

to a dark pink, and gradually washing out until we ended with a pale slate color, and the solubility made it very hard to know just when we got through, because the cobalt tests would show ferrocyanide to the very end. All the precipitates were washed in bulk of 6,700 cc., allowed to settle in bottles, then siphoned off as far as possible, and water added. Most of them had from twenty to thirty washings, and by adding barium chloride we were enabled to get four or five washings a day. Before doing that, we were well satisfied with one washing in two days. As you continue, the washing and settlings get slower and slower, but there seems to be some very curious change in the manganese salts during this washing. The precipitate changed color in parts entirely during the washing.

*Mr. Miller:* There is a difference in color where the manganese or ferrocyanide is in excess and you get changes in color going from one washing to another.

*Mr. Van Ingen:* I was referring to washing the precipitate where manganese was in excess. We started with pinkish purple and ended up with a slate color.

*Mr. Miller:* I don't remember seeing a purple color, but I noticed a change from pinkish to sort of slate color.

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

## HALIDES AND PERHALIDES OF PYRIDINE.<sup>1</sup>

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### ACTION OF BROMINE UPON IODIDES OF PYRIDINE.

*Pyridine Hydriodide Dibromide*,  $C_5H_5N.HI.Br_2$ , or  $C_5H_5N.HBr.IBr$ .—Reddish-brown, thin laminae or large, prismatic plates. Melting-point  $172^\circ-175^\circ$  C. Very soluble in alcohol, with difficulty in chloroform, and scarcely at all in water. The samples for analysis were crystallized from alcohol.

Pure pyridine hydriodide was dissolved in water and brominated by passing carbon dioxide through bromine and then through the solution. At first a very dark red precipitate formed which appeared to be nearly pure iodine. Upon continued bromination the precipitate became brownish yellow,

<sup>1</sup> Continuation of previous paper. This Journal, 19, 322.

flocculent, and readily floated in the liquid. Gradually the precipitate became heavier and finally settled as a dark brown, viscous mass. A small amount of heat was generated during the bromination. Upon standing the precipitate became crystalline and the solution showed the presence of some iodine. The pure product was obtained by several crystallizations from alcohol.

	Calculated for $C_5H_5N.HI.Br_2$ .	Found.	
		I.	II.
Titrated halogen .....	43.59	43.47 43.41	43.03
Total halogen.....	78.01	77.82 78.12	....

*Pyridine Methyl Iodide Dibromide*,  $C_5H_5N.CH_3I.Br_2$ , or  $C_5H_5N.CH_3Br.IBr$ .—Bright orange-yellow crystals, soluble in alcohol and acetone, does not crystallize well from the latter, insoluble in water and ether. From an absolute alcohol solution orange-yellow, short, prismatic, needle-like crystals were obtained. Melting-point  $61^{\circ}$ – $62^{\circ}$  C.

A water solution of pure pyridine methyl iodide was brominated in the same manner as the pyridine hydriodide. A heavy reddish brown oil formed, having a strong bromine-like odor. Potassium hydroxide decomposes the oil. When the oil is heated on the water-bath for several hours the bromine odor disappears and the oil becomes lighter in color. On cooling it forms a bright-orange crystalline mass. This was purified from alcohol.

	Calculated for $C_5H_5N.CH_3I.Br_2$ .	Found.
Total " .....	75.26	75.04

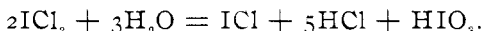
*Pyridine Ethyl Iodide Dibromide*,  $C_5H_5N.C_2H_5I.Br_2$ , or  $C_5H_5N.C_2H_5Br.IBr$ .—Orange-yellow crystals, soluble in alcohol. Melting-point  $25^{\circ}$ – $26^{\circ}$  C.

This preparation was made by aspirating air through bromine and into a water solution of pure pyridine ethyl iodide. A dark red oil formed, which was separated from the liquor (no iodine found in liquor), and heated for a time on the water-bath. The oil was then purified by dissolving in alcohol.

	Calculated for $C_5H_5N \cdot C_2H_5I \cdot Br_2$ .	Found.	
		I.	II.
Titrated halogen.....	40.49	{ 40.05 40.26	{ 40.45 40.34
Total " .....	72.59	72.34	72.89

## ACTION OF CHLORINE UPON IODIDES OF PYRIDINE.

Pictet and Kraft<sup>1</sup> report several mixed perhalides of pyridine, quinoline, and piperidine. By adding iodine trichloride to a water solution of pyridine hydrochloride they get pyridine hydrochloride iodine chloride,  $C_5H_5N \cdot HCl \cdot ICl$ . Melting-point  $180^\circ$ . Analysis not given. The water present decomposes the iodine trichloride according to the equation,



By treating the above hydrochloride with caustic alkali, pyridine iodine chloride is formed, white needles melting at  $132^\circ$  C. Close analytical results are given. They report analogous products of quinoline and piperidine. The  $C_8H_{11}N \cdot HCl \cdot ICl$ , melting at  $90^\circ$  C. is of especial interest as it is made by adding iodine chloride (ICl) to piperidine hydrochloride and also by adding hydrochloric acid to piperidine iodine chloride,  $C_8H_{11}N \cdot ICl$ .

Dittmar<sup>2</sup> uses iodine monochloride (ICl) and obtains the same bodies as reported by Pictet and Kraft. By chlorination of  $C_5H_5N \cdot HCl \cdot ICl$  he obtains  $C_5H_5N \cdot HCl \cdot ICl_3$ . This is an unstable body and according to Pictet and Kraft cannot be made by treating the pyridine hydrochloride with iodine trichloride.

In our study we did not attempt to confirm the results just cited. Our aim was to study the effect of chlorine on pyridine derivatives containing iodine, hence we did not make use of iodides of chlorine direct.

*Pyridine Hydriodide Trichloride*,  $C_5H_5N \cdot HI \cdot Cl_3$ ; or  $C_5H_5N \cdot HI \cdot Cl_2$ ,  $C_5H_5N \cdot HI \cdot Cl$ ; or  $C_5H_5N \cdot HCl \cdot ICl$ ,  $C_5H_5N \cdot HCl \cdot ICl_3$ .—Chlorine gas was passed through a water solution of pure pyridine hydriodide to complete saturation. At first iodine is set free. It then combines with more chlorine and a bright lemon-yellow flocculent precipitate is formed. It crystallizes nicely from alcohol. Melting-point  $176^\circ$  C. The precipitate contains an abundance of iodine.

<sup>1</sup> Bull. Soc. Chim. [5], 7, 72.

<sup>2</sup> Ber. d. chem. Ges., 18, 1613.

	Calculated for $C_5H_5N.HI.Cl_3$ .	I.	Found. II.	III.
Titrated halogen . . . . .	33.13	33.33	33.17	33.93
Total " . . . . .	74.09	74.76	73.83	73.18

We could not by this method of simple chlorination obtain a body having four atoms of chlorine. The body we obtained consists probably of equal portions of the dichloride and tetrachloride.

*Pyridine Methyl Iodide Tetrachloride*,  $C_5H_5N.CH_3I.Cl_4$ , or  $C_5H_5N.CH_3Cl.ICl_3$ .—A canary-yellow powder melting at  $185^\circ C$ .

	Calculated for $C_5H_5N.CH_3I.Cl_4$ .	Found.
Titrated halogen . . . . .	39.17	39.16

Made by passing chlorine into a water solution of pyridine methyl iodide to saturation.

Bally<sup>1</sup> reports the same body,  $C_5H_5N.CH_3Cl.ICl_3$ , by passing chlorine into a mixture of  $C_5H_5N.CH_3Cl.ICl$  and potassium hydroxide. He then acidifies and obtains a yellow body which melts at  $179^\circ-180^\circ C$ . He makes  $C_5H_5N.CH_3Cl.ICl$  by treating  $C_5H_5N.CH_3I$  with chlorine. Melting-point  $90^\circ C$ .

Ostermayer<sup>2</sup> reports this last body,  $C_5H_5N.CH_3Cl.ICl$ , but with a melting-point of  $81^\circ-82^\circ C$ ., by treating  $C_5H_5N.CH_3Cl$  with iodine chloride ( $ICl$ ). The iodine chloride is made by passing chlorine into iodine suspended in water.

*Pyridine Ethyl Iodide Tetrachloride*,  $C_5H_5N.C_2H_5I.Cl_4$ , or  $C_5H_5N.C_2H_5Cl.ICl_3$ .—Made by passing chlorine through a water solution of pyridine ethyl iodide. At first iodine is thrown out of solution. Gradually the solution assumes a lighter color, the iodine disappears, and finally a canary-yellow precipitate is obtained. Melting-point  $123^\circ C$ .

	Calculated for $C_5H_5N.C_2H_5I.Cl_4$ .	Found.
Titrated halogen . . . . .	37.71	37.43
Total " . . . . .	71.28	71.16

ACTION OF BROMINE UPON PYRIDINE.

Anderson<sup>3</sup> treats a water solution of pyridine with bromine water and reports (no analysis given) an addition product with probably more than one atom of bromine. He also treats dry

<sup>1</sup> *Ber. d. Chem. Ges.*, 21, 1772.

<sup>2</sup> *Ibid.*, 18, 591.

<sup>3</sup> *Ann. Chem.* (Liebig), 105, 341.

pyridine with dry bromine and reports pyridine hydrobromide as one of the products formed (no analysis given).

Hofmann<sup>1</sup> treats pyridine hydrochloride with bromine and gets a body which he does not analyze but erroneously assumes to have the formula  $C_5H_5N.Br_2$ . More is given in this paper concerning this product under "Action of Bromine upon Chlorides of Pyridine."

Grimaux<sup>2</sup> treats pyridine with three times its volume of bromine and obtains an unstable body, which he crystallizes from chloroform or alcohol. He gets thin red plates, melting at  $126^\circ C.$ , to which he assigns the formula  $(C_5H_5N.Br_2)_2.HBr$ . His analysis shows about two and one-half atoms of bromine to five atoms of carbon, but he does not report the action of reducing agents like sodium thiosulphate, which, if his formula be correct, would show four atoms of titrated bromine and five atoms of total bromine to ten atoms of carbon. We could not reproduce Grimaux's compound by this method. See further in this paper under "Action of Bromine upon Bromides of Pyridine."

After many ineffectual attempts to form a definite compound by the action of bromine in varying quantities upon dry pyridine and pyridine in water solution, pyridine was dissolved in a large excess of chloroform and treated with bromine vapors. A red oil separated at first which rapidly went into solution. As the solution became saturated with the bromine, fine dark red needle-like crystals separated out. These were carefully and rapidly dried and analyzed. Melting-point  $58.5^\circ C.$

	Calculated for $C_5H_5N.Br_4$ .	Calculated for $C_5H_5N.HBr.Br_3$ .	I. Found.	II.
Titrated bromine..	80.16	59.97	{ 80.23	79.31
			{ 80.15	
Total " ..	80.16	79.96	{ 79.30	....
			{ 79.91	

The tetrabromide is unstable and loses bromine upon exposure, becoming lighter in color. After several days it ceases to lose bromine and becomes light yellow with a melting-point of  $94^\circ-95^\circ C.$  Titration gives 66.71 per cent. of bromine; theory for  $C_5H_5N.Br_2$  gives 66.89 per cent. of bromine.

#### BROMIDES OF PYRIDINE.

*Pyridine Hydrobromide*,  $C_5H_5N.HBr$ .—Colorless transparent

<sup>1</sup> *Ber. d. chem. Ges.*, 1879, 988.

<sup>2</sup> *Compt. rend.*, 95, 85.

feathery scales, slightly deliquescent, soluble in alcohol, chloroform, and water, insoluble in ether, melts at 200° C. with decomposition. Made by neutralizing pure pyridine with hydrobromic acid and evaporating gently to crystallization.

	Calculated for C <sub>5</sub> H <sub>5</sub> N.HBr.	Found.
Bromine .....	49.93	{ 49.17 49.93

*Pyridine Methyl Bromide*, C<sub>5</sub>H<sub>5</sub>N.CH<sub>3</sub>Br,  $\frac{1}{2}$ H<sub>2</sub>O.—Forms large translucent crystals from alcoholic solution, soluble in water, alcohol, and chloroform, insoluble in ether. Melts with slight decomposition at 135.5° C. Made by passing methyl bromide gas through pure pyridine cooled in salt and ice. The fine, white crystals were washed with ether and crystallized from alcohol.

	Calculated for C <sub>5</sub> H <sub>5</sub> N.CH <sub>3</sub> Br, $\frac{1}{2}$ H <sub>2</sub> O.	Calculated for C <sub>5</sub> H <sub>5</sub> N.CH <sub>3</sub> Br.	Found.
Bromine .....	43.88	45.33	{ 44.23 43.72

We have not yet succeeded in preparing a sample that gives sufficient bromine for the pure bromide without some water of crystallization.

*Pyridine Ethyl Bromide*, C<sub>5</sub>H<sub>5</sub>N.C<sub>2</sub>H<sub>5</sub>Br.—White crystals melting at 111°–112° C., soluble in alcohol and water, insoluble in ether. Made by adding ethyl bromide to pure pyridine. At ordinary temperature the action is very slow and almost no heat is generated. When the mixture is warmed a violent action takes place with the generation of heat. An excess of ethyl bromide should be used and the flask provided with a reflux condenser. After the reaction has ceased (one-half hour) the ethyl bromide may be distilled off before crystallization from alcohol.

	Calculated for C <sub>5</sub> H <sub>5</sub> N.C <sub>2</sub> H <sub>5</sub> Br.	Found.
Bromine .....	42.49	{ 41.82 41.88

ACTION OF IODINE UPON BROMIDES OF PYRIDINE.

*Pyridine Hydriodide Periodide*, C<sub>5</sub>H<sub>5</sub>N.HI.I.<sup>1</sup>—Iodine in alcoholic or potassium iodide solution displaces bromine in pyridine hydrobromide. The particular periodide formed depends upon temperature of experiment and amount of iodine used. When

<sup>1</sup> This Journal, 19, 327.

the crystals obtained are well washed with ether and recrystallized from alcohol, they are found to be entirely free from bromine. In this manner  $C_5H_5N.HI.I$  was obtained and also higher periodides, which were only tested to prove the absence of bromine.

*Pyridine Methyl Iodide Tetriodide*,  $C_5H_5N.CH_3I.I_4$ .<sup>1</sup>—To an aqueous solution of pyridine methyl bromide a potassium iodide solution of iodine was added. Bronze-green crystals were formed at once. These, upon purification, showed entire absence of bromine and on analysis gave good figures for  $C_5H_5N.CH_3I.I_4$ . The same results were obtained using an alcoholic solution of iodine.

*Pyridine Ethyl Iodide Periodide*,  $C_5H_5N.C_2H_5I.I_3$ .—On treatment of pyridine ethyl bromide with alcoholic or with potassium iodide solution of iodine, an oil was obtained entirely free from bromine. This body could not be obtained in a crystalline condition. Analysis gives figures too high for the triiodide,  $C_5H_5N.C_2H_5I.I_3$ ,<sup>2</sup> which melts at  $51^\circ C$ . This is probably the pentiodide,  $C_5H_5N.C_2H_5I.I_5$ , not entirely pure.

#### ACTION OF BROMINE UPON BROMIDES OF PYRIDINE.

*Pyridine Hydrobromide Perbromide*,  $(C_5H_5N.HBr)_2Br_8$ , or  $C_5H_5N.HBr.Br.C_5H_5N.HBr.Br_2$ .—Very stable, dark orange-colored prismatic crystals. Melting-point  $125^\circ C$ . Made by aspirating bromine through a water solution of pyridine hydrobromide until the orange crystals which first formed were dissolved in the excess of bromine. The oil was separated and became a crystalline solid upon exposure for the evaporation of the excess of bromine. This solid was heated on the water-bath for some time and then crystallized from alcohol.

	Theory for $(C_5H_5N.HBr)_2Br_8$ .	Theory for $C_5H_5N.HBr.Br.C_5H_5N.HBr.Br_2$ .	Theory for $C_5H_5N.HBr.Br_2$ .	Found.
Titrated bromine.	42.82	33.30	51.58	41.95
Total	71.37	66.61	74.95	70.86

It is very probable that this is the same body reported by Grimaux<sup>3</sup> and referred to in this paper under "Action of Bromine upon Pyridine." However, he reports his product unstable, melting at  $126^\circ C$ . The body we obtain is perfectly stable, does

<sup>1</sup> This Journal, 19, 324.

<sup>2</sup> This Journal, 19, 329.

<sup>3</sup> *Compt. rend.*, 95, 85.

not give off bromine when heated on the water-bath and melts at 125° C. Grimaux assigns the formula  $(C_5H_5NBr_2)_2HBr$ , which differs from our formula in total amounts of the elements by one hydrogen atom, but differs widely in the structural relation. The total bromine and the combustion would give the same results for both formulas. Total bromine for Grimaux 71.50 per cent. According to his formula four atoms of the bromine are *per* halogen and should react with sodium thiosulphate, giving 57.38 per cent. of titrated bromine. Our formula calls for 42.85 per cent. of titrated bromine, which is confirmed by the analysis. This body is then a mixture of one molecule each of the mono- and dibromide of pyridine hydrobromide, and not the monohydrobromide of two molecules of pyridine dibromide.

By checking the bromination of the pyridine hydrobromide at the formation of the first crystals a lighter orange-colored body is obtained, which crystallizes nicely from alcohol and is perfectly stable. Melting-point 93° C.

	Calculated for $C_5H_5N.HBr.Br.$	Found.
Titrated bromine .....	33.30	32.66

*Pyridine Methyl Bromide Dibromide*,  $C_5H_5N.CH_3Br.Br_2$ .—A dark orange-red crystalline body. Melting-point 66° C. Soluble in alcohol and acetic ether, insoluble in carbon bisulphide, chloroform, water, and ether. It is decomposed by acetone. Made by aspirating bromine through a water solution of pyridine methyl bromide. The excess of bromine was driven off on the water-bath and the crystalline mass further purified by recrystallization from alcohol.

	Calculated for $C_5H_5N.CH_3Br.Br_2$ .	I.	Found. II.
Titrated bromine.....	47.87	48.03	48.08
Total           " .....	71.80	71.74	71.60

Ostermayer<sup>1</sup> treats pyridine methyl chloride with bromine and obtains a body melting at 48° C., which loses bromine in the air. He assigns the formula  $C_5H_5N.CH_3Br.Br_2$ , but reports no analysis.

*Pyridine Ethyl Bromide Dibromide*,  $C_5H_5N.C_2H_5Br.Br_2$ .—The same in appearance and properties as the methyl compound just

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 599.



described, and made in the same manner. Melting-point  $35^{\circ}$  C.

	Calculated for $C_5H_5N.C_2H_5Br.Br_2$ .	Found.	
		I.	II.
Titrated bromine.....	45.94	45.55	45.35
Total " .....	68.91	68.90	68.40

#### ACTION OF CHLORINE UPON THE BROMIDES OF PYRIDINE.

*Pyridine Hydrobromide Perchloride* (?).—When chlorine is passed into a water solution of pyridine hydrobromide, some bromine is evolved and a reddish-yellow crystalline precipitate is formed. This precipitate becomes a yellow oil upon complete saturation with chlorine. Upon exposure or warming on the bath this becomes solid. Qualitative tests show an abundance of bromine and chlorine. The yellow crystals assume a reddish tinge when washed with water; this disappears if the crystals are then washed with ether. The compound is not stable; chlorine is evolved on standing, and possibly some bromine, although the bromine odor was not observed. This preparation was made several times, giving to all appearances exactly the same body, and having approximately the same melting-point,  $51^{\circ}$  C. Analysis, however, shows widely different results. It seems quite probable that  $C_5H_5N.HCl.BrCl$  is formed, but in all cases impure, owing to the volatilization of some of the bromine as soon as it is set free by the chlorine and before it can enter into combination with more chlorine. Samples IV and V were given an extra long treatment with chlorine.

	Calculated for $C_5H_5N.HBr.Cl$ .	Calculated for $C_5H_5N.HCl.BrCl$ .	Found.				
			I.	II.	III.	IV.	V.
Titrated halogen	18.17	30.68	25.59	15.63	13.48	16.95	16.85
			25.28	14.72	13.30	16.75	16.62
			24.16	14.79	13.62	.....	.....
			25.12	.....	15.22	.....	.....
			23.60	.....	11.90	.....	.....
Total	59.01	65.29	23.29	.....	.....	.....	.....
			57.30	.....	53.04	65.02	63.69
			57.46	.....	54.89	65.82	62.41

*Pyridine Methyl Bromide Dichloride*,  $C_5H_5N.CH_3Br.Cl_2$ , or  $C_5H_5N.CH_3Cl.BrCl$ .—When pyridine methyl bromide in water solution is treated with chlorine some bromine escapes and a light yellow precipitate forms, becoming a red oil upon complete saturation with chlorine. This body is not stable, but upon standing or gently warming loses most of its halogen odor and becomes solid at about  $19^{\circ}$  C.

	Calculated for	Calculated for	Found.	
	$C_5H_5N.C_2H_5Br.Cl_2$ .	$C_5H_5N.C_2H_5Br.Cl$ .	I.	II.
Titrated halogen..	29.00	16.90	{ 27.96	27.94
			{ 27.86	27.85
Total " ..	61.56	55.06	61.00	61.12

*Pyridine Ethyl Bromide Dichloride*,  $C_5H_5N.C_2H_5Br.Cl_2$ , or  $C_5H_5N.C_2H_5Cl.BrCl$ .—A pale yellow precipitate is first formed, when chlorine is passed into a water solution of pyridine ethyl bromide. Some bromine escapes. This precipitate becomes a red oil upon complete saturation with chlorine. This oil could not be purified so as to obtain a crystalline body. The oil was gently warmed for some time and analyzed.

	Calculated for	Calculated for	Found.	
	$C_5H_5N.C_2H_5Br.Cl_2$ .	$C_5H_5N.C_2H_5Br.Cl$ .	I.	II.
Titrated halogen..	27.43	15.84	{ 27.19	27.77
			{ 26.13	27.81
Total " ..	57.49	51.60	55.15	55.75

#### ACTION OF CHLORINE UPON PYRIDINE.

Anderson<sup>1</sup> treats pyridine with chlorine and gets pyridine hydrochloride and a white product having the hypochlorite odor. No analysis reported.

Kaiser<sup>2</sup> treats pure pyridine with dry chlorine and obtains ultimately a hydrochloride of dichlorpyridine,  $C_5H_5Cl_2N.HCl$ , a substituted body and pyridine chloride,  $C_5H_5N.Cl$ , an addition body. He also treats pyridine dissolved in water with chlorine gas and obtains an addition-product having a chloride of lime odor. He concludes that this is pyridine hypochlorite,  $C_5H_5N.HOCl$ . Upon passing more chlorine into this product pyridine is decomposed with evolution of carbon dioxide, nitrogen, etc. When he treats pyridine and potassium hydroxide with chlorine, chloroform, dichloroacetic acid, carbon dioxide, and nitrogen are formed.

We treated a chloroform solution of pyridine with dry chlorine to complete saturation. A few oily drops formed at the first which almost immediately went into solution, and no further change was noticed during the long-continued chlorination. The solution was then gently evaporated to expel the excess of chlorine and the chloroform. A brownish colored oil was left behind which did not solidify upon standing. On addition of a

<sup>1</sup> *Ann. Chem.* (Liebig), 105, 340.

<sup>2</sup> *Am. Chem. J.*, 8, 312.

few drops of water the oil becomes a white flocculent powder, which does not dissolve in great excess of water. This oil has an odor somewhat like chloride of lime. When a crystal of potassium iodide is added to the oil no iodine is set free, nor when to this water and hydrochloric acid are added. Iodine is not set free when potassium iodide is added to the oil after the addition of water. This seems to be conclusive proof that the body is not a hypochlorite or a perchloride of pyridine. We hope later to investigate this body more fully.

#### CHLORIDES OF PYRIDINE.

*Pyridine Hydrochloride*,  $C_5H_5N.HCl$ .—Transparent, colorless crystals, soluble in alcohol, chloroform, hydrochloric acid, and water; insoluble in ether, and is thrown down from its alcoholic solution by the addition of ether. It crystallizes in scales from a solution in absolute alcohol. It cannot be crystallized from its water solution. It is made by adding concentrated hydrochloric acid in excess to pure pyridine. The solution is heated on the bath and then cooled over sulphuric acid. The salt separates out as a mass of thin scales, which are purified by recrystallization from absolute alcohol. Melting-point  $82^\circ C$ .<sup>1</sup>

	Calculated for $C_5H_5N.HCl$ .	Found.
Chlorine.....	30.73	{ 30.23 30.28

*Pyridine Methyl Chloride*,  $C_5H_5N.CH_3Cl$ .—Ostermayer<sup>2</sup> has reported the formation of this salt by heating pyridine, hydrochloric acid, and methyl alcohol to  $230^\circ C$ . for ten hours. He fails to obtain stable crystals but proves the purity of his syrupy solution by the formation and analysis of the gold and platinum double salts.

Lange<sup>3</sup> makes the pyridine methyl chloride by shaking the iodide with moist silver chloride. We tried to obtain the chloride in crystalline form by saturating pure pyridine with methyl chloride; failing in this we adopted the method of Lange. This

<sup>1</sup> The sample from which the melting-point was obtained was made by passing dry hydrochloric acid gas into dry pyridine cooled in ice. This was well washed with ether, and melting-point taken. This preparation distills with some decomposition. A strong odor of pyridine is observed. Voluminous white vapors are formed, which condense on the sides of the flask and thermometer, and solidify when cooled to  $118^\circ C$ .

<sup>2</sup> *Ber. d. chem. Ges.*, 18, 591.

<sup>3</sup> *Ibid*, 1885, 3438.

same method was used in the preparation of pyridine ethyl chloride. Whenever the pyridine methyl or ethyl chloride was desired the corresponding iodide was shaken with an excess of freshly precipitated silver chloride, till a portion of the clear liquid gave no test for iodine. The chloride was always used in solution. All attempts to obtain the crystalline body failed.

ACTION OF IODINE UPON CHLORIDES OF PYRIDINE.

*Pyridine Hydriodide Hexiodide*,  $C_5H_5N.HI.I_6$ .<sup>1</sup>—When an alcoholic solution of iodine is added to pyridine hydrochloride, the latter being in excess, a dark crystalline body is obtained which, when crystallized from alcohol, gives tests for chlorine. When an excess of alcoholic solution of iodine is added to pyridine hydrochloride the heptiodide,  $C_5H_5N.HI.I_7$ , fairly pure, is obtained perfectly free from chlorine after a second crystallization from alcohol. Melting-point  $71^\circ-72^\circ$  C.

*Pyridine Methyl Iodide Tetriodide*,<sup>2</sup>  $C_5H_5N.CH_3.I.I_4$ .—When an excess of alcoholic solution of iodine is added to pyridine methyl chloride, a dark green oil is at once formed. This is carefully separated and dissolved in alcohol. From this solution, after a second treatment with alcohol, fine needle-like crystals are obtained free from chlorine. Analysis shows these crystals to be the pentiodide.

*Pyridine Ethyl Iodide Periodide*,  $C_5H_5N.C_2H_5.I.I_9$ .—When an alcoholic solution of iodine, in excess, is added to pyridine ethyl chloride, a dark green oil is formed. This is carefully separated and dissolved in alcohol and is again obtained as an oil which does not contain chlorine. All attempts to obtain a crystalline body failed, and analysis of the oil showed it to be an impure periodide, but containing more iodine than required for  $C_5H_5N.C_2H_5.I.I_9$ , which melts at  $51^\circ$  C.<sup>3</sup>

ACTION OF BROMINE UPON CHLORIDES OF PYRIDINE.

*Pyridine Hydrobromide Dibromide*,  $C_5H_5N.HBr.Br_2, 2H_2O$ .—Pure pyridine was treated with an excess of dilute hydrochloric acid and then saturated with bromine. A bromine-colored oil is formed, which becomes solid upon exposure and loses its bro-

<sup>1</sup> This Journal, 19, 328.

<sup>2</sup> This Journal, 17, 859.

<sup>3</sup> This Journal, 19, 329.

mine odor upon warming. The crude product melts at  $94^{\circ}\text{C}$ ., and that crystallized from alcohol at  $118^{\circ}\text{--}120^{\circ}\text{C}$ . The crystals are orange-yellow. In sample I, the crude product was well washed with chloroform but not crystallized, II is the crude product, III is the crude product washed with chloroform and then crystallized from alcohol. I and II do not contain even a trace of chlorine. When dissolved in absolute alcohol and placed in a freezing mixture, the crystals form as prismatic bars very sharply defined.

	Calculated for $\text{C}_5\text{H}_5\text{N.HBr.Br}_2.2\text{H}_2\text{O}$ .	Calculated for $\text{C}_5\text{H}_5\text{N.HBr.Br}$ .	I.	Found. II.	III.
Titrated bromine..	44.59	33.30	{ 44.33	43.74	44.24
			{ 44.08	43.20	44.23
Total	67.36	66.61	{ 67.55	66.38	67.96
			{ 66.51	66.01	...

*Pyridine Hydrobromide Perbromide*,  $\text{C}_5\text{H}_5\text{N.HBr.Br}$ .—Pure pyridine hydrochloride was dissolved in chloroform and brominated. Stellate masses of flat golden needles were obtained. These were dried and crystallized from alcohol. Free from chlorine. Melting-point  $88^{\circ}\text{C}$ .

	Calculated for $\text{C}_5\text{H}_5\text{N.HBr.Br}$ .	Found.
Titrated bromine .....	33.30	{ 33.18
		{ 33.39
Total	66.61	{ 66.66
		{ 66.82

*Pyridine Methyl Bromide Perbromide*,  $\text{C}_5\text{H}_5\text{N.CH}_3\text{Br.Br}$ .—Ostermayer<sup>1</sup> treats pyridine methyl chloride with bromine and obtains  $\text{C}_5\text{H}_5\text{N.CH}_3\text{Br.Br}_2$ , melting-point  $48^{\circ}\text{C}$ . Loses bromine in the air. Great difficulty was experienced in confirming Ostermayer's work. In one experiment a yellow compound was obtained free from chlorine, melting at  $82^{\circ}\text{--}83^{\circ}\text{C}$ ., which gave fairly good results for  $\text{C}_5\text{H}_5\text{N.CH}_3\text{Br.Br}$ .

	Calculated for $\text{C}_5\text{H}_5\text{N.CH}_3\text{Br.Br}$ .	Found.
Titrated bromine .....	31.46	32.09
Total	62.93	64.41

*Pyridine Methyl Bromide Dibromide*,  $\text{C}_5\text{H}_5\text{N.CH}_3\text{Br.Br}_2$ .—Most of the experiments gave results indicating a compound between the dibromide and the tribromide. Finally, after several hours bromination, a product was obtained which crystallized from

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 599.

absolute alcohol in orange-colored needles and was entirely free from chlorine. Melting-point  $55^{\circ}$  C., not  $48^{\circ}$  C. as reported by Ostermayer. We brominated  $C_5H_5N.CH_2Br$  and get  $C_5H_5N.CH_2Br.Br_2$ . Melting-point  $66^{\circ}$  C.

	Calculated for $C_5H_5N.C_2H_5Br.Br_2$ .	Found.
Titrated bromine .....	47.87	{ 46.29
		{ 46.47
Total " .....	71.80	{ 71.59
		{ 70.97

*Pyridine Ethyl Bromide Dibromide*,  $C_5H_5N.C_2H_5Br.Br_2, 2H_2O$ .—Bromine vapors were passed through a water solution of pyridine ethyl chloride. A dark red oil was obtained which was warmed on the water-bath to remove excess of bromine. This oil would not solidify in a freezing mixture until a small piece of ice was added, when it became a mass of thin, reddish brown laminae, melting at  $15^{\circ}$  C., and solidifying at once when cooled below that temperature. This body was dissolved in absolute alcohol, using very gentle heat. It is decomposed by hot alcohol. Again, upon cooling, crystals could not be obtained until a small piece of ice was added, when it solidified as before. Melting-point  $15^{\circ}$  C. A qualitative test shows entire absence of chlorine.

	Calculated for $C_5H_5N.C_2H_5Br.Br_2, 2H_2O$ .	Found.
Titrated bromine .....	41.62	41.65
Total " .....	62.44	62.61

#### ACTION OF CHLORINE UPON CHLORIDES OF PYRIDINE.

The effect of chlorine was studied upon the hydrochloride, methyl chloride, and ethyl chloride of pyridine in water solution. No perchloride is formed, for upon heating on the water-bath to remove the excess of chlorine the solutions do not liberate iodine from a potassium iodide solution.

*Molecular Weight Determinations.*—The cryoscopic method was used with a number of the above-described mixed perhalides, using phenol as a solvent. In most cases the results were not close but all plainly indicated the monopyridine molecule as the probable structure.

#### SUMMARY.

The range of formation with the periodides is great,  $C_5H_5N$ .

HI.I to  $C_5H_5N.HI.I_3$ , with the perbromides slight, and zero with the perchlorides. With the normal perhalides, increase in halogen lowers the melting-point. With the normal halide the hydrogen halide melts highest, the methyl halide lower, and the ethyl halide lowest.

In the mixed perhalides the power of displacement and the position of the halogen atoms in the molecule are points of great interest. Iodine in excess displaces bromine and chlorine completely, forming periodides from the normal bromides and chlorides. Bromine seems to displace iodine from the pyridine normal iodides and then combines with it to form a bromoiodide of a normal bromide. Bromine displaces chlorine completely, forming perbromides from the normal chlorides. Chlorine seems to displace both iodine and bromine at first to form normal chlorides, then it combines with the displaced halogen (some of the bromine always escapes) to form mixed perhalides,  $ICl$ ,  $ICl_3$ ,  $BrCl$ ,  $BrCl_3$ , of the normal chlorides, *e. g.*,  $C_5H_5N.HCl.ICl_3$  from  $C_5H_5N.HI$  and  $Cl_2$ . The mixed perhalides containing bromine and iodine show color reaction for iodine when treated with carbon bisulphide, indicating that the iodine is probably present as *periodine*. Also the mixed perhalides containing bromine and chlorine show color tests for bromine, indicating that the bromine is *perbromine*. When an alcoholic solution of the perhalide containing bromine and iodine is titrated with sodium thio-sulphate, evaporated to dryness, and the organic body thoroughly extracted; both bromine and iodine are found in the residue of sodium salts. In the following summary, unless references are given, the description of the preparations and needed references are found in the body of this paper :

1. *Action of Iodine upon Pyridine.*<sup>1</sup>  
 $C_5H_5N.I_4$ . Greenish black. Melting-point  $85^\circ C$ .
2. *Action of Bromine upon Pyridine.*  
 $C_5H_5N.Br_2$ . (?) Hofmann.  
 $(C_5H_5N.Br_7)_2HBr$ . (?) Grimaux.  
 $C_5H_5N.Br_4$ . Dark red. Melting-point  $58.5^\circ C$ .  
 $C_5H_5N.Br_2$ . Light yellow. Melting-point  $94^\circ-95^\circ C$ .
3. *Action of Chlorine upon Pyridine.*  
 $C_5H_5N.HCl$ . Anderson.  
 $C_5H_5Cl_2N.HCl$ . Kaiser.

<sup>1</sup> This Journal, 17, 865.

- $C_5H_5N.Cl.$  (?) Kaiser.  
 $C_5H_5N.HOCl.$  (?) Kaiser.
4. *Iodides of Pyridine.*  
 $C_5H_5N.HI.$  Colorless. Melting-point  $268^\circ C.$ <sup>1</sup>  
 $C_5H_5N.CH_3I.$  Colorless. Melting-point  $117^\circ C.$ <sup>2</sup>  
 $C_5H_5N.C_2H_5I.$  Colorless. Melting-point  $90.5^\circ C.$ <sup>3</sup>  
 $C_5H_5N.C_3H_7I.$  Baer. Colorless. Melting-point  $52^\circ-53^\circ C.$ <sup>4</sup>  
 $C_5H_5N.C_3H_7I(iso).$  Baer. Colorless. Melting-point  $114^\circ-115^\circ C.$ <sup>5</sup>
5. *Bromides of Pyridine.*  
 $C_5H_5N.HBr.$  Colorless. Melting-point  $200^\circ C.$   
 $C_5H_5N.CH_3Br, \frac{1}{2}H_2O.$  Colorless. Melting-point  $135.5^\circ C.$   
 $C_5H_5N.C_2H_5Br.$  Colorless. Melting-point  $111^\circ-112^\circ C.$
6. *Chlorides of Pyridine.*  
 $C_5H_5N.HCl.$  Colorless. Melting-point  $82^\circ C.$   
 $C_5H_5N.CH_3Cl.$  Ostermayer, Lange. Not obtained in crystals.  
 $C_5H_5N.C_2H_5Cl.$  Not obtained in crystals.
7. *Action of Iodine upon the Iodides of Pyridine.*  
 $C_5H_5N.HI.I.$  Dark brown. Melting-point  $188^\circ-192^\circ C.$ <sup>6</sup>  
 $C_5H_5N.HI.I_2.$  Has not been prepared.  
 $C_5H_5N.HI.I_3.$  This and the  $I.I_3$  probably do not exist.  
 $C_5H_5N.HI.I_4.$  Brownish black. Melting-point  $78^\circ-85^\circ C.$ <sup>7</sup>  
 $C_5H_5N.HI.I_5.$  Lustrous green scales. Melting-point  $63^\circ-64^\circ C.$ <sup>8</sup>  
 $C_5H_5N.CH_3I.I.$  Reddish brown. Melting-point  $91.5^\circ C.$ <sup>9</sup>  
 $C_5H_5N.CH_3I.I_2.$  Dark red. Melting-point  $50^\circ C.$ <sup>10</sup>  
 $C_5H_5N.CH_3I.I_3.$  This and the  $I.I_3$  probably do not exist.  
 $C_5H_5N.CH_3I.I_4.$  Greenish black. Melting-point  $47.5^\circ C.$ <sup>11</sup>  
 $C_5H_5N.CH_3I.I_5.$  Green. Melting-point  $26^\circ C.$ <sup>12</sup>  
 $C_5H_5N.C_2H_5I.I.$  Has not been prepared.  
 $C_5H_5N.C_2H_5I.I_2.$  Bluish black. Melting-point  $51^\circ C.$ <sup>13</sup>  
 $C_5H_5N.C_2H_5I.I_4.$  (?) Black. Melting-point  $83^\circ C.$ <sup>14</sup>  
 $C_5H_5N.C_2H_5I.I_5.$  Has not been made.
8. *Action of Bromine upon the Iodides of Pyridine.*  
 $C_5H_5N.HBr.IBr.$  Reddish brown. Melting-point  $172^\circ-175^\circ C.$   
 $C_5H_5N.CH_3Br.IBr.$  Orange yellow. Melting-point  $61^\circ-62^\circ C.$   
 $C_5H_5N.C_2H_5Br.IBr.$  Orange yellow. Melting-point  $25^\circ-26^\circ C.$
9. *Action of Chlorine upon the Iodides of Pyridine.*  
 $C_5H_5N.HCl.ICl.$  Melting-point  $180^\circ C.$  Pictet and Kraft, Dittmar.  
 $C_5H_5N.ICl.$  White needles. Melting-point  $132^\circ C.$  Pictet and Kraft.

<sup>1</sup> This Journal, 19, 327.<sup>2</sup> This Journal, 18, 92.<sup>3</sup> This Journal, 18, 93.<sup>4</sup> This Journal, 17, 867, and 19, 328.<sup>5</sup> This Journal, 17, 860.<sup>6</sup> This Journal, 19, 322.<sup>7</sup> This Journal, 19, 329.<sup>8</sup> This Journal, 18, 91.<sup>9</sup> This Journal, 18, 92.<sup>10</sup> This Journal, 19, 327.<sup>11</sup> This Journal, 19, 328.<sup>12</sup> This Journal, 17, 860.<sup>13</sup> This Journal, 19, 323.<sup>14</sup> This Journal, 19, 32.



- $C_5H_5N.HCl.ICl_3$ . Dittmar.  
 $C_5H_5N.HCl.ICl$ ,  $C_5H_5N.HCl.ICl_3$ . Lemon yellow. Melting-point  $176^\circ C$ .  
 $C_5H_5N.CH_3Cl.ICl_3$ . Canary yellow. Melting-point  $185^\circ C$ .  
 $C_5H_5N.CH_3Cl.ICl_3$ . Yellow. Bally. Melting-point  $179^\circ-180^\circ C$ .  
 $C_5H_5N.CH_3Cl.ICl$ . Bally. Melting-point  $90^\circ C$ .  
 $C_5H_5N.CH_3Cl.ICl$ . Ostermayer. Melting-point  $81^\circ-82^\circ C$ .  
 $C_5H_5N.C_2H_5Cl.ICl_3$ . Canary yellow. Melting-point  $123^\circ C$ .
10. *Action of Iodine upon the Bromides of Pyridine.*  
 $C_5H_5N.HI.I$ , and higher periodides.  
 $C_5H_5N.CH_3I.I_4$ .  
 $C_5H_5N.C_2H_5I.I_2$ .
11. *Action of Bromine upon the Bromides of Pyridine.*  
 $C_5H_5N.HBr.Br$ ,  $C_5H_5N.HBr.Br_2$ . Dark orange. Melting-point  $125^\circ C$ .  
 $(C_5H_5N.Br_2)_2HBr$ . (?) Grimaux. Melting-point  $126^\circ C$ .  
 $C_5H_5N.HBr.Br$ . Light orange. Melting-point  $93^\circ C$ .  
 $C_5H_5N.CH_3Br.Br_2$ . Dark orange-red. Melting-point  $66^\circ C$ .  
 $C_5H_5N.CH_3Br.Br_2$ . Ostermayer. Melting-point  $48^\circ C$ .  
 $C_5H_5N.C_2H_5Br.Br_2$ . Dark orange-red. Melting-point  $35^\circ C$ .
12. *Action of Chlorine upon the Bromides of Pyridine.*  
 $C_5H_5N.HCl.BrCl$ . (?) Yellow. Melting-point  $51^\circ C$ .  
 $C_5H_5N.C_2H_5Cl.BrCl$ . Yellow. Melting-point  $19^\circ C$ .  
 $C_5H_5N.C_2H_5Cl.BrCl$ . Red oil.
13. *Action of Iodine upon the Chlorides of Pyridine.*  
 $C_5H_5N.HI.I_6$ .  
 $C_5H_5N.CH_3I.I_4$ .  
 $C_5H_5N.C_2H_5I.I_2$ .
14. *Action of Bromine upon the Chlorides of Pyridine.*  
 $C_5H_5N.HBr.Br_2, 2H_2O$ . Orange-yellow. Melting-point  $118^\circ-120^\circ C$ .  
 $C_5H_5N.HBr.Br$ . Golden yellow. Melting-point  $88^\circ C$ .  
 $C_2H_5N.CH_3Br.Br$ . Ostermayer. Melting-point  $48^\circ C$ .  
 $C_5H_5N.CH_3Br.Br$ . Yellow. Melting-point  $82^\circ-83^\circ C$ .  
 $C_5H_5N.CH_3Br.Br_2$ . Orange. Melting-point  $55^\circ C$ .  
 $C_5H_5N.C_2H_5Br.Br_2, 2H_2O$ . Reddish brown. Melting-point  $15^\circ C$ .
15. *Action of Chlorine upon the Chlorides of Pyridine.*  
 No perchlorides formed. (See body of paper.)

We wish to express our thanks to Professor A. B. Prescott, in whose laboratory and under whose general supervision the work has progressed. A paper on "Perhalides of Quinoline" is nearly ready, and work is continued upon "Halogen Derivatives of the Alkaloids with a View to Methods of Analysis."