I.I_2$
4	44	86.12	87.06	66.47	69.65	$C_5H_5N.CH_3I.I_4$
4	liquor 50	79.40	80.14	53.13	53.43	$C_5H_5N.CH_3I.I_2$
5	..	85.73	84.33	66.76	63.25	$C_5H_5N.CH_3I.I_3$
5	" ..	80.17	84.43	63.80	63.25	$C_5H_5N.CH_3I.I_3$
6	
6	" ..	86.30	87.06	70.08	69.65	$C_5H_5N.CH_3I.I_4$
7	44	86.50	87.06	68.56	69.65	$C_5H_5N.CH_3I.I_4$
7	" 45	85.92	87.06	70.08	69.65	$C_5H_5N.CH_3I.I_4$
8	..	86.31	87.06	69.51	69.65	$C_5H_5N.CH_3I.I_4$
8	" 44.5	86.57	87.06	68.24	69.65	$C_5H_5N.CH_3I.I_4$
9	44.5	86.88	87.06	69.17	69.65	$C_5H_5N.CH_3I.I_4$
9	" ..	86.81	87.06	68.99	69.65	$C_5H_5N.CH_3I.I_4$
10	
10	" 44	86.26	87.06	68.87	69.65	$C_5H_5N.CH_3I.I_4$

In further studying the limits of iodine addition with pyridine methyl iodide, another series of experiments was made, in which pyridine was added to an alcoholic solution of iodine containing methyl iodide. The iodine was so taken that (1) gave iodine for one additive atom, (2) for two, etc., temperature conditions being the same as in the preceding series. In all cases there was formed at first the pyridine tetriodide, which was rapidly separated by filtration and the liquor set aside for evaporation and crystallization. The products obtained were purified by recrystallization and then carefully analyzed.

(1) and (2) gave a mixture of the pyridine methyl diiodide and triiodide. (3) gave the triiodide in most excellent conditions of purity. (4) and (5) gave the pentiodide very pure.

From the above series of experiments we must conclude that, at ordinary temperature and with small amounts of iodine, the triiodide is usually formed, and with larger amounts of iodine the pentiodide; and this latter is the highest periodide that will form of pyridine methyl iodide at ordinary temperature, no matter how much iodine be used. Some of the preparations are evidently mixtures of the triiodide and the pentiodide. There is no satisfactory evidence of the formation of a pyridine methyl tetriodide.

Pyridine Hydriodide, $C_5H_5N.HI.H_2O$.—White needle-like

crystals, soluble in water and alcohol, insoluble in ether, melt at about 268° C. with some decomposition. Upon standing, the crystals become brownish in color and after a few days give off pyridine. Dilute hydriodic acid freshly distilled from red phosphorus was added to pyridine diluted with water. The crystals were obtained by partial evaporation and then cooling. These were purified by crystallizing from water and drying over sulphuric acid.

0.4501 gram gave 0.4728 gram silver iodide, or 0.2554 gram iodine, or 56.74 per cent. iodine.

Theory for $C_5H_6N.HI.H_2O = 56.34$ per cent.

Theory for $C_5H_6N.HI = 61.25$ per cent.

Pyridine Hydriodide, $C_5H_6N.HI$.—This preparation has the same properties as that just described. It is made by adding freshly distilled hydriodic acid, sp. gr. 1.96, to pure pyridine cooled in a mixture of salt and ice. The pure white crystals formed at once and were purified by washing repeatedly with absolute ether. After being thus purified they do not take up a molecule of water when recrystallized from water. Neither the salt purified by washing with ether nor that crystallized from water loses an appreciable amount on being heated for six hours at 100° C.

Iodine found before drying.	Iodine found after drying six hours.	Theory for $C_5H_6N.HI$.
61.21	60.88	61.25
60.93	60.65	...
61.00

Pyridine Hydrogen Diiodide, $C_5H_6N.HI.I$.—Dark-brown short needles, perfectly stable, slightly soluble in water, very soluble in alcohol. Melting-point 188°–192° C. Crystallizes from absolute alcohol as brown overlapping plates. This preparation was made (1) by treating pyridine with hydriodic acid containing some free iodine, and then allowing to stand; (2) by adding an alcoholic solution of iodine to pure pyridine hydriodide in the cold.

	Found.		Calculated for $C_5H_6N.HI.I$.
	1.	2.	
Total iodine.....	75.66	75.75	75.97
Titrated iodine.....	37.32	37.95	37.98
	37.93
	37.94

Hollow Crystals of the Pyridine Hydrogen Diiodide.—The liquor from the first crystallization of the $C_5H_5N.HI.H_2O$, was treated with an alcoholic solution of iodine (not a great excess), and allowed to stand for twenty-four hours. A large bulk of crystals was obtained, fully fifty grams. They were reddish-brown hexagonal hollow prismatic crystals of very uniform size and many of them fully two inches long. Melting-point $188^\circ-191^\circ$ C. These crystals are the pyridine hydrogen diiodide but not quite pure. Analytical results are about one per cent. too low, both in total and titrated iodine. When these hollow crystals are recrystallized from alcohol the pure diiodide is obtained in fine needle-like crystals. I have tried repeatedly to reproduce the hollow crystals, but without success. Hollow crystals have been reported by Kebler.¹

Pyridine Hydrogen Pentiodide, $C_5H_5N.HI.I_4$.—Stable, very dark, brownish-black, short crystals, melting-point $78^\circ-82^\circ$ C. Obtained (1) from the liquor of the heptiodide described below, by evaporation and several recrystallizations from alcohol; (2), by dissolving iodine in hydriodic acid, warming, and adding a calculated quantity of pyridine. Crystals form and are purified from alcohol, in which they are very soluble.

	Found.		Calculated for $C_5H_5N.HI.I_4$.
	1.	2.	
Titrated iodine.....	71.09	69.91	71.01
Total iodine.....	87.66	88.77

Pyridine Hydrogen Heptiodide, $C_5H_5N.HI.I_6$.—Lustrous green scales, fairly stable, soluble in alcohol, melting-point $63^\circ-64^\circ$ C. Hydriodic acid was added to pyridine and then heated on the water-bath. To this a hot saturated alcoholic solution of iodine was added. An abundance of crystals was obtained upon cooling. Purified by recrystallization from alcohol.

	Found.	Calculated for $C_5H_5N.HI.I_6$.
Total iodine	92.23	91.71
Titrated iodine	78.65	78.67

Not being successful in any of the previous experiments in making pyridine hydrogen triiodide, a series of experiments was started, from which it was hoped to obtain the desired periodide. Pure pyridine hydriodide was dissolved in dilute alcohol, and iodine in alcoholic solution was added. (1) contained

¹ *Am. J. Pharm.*, 67, 602.

iodine sufficient for one-half atom of additive iodine, (2) for one atom, (3) two atoms, (4) three atoms, (5) four atoms, (6) five atoms, (7) six atoms, (8) seven atoms, (9) ten atoms, and (10) fifteen atoms.

In (1) to (6) no heat was used, in the others the solution of pyridine hydriodide was heated and the iodine added as a hot saturated alcoholic solution.

(1). After several crystallizations the pure $C_6H_5N.HI.I$ was obtained in needles one-half inch long.

(2). Same as (1).

(3). Same as (1), but impure.

(4) and (5). $C_6H_5N.HI.I_4$, but impure.

(6). $C_6H_5N.HI.I_4$, pure.

(7). $C_6H_5N.HI.I_6$, pure.

(8), (9), and (10). $C_6H_5N.HI.I_8$, fairly pure in each case.

Thus far we have been unable to make the triiodide, $C_6H_5N.HI.I_3$. The corresponding periodides of the methyl and ethyl series are very easily made.

Pyridine Ethyl Triiodide,¹ $C_6H_5N.C_2H_5I.I_3$.—To 23.4 grams pure pyridine ethyl iodide dissolved in a small amount of alcohol, 12.6 grams of iodine dissolved in alcohol were added. No crystals formed on standing twenty-four hours, lightly covered, but after a second twenty-four hours, several large clusters of crystals were formed. These are bluish-black, thin, rhomboidal, overlapping plates. Melting-point $51^\circ C$.

In a second preparation a greater quantity of iodine was taken and the pure crystals obtained free from adhering oil by several recrystallizations. Melting-point $51^\circ C$. In a third and fourth preparation the above periodide was made in the attempt to make pyridine ethyl chloride periodide. A water solution of pyridine ethyl iodide was shaken with a slight excess of freshly precipitated silver chloride until the filtrate gave no test for iodine. This filtrate was treated with a potassium iodide solution of iodine. A heavy black oil formed, which was carefully separated and placed in tightly stoppered bottles. Owing to other work, these stood for three months. The oily products had become crystalline with some adhering oil. The crystals were very compact, hard, lustrous, and greenish-black.

¹ This Journal, 17, 862.

Careful tests showed entire absence of chlorine. They were recrystallized from absolute alcohol, when lustrous, greenish-black, overlapping plates were formed. Some of these plates are fully one inch long, with very definite angles. Melting-point, (3), 52° C., (4), 51° C.

	Found.				Calculated for
	1.	2.	3.	4.	$C_5H_5N.C_2H_5I.I_2$.
Total iodine	77.91	77.68	78.33	77.85
	77.27	77.57
Titrated iodine ...	50.77	51.83	52.42	52.15	51.90
	51.48	51.91	51.80	51.80
	51.06	51.86

Work is being continued on periodides of quinoline piperidine and mixed perhalides of pyridine and quinoline.

Molecular Weight Determinations.—Much difficulty has been experienced in determining the probable molecular composition of the pyridine periodides. Since alcohol is such a ready solvent for them and heat so readily decomposes them, it was deemed advisable to try the vapor-tension method of Will and Bredig.¹ We find that this method is not at all applicable to the perhalides, but as a check on our own work, we very easily confirmed Will and Bredig's work on nitrobenzene.

The freezing-point method was tried, using nitrobenzene, formic acid, glacial acetic acid, and phenol. None of these solvents seem to decompose the perhalides, but phenol is the only solvent that gives sufficient deviation of the freezing-point.

	Found.	Theory.
$C_5H_5N.HI.I$	387	
	375	
	386	333
	398	
$C_5H_5N.CH_3I.I$	398	
	334	347
$C_5H_5N.C_2H_5I.I_2$	403	
	423	487
$C_5H_{11}N.CH_3I.I_2.H_2O$	496.8	497.5
$C_5H_5N.CH_3I.I_4$. No accurate results.		

It is of much significance that two different diiodides, having but one atom of additive iodine to one atom of normal iodine, are clearly found to be monopyridine compounds, the same as those with even numbers of additive iodine. It would appear, therefore, that in the diiodides one of the two iodine atoms exer-

¹ *Ber. d. chem. Ges.*, 22, 1084.

cises an even valence, as in $C_6H_5N \leftarrow \begin{matrix} R \\ I-I \end{matrix}$, or perhaps $C_6H_5N \leftarrow \begin{matrix} R \\ I=I \end{matrix}$. With the higher perhalides the burden of experiment points very strongly to the formation of compounds having only an even number of additive halogen atoms. The

structure may be $C_6H_5N \leftarrow \begin{matrix} R \\ I \left\langle \begin{matrix} I-I \\ | \\ I-I \end{matrix} \right. \end{matrix}$, etc., at all events indicating

uneven valence for all halogen atoms. It is quite probable that all the pyridine perhalides exist in monopyridine molecules.

If there be an analogy between the perhalides of the tertiary amines and the ammonium salts of the oxyacids of chlorine, then

the structure may be $\equiv N \leftarrow \begin{matrix} R \\ (I=I)-I \end{matrix}$, $\equiv N \leftarrow \begin{matrix} R \\ (I=I)-I \left\langle \begin{matrix} I \\ | \\ I \end{matrix} \right. \end{matrix}$,

etc., where $(I=I) = O$. In this case the single additive halogen would be divalent and a substitute for oxygen, *i. e.*, $\begin{matrix} H \\ H \\ H \end{matrix} \equiv N \leftarrow \begin{matrix} H \\ O-Cl \end{matrix}$ and $\equiv N \leftarrow \begin{matrix} R \\ I-I \end{matrix}$. In the mixed perhalides to be reported in a later paper, the single additive halogen is of more frequent occurrence.

I wish to express my thanks to Professor A. B. Prescott, to whom I have gone for advice and under whose general supervision the work has progressed; also to Messrs. O. C. Diehl² and R. E. Knapp for their assistance in the laboratory.

ANN ARBOR, MICH., Jan. 23, 1897.

MODIFICATION OF THE THALLEOQUIN TEST FOR QUININE.

BY F. S. HYDE.

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IT is extremely important for the success of this test that the reagents employed should be dilute. Some authorities give the quantity of each reagent necessary, without stating the proper dilution, thereby causing much inconvenience.

The light green coloration produced on porcelain by contact of the quinine salt with weak bromine or chlorine water and

¹ This Journal, 17, 780.

² This is the beginning of Mr. Diehl's work upon "Foundations for the Estimation of Alkaloids. Conducted for the Committee of Revision of the U. S. Pharmacopeia," by Prof. A. B. Prescott. The next following work has been upon "Mixed Perhalides of Pyridine and Piperidine," now nearly ready for publication.