there seems no question that it is the 1-benzoylphenyl-2,3-dimethyl-5-pyrazolone, from the method of its formation and the fact that ferric chloride gives a dark red color with its aqueous solution. It is very soluble in alcohol, or benzene; somewhat soluble in cold, soluble in hot water; soluble in strong hydrochloric acid. The melting point obtained by us (125°) was probably too low, as the amount at our disposal was too small to make certain of the purity of our specimen.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

NOTE ON SOME PROPERTIES OF PIPERONYLOIN.

BY HENRY A. TORREY AND J. B. SUMNER.[1]

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The object of this work was to compare the behavior of piperonyloin and benzoin under similar conditions. The number of results obtained is small, partly because we had but little time at our disposal, but still more because the piperonyloin, $CH_2O_2C_6H_3COCHOHC_6H_3O_2CH_2$, proved to be much less reactive than benzoin; thus no substance corresponding to desoxybenzoin could be obtained under the usual conditions for forming that substance, or a variety of modifications of them. Most of the piperonyloin remained unaltered, the product of the reaction being little more than a trace of what seemed to be a pinacone. No oxime could be made: in fact there was no reaction, as far as we could find, under conditions which give the oxime of benzoin with ease; and no more than a trace of an acetyl compound was formed by long continued and varied action of acetyl chloride on the piperonyloin. These differences between benzoin and piperonyloin form the most important result of this research, but until more observations have been made, it is not worth while to speculate on their cause.

The only substances we have found which react easily with piperonyloin are urea and ammonium thiocyanate. The ureide decomposes at 262° the thioureide near 260°, but the formula of the latter has not been established by us with certainty.

We also describe a modification of Perkin's method of preparing piperonyloin, which makes it possible to use larger quantities of substance.

Experimental Part.

The piperonyloin used in this work was prepared by the method of Perkin,[2] but we found that we obtained a better result, when instead of heating the mixture of 5 grams piperonal, 20 grams of 50 per cent. alcohol, and 2 grams of potassium cyanide for 6–8 hours, as recommended by

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[1] This research was suggested by the late Professor H. A. Torrey, and somewhat more than half of the experimental work was done under his direction, but the remainder of the experimental work and the writing of the paper were deprived of the benefit of his supervision by his too early death. C. L. JACKSON.

[2] *J. Chem. Soc.*, 59, 164.

him, the heating was carried on for only 3 hours, or the materials were allowed to stand at ordinary temperatures a few days. Under these latter conditions a yield of 80 per cent. of crude piperonyloin was obtained from 100 grams of piperonal, whereas Perkin states that the amount of piperonal used must be restricted to 5 grams in order to get a good result.

Treatment of piperonyloin with zinc and 80 per cent. alcohol, saturated with hydrochloric acid, under the same conditions, which give desoxybenzoin, gave on dilution a black tar, which could not be purified by distillation. Treatment with ether dissolved the tarry impurities, leaving a mass of yellow crystals, which proved to be unaltered piperonyloin, and made up the greater part of the product. It follows, therefore, that piperonyloin is much less affected by this reducing agent than benzoin. On trying to distil under a pressure of 1.5 cm. the tar obtained from the ether, a drop of distillate came over at 110°, and after this nothing till 246°, when about two-thirds of the substance passed over, leaving a black viscid mass. By crystallization of this distillate a body melting at 170° was obtained, probably a pinacone, but we did not obtain it in sufficient quantity for investigation. Many of the reducing processes were tried, but with no success.

According to Goldschmidt and Polonowska,[1] the oxime of benzoin is obtained with no difficulty; but with the piperonyloin we could obtain no reaction, although the conditions were varied in a number of different ways. In every case the piperonyloin was recovered unaltered.

Zinin[2] made the acetate of benzoin by heating it with acetyl chloride at 40–50° and finally at 100°, until there was no more action. Piperonyloin gave no perceptible action with acetyl chloride under these conditions, or any others we could find. By extracting the product with ether, in which piperonyloin is nearly insoluble, a trace of a yellow substance melting near 135° was obtained, but the quantity was so small that it was useless to think of obtaining enough for study.

Piperonyloinureide, $C_{17}H_{12}O_5N_2$.—This substance was made by heating 5 grams of piperonyloin with an excess of urea and amyl alcohol in a sealed tube at about 190° for three hours. The tube contained some large crystals and a black liquid. The crystals were washed with cold water and recrystallized four times from glacial acetic acid, after which the acid was washed off with alcohol and the substance dried at 110° for analysis.

The analyses gave 7.78 and 8.90 per cent. N; calculated, 8.64 per cent.

Properties.—The ureide forms pale pinkish crystals, as obtained by us, which decompose at about 265°. The substance is slightly soluble in hot alcohol, moderately soluble in hot amyl alcohol; slightly soluble in

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[1] *Ber.*, **20**, 492.

[2] *Ann.*, 104, 120.

cold, very soluble in hot glacial acetic acid; essentially insoluble in water, or benzene, even if hot.

The *thioureide* was prepared by heating piperonyloin with an excess of ammonium thiocyanate in a sealed tube to 170°. The crystals obtained in this way were washed with cold water and purified by crystallization from hot methyl alcohol.

The analyses gave 8.61 and 8.50 per cent. S; calculated for $C_{17}H_{12}O_4N_2S$, 9.41; for $C_{17}H_{14}O_5N_2S$, 8.99.

The analyses cannot distinguish between the two formulas, and we are inclined to adopt the first in spite of the fact that it agrees less well with the percentages found than the second, since this formula is analogous to that of the ureide, and the difference in results might be caused by a little of some impurity, which could not be removed from the small amount of substance at our disposal.

Properties.—The thioureide crystallizes in long, felted, nearly white needles, which decompose near 260°; slightly soluble in ethyl alcohol, methyl alcohol, acetone, or glacial acetic acid, when cold; moderately soluble in hot methyl alcohol, or carbon disulphide; very soluble in pyridine; insoluble in water.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 182.]

SOME DERIVATIVES OF *p*-AMINOBENZONITRILE.

BY MARSTON TAYLOR BOGERT AND LOUIS ELSBERG WISE.

Received September 11, 1910.

In 1903, Bogert and Kohnstamm[1] published a brief article on *p*-aminobenzonitrile, giving its method of preparation and properties, and describing also its acetyl and propionyl derivatives.

The present paper is a continuation of this work. In it are described improved methods for the production of the *p*-nitro- and *p*-aminobenzonitriles and of the acetyl derivative of the latter, as well as certain new substances.

By the action of glacial formic acid, of benzoyl chloride, and of benzenesulphonyl chloride, upon the aminonitrile, the corresponding acyl derivatives were obtained, while with oxalic esters, cyano-oxanilic esters and cyano-oxanilide were secured. The acetaminonitrile yielded the acetaminobenzamide with alkaline hydrogen dioxide, and the *m*-nitro-*p*-acetaminobenzonitrile on direct nitration. By reduction of the latter, the 3,4-diaminobenzonitrile was prepared, a most interesting orthodiamine.

The work is being continued and another paper will appear shortly. The fact that other chemists are working in closely related fields, or are

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[1] THIS JOURNAL, 25, 478 (1903)