

NOTES ON A FEW PYRIDINE ALKYL IODIDES.¹

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PYRIDINE METHYL IODIDE.²

Preparation.—Of rectified pyridine, boiling at 116°–118° C., fifteen cc. are taken in a flask immersed in cold water and carrying a reflux condenser, and twelve cc. methyl iodide added, in very small portions at first, when the reaction is violent. Boiling is moderated by the rate of the addition. After standing half an hour, the resulting crystalline mass, light straw colored, is warmed on the water-bath without the condenser, and more methyl iodide very gradually added until, as a result, the odor of pyridine disappears. Any excess of methyl iodide is distilled off on the water-bath. The mass is now dissolved in sufficient warm absolute alcohol, from which it crystallizes on cooling, and the product recrystallized in the same way several times, until colorless crystals are obtained. Colorless crystals are sometimes obtained in the second crystallization. From alcohol of ninety to ninety-five per cent. strength the crystallization is much less satisfactory. The mother liquids, on the addition of ether, yield a considerable precipitate of the product, and this can be crystallized from absolute alcohol.

Properties.—The crystals are flat pencils, sometimes aggregated in rosettes. They are very soluble in water, soluble in alcohol, methyl alcohol, chloroform, acetone, and in glacial acetic acid; not soluble in ether, or benzene, or carbon disulphide. The crystals are very slowly deliquescent, to a degree scarcely affecting weight after several hours exposure to the air. The melting point is 117° C.

¹ Read at the Springfield meeting of the American Association for the Advancement of Science, Aug. 30, 1895.

² From the experimental work of Mr. P. F. Trowbridge. Anderson stated the additive reaction of pyridine with alkyl iodides in 1855. In making such an addition-product, as a means of distinguishing pyridine from its homologues in analysis, he took ethyl iodide, *Ann. Chem.* (Liebig), 94, 364. Hofmann resorted to pyridine in his study of the reaction of dihalogen substituted hydrocarbons with tertiary bases, but not earlier, that I have been able to find.—1861: *Proc. Roy. Soc.*, 11, 261. O. Lange, in 1885, in the course of work on the formation of picolines by Ladenburg's method of transposition, gives some account of pyridine methiodide.—*Ber. d. chem. Ges.*, 18, 3436. O. de Coninck, in 1883, proposed the additive reactions with methyl iodide in contrast with those of ethyl iodide for distinction between pyridine derivatives and quinoline derivatives.—*Bull. Soc. Chim.* [2], 40, 276.

PYRIDINE ETHYL IODIDE.¹

Preparation.—It has been directed to bring about the addition of ethyl iodide to pyridine by heating the mixture of the two in sealed tubes. Trial was made of three ways, (1) by heating in sealed tubes at 120° C.; (2) by heating in pressure flasks at 100° C.; (3) by occasionally shaking in a flask at the temperature of the room. The last stated method gives much the best results. The ethyl iodide should be taken in a slight excess of the chemical proportion, and added all at once. With considerable quantities the heat of chemical action after a short time needs to be moderated by cooling, to prevent vaporization of the materials. The action is usually complete within two hours, the contents of the flask becoming solid. The crystalline mass is dissolved in enough warm absolute alcohol, and crystallized, more perfectly by the low temperature of a freezing mixture, recrystallizing until white. Addition of ether to the absolute alcoholic solution causes crystalline precipitation, and in this way the mother liquids may be made to yield final portions. Like addition of chloroform precipitates an oily mass.

Properties.—The crystals are colorless plates, permanent or slightly deliquescent, soluble in water, alcohol, methyl alcohol, acetone, and glacial acetic acid, from which it crystallizes, and slightly soluble in ethyl acetate; insoluble in ether, benzene, carbon disulphide, and in chloroform. The melting point is 90.5° C.

PYRIDINE PROPYL IODIDE,² C₅H₅N.CH₂CH₂CH₂I.

Preparation.—Pyridine rectified to boil at 116.5°–118.5°, and normal propyl iodide distilling at 102° C., are taken in molecular proportions of the two, but with a slight excess of the iodide. The two are digested together under pressure in a sealed tube at 130° C., for an hour. On cooling the resulting yellowish mass is dissolved in warm absolute alcohol, from which plate-form crystals of the addition product separate on cooling. If

¹ From the experimental work of P. F. Trowbridge in this laboratory. T. Anderson, 1855; *Trans. Roy. Soc. Edinb.*, 21, (4) 571; *Ann. Chem.* (Liebig), 94, 364. O. de Coninck, 1883; *Bull. Soc. Chim.* [2], 40, 276.

² From the experimental studies of Mr. S. H. Baer. In Ladenburg's account of the formation of propylpyridine hydriodide, by transposition of pyridine propyl iodide (*Ber. d. chem. Ges.*, 17, 772) no description of the last named body is given.

not white it is to be recrystallized from the same solvent. Addition of ether to the absolute alcohol solution throws it down in a crystalline precipitate. Like addition of chloroform separates it as an oil-like liquid. From alcohol of ninety-five per cent. it is precipitated as an oil by addition of ether. In analysis of the preparation, it gave for iodine 50.63 per cent. in comparison with 51.00 per cent. by calculation.

Properties.—In colorless plate-form crystals, deliquescent, soluble in water, alcohol, amyl alcohol, ethyl acetate, and in benzene; insoluble in ether and in chloroform. The melting-point is between 52° and 53° C.

PYRIDINE ISOPROPYL IODIDE,¹ $C_6H_5N.(CH_3)_2CHI$.

Preparation.—By the same method, and under the same conditions already given for the corresponding normal propyl compound, but using a greater excess of the alkyl iodide, namely about one and a half molecules of the isopropyl iodide (boiling at 89°–90° C.) to one molecule of pyridine. The product solidifies in a crystalline mass while in the sealed tube, more readily and completely than the product of normal propyl iodide and pyridine, and it crystallizes more readily from absolute alcohol. In analysis, the iodine found was 50.64 and 50.50 per cent. in comparison with 51.00 per cent by calculation.

Properties.—Colorless crystals, soluble in water, alcohol of ninety-five per cent., and in ethyl acetate; less freely soluble in absolute alcohol, amyl alcohol, or chloroform; insoluble in ether. The melting point is 114°–115° C.

COMPARISON OF MELTING POINTS.

As set forth below the addition compounds of the one base pyridine with different alkyl iodides, $C_nH_{2n+1}I$ show a gradation of melting points, a gradation which appears among the homologous normal members of the series, and again appears between isomeric members. The solubilities of these addition compounds show a correspondence to their melting points, agreeing with the generalization of Carnelly.² Pyridine

¹ From the work of Mr. S. H. Baer in this laboratory. Schrader (Inaug. Diss. at Kiel, 1884) obtained this quaternary iodide, by treatment at 100° C., as a yellow-white crystalline mass, convertible to the corresponding chloride (Ladenburg's *Handwörterbuch*, 9, 464. Ladenburg and Schrader, *Ber. d. chem. Ges.*, 17, 1121).

² *Phil. Mag.*, (5) 13, 180; *J. Chem. Soc.*, 53, 782.

combination has been resorted to for various characteristics distinctive of alcohol radicals, by de Coninck, as cited in the beginning of this paper, and by Lippert¹ in 1893. The iodides of these quaternary bases give constants more distinctive of composition than do the platinum chlorides, at least so far as melting points of the iodides are available. In tabulating the melting points of the pyridine alkyl iodides it appears that, comparing homologues and again comparing isomers, the melting points of the addition products *fall* as the boiling points of the free alkyl iodides *rise*.² The same reverse ratio appears among picoline alkyl iodides. On the contrary, comparing pyridine methyl iodide with picoline methyl iodide, the two tertiary bases being homologous and the alkyl iodide being the constant factor, it is found that the melting point of the addition compound rises as the boiling point of the tertiary base rises, and in an extreme proportion.

QUATERNARY BASE IODIDES.

With homologous alkyls :

	Melting points	Boiling points of the free alkyl iodides.
Pyridine methyl iodide.....	117° ³	45°
Pyridine ethyl iodide.....	90.5° ³	72°
Pyridine propyl iodide	52-53° ⁴	102°
(Pyridine butyl iodide decomposes before melting) ⁵		130°)
<i>α</i> -Picoline methyl iodide	226.5-227° ⁶	45°
<i>α</i> -Picoline ethyl iodide;.....under.....	100° ⁷	72°

With isomeric alkyls :

Pyridine isopropyl iodide.....	114-115° ⁴	89°
Pyridine propyl iodide	52-53° ⁴	102°

QUATERNARY BASE METALLIC CHLORIDES.

(Pyridine tertiary butyl salts are not formed) ⁵		100°
Pyridine isobutyl platinum chloride.....	220° ⁵	119°
“ “ gold chloride.....	139° ⁵	

¹ *Ann. Chem.* (Liebig), 276, 182.² This reverse ratio does not hold good between ethyl and isopropyl, in their pyridine iodo-products, the one being not the direct homologue, but the isomer of the homologue of the other. In 1882 Carnelly remarked of "isomeric compounds" as shown by many instances, that their melting points follow a rule the reverse of that accepted for their boiling points, namely that "those melt the highest in which there are the greatest number of side chains." (*Phil. Mag.* (5), 13, 126).³ Trowbridge. ⁴ Baer. ⁵ Lippert : *Ann. Chem.* (Liebig), 276, 182.⁶ Ramsay : *Phil. Mag.* (5), 4, 241. Before the constitution of picoline was established. It is not necessary here to distinguish between isomeric picolines.⁷ Anderson : *Ann. Chem.* (Liebig), 94, 361.

	Melting points.	Boiling points of the free alkyl iodides.	
Pyridine secondary butyl platinum chloride	191° ¹	119°	
“ “ gold chloride.....	129° ¹		
Pyridine normal butyl platinum chloride ..	205° ¹	130°	
“ “ “ gold chloride	111° ¹		
<i>With homologous tertiary bases :</i>		The free tertiary bases.	
Pyridine methyl iodide.....	117° ²	116°	
Picoline methyl iodide	226.5-227° ³	132-140°	
<i>Comparing two isomeric addition compounds :</i>		Ter.	Alk.
Pyridine ethyl iodide, C ₅ H ₅ N.C ₂ H ₅ I =		base.	iod.
C ₇ H ₁₀ NI	90.5° ²	116°	72°
Picoline methyl iodide, CH ₃ .C ₅ H ₄ N.CH ₃ I =			
C ₇ H ₁₀ NI.....	227° ³	132°	45°

In the comparison last above, there are two quaternary base iodides having the same empirical formula, and having near the same mean of boiling points of the uniting constituents, while the difference between their quoted melting points is something surprising. We should expect, however, from analogy with the previous comparisons, to find a double homologous difference in this case. The transfer of the homologous CH₃, so to speak, *from* the alkyl of one compound *to* the amine of the other compound, should exert a two-fold effect in raising the melting point.

In a paper by Mr. Flintermann⁴ and myself, some data are given in small part from our own work and more from the work of others, as to the limits of additive combination of isomeric alkyls with tertiary amines, especially with pyridine, in formation of quaternary bases. It would seem desirable to compare these apparent limits of additive formation with the generalizations of Carnelly and others upon the cohesion constants of isomers at large. Therewith these few facts of the melting points of pyridine quaternary bases are presented, though requir-

¹ Lippert: *Ann.Chem.* (Liebig), 276, 182.

² Trowbridge.

³ Ramsay: *Phil. Mag.* (5), 4, 241. Before the constitution of picoline was established. It is not necessary here to distinguish between isomeric picolines.

⁴ Dipyrindene trimethylene dibromide, etc., this Journal, 18, 28.

ing more data, with the re-examination of figures of early date, as a part of the study of the chemical character of the nitrogen bases. To the same end some work upon the hydroxides of these bases is nearly ready for presentation from this laboratory. And to the same end work is being continued upon the periodides,¹ and other super halides, that these extreme additive combinations may show something of the base making power of nitrogen.

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

AN ELECTROLYTIC METHOD FOR THE DETERMINATION OF MERCURY IN CINNABAR.

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WHEN a rapid solution of cinnabar is desired, heretofore, oxidation with aqua regia has seemed most convenient; the length of time required to expel the nitric acid used, and the likelihood of loss of mercury by distillation in hydrochloric acid, are serious hindrances to the use of this method. Hydrobromic acid dissolves very readily mercuric sulphide, as well as many other naturally occurring sulphides with the evolution of hydrogen sulphide and the formation of the bromide.

If this solution be nearly neutralized with caustic potash, pure potassium cyanide added in sufficient excess to dissolve the cyanide first precipitated (Smith, *Electro-Chemical Analysis*, p. 58), and electrolyzed with a weak current, the mercury will be readily deposited as metal on a platinum dish used as a negative electrode. The use of hydrobromic acid is to be recommended, as it gives such a ready method of decomposition, and can be used at low temperatures, when there will be no loss of mercury by distillation.

The hydrobromic acid used in the following experiments was prepared by treating potassium bromide with sulphuric acid of 56° Baumé; the gas was conducted into water, as in the preparation of hydrochloric acid. By using potassium bromide

¹ This Journal, 17, 775, 859.