DIPYRIDINE METHYLENE IODIDE AND THE NON-FORMATION OF THE CORRESPONDING MONOPYRIDINE PRODUCTS.[1]

BY S. H. BAER and A. B. PRESCOTT.

Received September 7, 1896.

THE addition compound of pyridine and methylene iodide was formed in different ways, varying the conditions of mass, temperature, pressure, and time, as follows. The method of preparation recommended is that of No. V.

Preparation I.—Pyridine and methylene iodode in equimolecular proportions, reacting at laboratory temperature, for two days, form a dark-red crystalline mass. This was washed in cold alcohol, which does not dissolve it.

Preparations II and III.—The same proportions (those of a monopyridine product) were taken in reaction at 120° C. The methyl iodide for I and II was colored with free iodine, that for III was obtained colorless by distillation in vacuum. In each case the crystals, washed with cold alcohol, were dark-red. This color was not affected by treating the crystals with thiosulphate solution, and therefore not due to free iodine or to periodides.

Preparation IV.—By reaction of colorless methylene iodide, in the same proportions, with the pyridine, but without heat, an orange precipitate settles slowly. This was washed as the others.

Preparation V.—Pyridine of boiling point 118° C., and methylene iodide either colorless or tinged with iodine, in about equal molecular quantities, are placed in a flask, alcohol in volume equal to the two reacting materials is added, a return-condenser adjusted, and the heat of a water-bath applied for an hour. On cooling, long yellow needles separate out. To purify further, dissolve in hot fifty per cent. alcohol, cool, and add a little ether, when fine crystals are formed.

So obtained, the product is in fine needles, of yellow color, decomposing, not melting, at 220° C.; soluble in water, from which it crystallizes at 0° C.; insoluble in cold alcohol, sparingly soluble in hot alcohol; insoluble in ether, or chloroform, or benzene, or amyl alcohol; sparingly soluble in methyl alcohol.

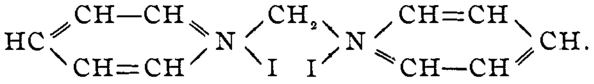
Analysis gave us percentages as follows:

	Calculated for	Found.				
	$(C_5H_5N)_2CH_2I_2$.	I.	II.	III.	IV.	V.
I	59.61	58.95	58.91	57.98	58.4	59.6
N........	6.57	....	....	....	...	6.72

---

[1] Read at the Buffalo meeting of the American Association for the Advancement of Science.

The product, therefore, not quite pure in the first four experimental preparations, is substantially the same under the different conditions employed, and with whatever excess of the diiodomethane, is always the dipyridine addition compound. And its formula, agreeing with those of its bromine homologues,[1] may be confidently written, to express the relations of the methylene group and the halogen atoms :



Kleine found[2] that trimethylamine, in combination with dihalogen substituted hydrocarbons, forms both the monammonium and the diammonium products, the former prevailing, especially when there are not more than two atoms of carbon in the halide.

It seemed now desirable to subject pyridine to various conditions of additive reaction with various dihalides, in order to know whether it can in any case form such monamine compounds as the fatty amines sometimes form.[3] Pyridine and ethylene bromide, in equal molecular proportions, were digested together in a sealed tube for two weeks, when the entire content, a crystalline mass, was dissolved in hot alcohol of ninety-five per cent., and fractionally crystallized in successive crops, washing each with cold absolute alcohol. These crops of crystals gave, of bromine, respectively, 46.15, 46.15, 46.18, and 46.03 per cent., the calculated per cent. in $(C_5H_5N)_2C_2H_4Br_2$ being 46.21.

Next pyridine with excess of ethylene bromide was digested in a pressure flask, in water-bath, with agitation. The crystallized product gave 46.26 per cent. of bromine. Finally dipyridine ethylene bromide was heated with excess of ethylene bromide in a sealed tube to 170° C. There was some charring in the mixture. By recrystallizing from it a product was obtained which gave 45.84 per cent. of bromine.

Dipyridine ethylene bromide crystallizes in colorless plates, insoluble in ether, and melting with decomposition at 295° C.

UNIVERSITY OF MICHIGAN.

---

[1] The ethylene bromide, (Hofmann) Davidson, 1861 : *Proc. Roy. Soc.*, page 261 ; The trimethylene bromide, Flintermann and Prescott, 1895 : *J. Am. Chem. Soc.*, **18**, 28.

[2] G. Kleine, 1894 : *Chem. Centrbl.*, page 161.

[3] This in continuation of the inquiry of Flintermann and Prescott, 1895 : *J. Am. Chem. Soc.*, **18**, 33.