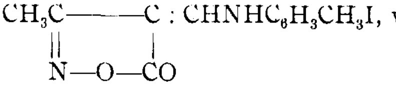
isoxazolone,  $\begin{array}{l} CH_3C\text{———}C : CHNHC_6H_3CH_3I \\ \;\| \qquad\qquad | \\ N\text{—}O\text{—}CO \end{array}$ which separates from glacial acetic acid in needles melting at 209°.

Calculated for $C_{12}H_{11}O_2N_2I$; N, 8.19; found: N, 8.19.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

THE CONDENSATION OF VANILLIN AND PIPERONAL WITH CERTAIN AROMATIC AMINES.

BY ALVIN S. WHEELER.

Received June 6, 1913.

In extension of the work done in this laboratory upon the condensation of chloral with aromatic amines,[1] we have carried out the condensation of the aldehydes, vanillin and piperonal, with *p*-aminobenzoic acid, its ethyl ester, and also with *p*-anisidine. Pawlewski[2] has described the product obtained by the condensation of anthranilic acid with vanillin, stating it to be an amorphous substance. We find that the para acid yields with vanillin a crystallin product with a melting point 40° higher. The condensation of anthranilic acid with piperonal was carried out by H. Wolf.[3] Our product with the para acid melts 44° higher. The products with the ethyl ester have very much lower melting points. The work with the ester was undertaken with the hope of discovering more cases of isomerism, a few cases having already been observed in similar reactions. No indications of isomerism, however, were noted in handling the two ester derivatives.

The condensations take place readily in a boiling solvent with the loss of one molecule of water, one molecule of each constituent taking part in the reaction. By working at low temperatures it is sometimes possible to bring two molecules of the amine into combination with one of the aldehyde. In the reaction between the free para acid and piperonal a small quantity of a low melting substance, m. 171–3°, was isolated and the amount was greatly increased by using two molecules of the acid. Notwithstanding many analyses, no satisfactory figures could be obtained for a dibenzylidene derivative.

The condensation product of *p*-aminobenzoic acid with vanillin is unique among the benzylidene derivatives in that it is the only one that takes up a molecule of water of crystallization. Exposed to a moist atmosphere it gradually assumes a reddish color. If it is recrystallized

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[1] Wheeler and Weller, THIS JOURNAL, **24**, 1063 (1902). Wheeler, *Ibid.*, **30**, 136 (1908). Wheeler and Jordan, *Ibid.*, **31**, 937 (1909).

[2] *Ber.*, **37**, 596 (1904).

[3] *Monatsh.*, **31**, 903.

from water, it becomes brilliant red. It is not a case of isomerism, for it loses one molecule of water at 100° and regains its yellow color.

Experimental Part.

3-Methoxy-4-hydroxybenzal-p-aminobenzoic Acid, $CH_3O.OH.C_6H_3CH:NC_6H_4CO_2H$, is prepared by boiling 1.37 grams (one mol) *p*-aminobenzoic acid and 1.52 grams (one mol) vanillin in 100 cc. toluene with the addition of 5 cc. alcohol. A little alcohol greatly diminishes the amount of toluene required. After boiling five hours under a reflux condenser, the solution is allowed to cool, the condensation product crystallizing out abundantly. A second crop of crystals from the mother liquor increased the yield to a total of 2.6 grams or 96% of the theoretical. The crude product, which melts at 204–6° was recrystallized from 200 cc. of toluene. The pure substance is deep yellow, consists of thin plates and melts at 211–2°.

Calculated for $C_{15}H_{13}O_4N$: C, 66.42; H, 4.80; N, 5.15
Found: C, 66.44; H, 5.12; N, 5.69

It was noticed that the rich, yellow crystals were often mixed with red ones. The first thought was that an isomeric compound was present, since some cases among analogous compounds are known, as the *o*-hydroxybenzalanthranilic acid described by Wolf. The whole mass turned red however in water and upon recrystallizing from boiling water a brilliant red substance, m. 104–6°, was obtained. After complete drying in the air, the product was heated to constant weight at 100°.

1.7860 g. lost at 100° 0.1150 g. H_2O.

Calculated for $C_{15}H_{13}O_4N.H_2O$: H_2O, 6.22; found: H_2O, 6.44.

3-Methoxy-4-hydroxybenzalethyl-p-aminobenzoate, $CH_3O.OH.C_6H_3CH:NC_6H_4CO_2C_2H_5$, is prepared by boiling 1 gram-molecule of ethyl-*p*-aminobenzoate with 1 gram-molecule vanillin in 10 cc. benzene for six hours under a reflux condenser. The solvent was then evaporated off and the residue recrystallized three times from alcohol. The crystals, which are thin yellow plates, melt at 145° (cor.).

Calculated for $C_{17}H_{17}O_4N$: C, 68.18; H, 5.73
Found: C, 68.53; H, 5.79

3-Methoxy-4-hydroxybenzal-p-anisidine, $CH_3O.OH.C_6H_3CH:NC_6H_4.OCH_3$, is prepared by boiling 1 gram-molecule of *p*-anisidine with 1 gram-molecule vanillin in 10 cc. benzene for six hours. Then after evaporation of the solvent, the product is recrystallized from ligroin. The pale yellow crystals deposit in radiating clusters, are easily soluble in most organic solvents and melt at 133.5° (cor.).

Calculated for $C_{15}H_{15}O_3N$: C, 70.00; H, 5.88
Found: C, 69.96; H, 6.09

3,4-Methyleneoxybenzal-p-aminobenzoic Acid, $CH_2:O_2:C_6H_3CH:NC_6H_4CO_2H$, is prepared by boiling 1.50 gram (one mol) piperonal and

1.37 grams (one mol) *p*-aminobenzoic acid in 100 cc. toluene for nine hours under a reflux condenser. The time was increased in this case to reduce the amount of a by-product melting at 171–3°. The chief product, which crystallized out on cooling, consisted of pale yellow prisms and could be recrystallized from toluene or water. The pure substance melts at 233°–4°.

Calculated for $C_{15}H_{11}O_4N$: C, 66.90; H, 4.08
Found: C, 67.14; H, 4.64

If in the preparation of this compound the boiling was interrupted after two or three hours, a small amount of a substance melting at 171–3° could be readily isolated. The amount could be greatly increased by employing two molecules of the acid for one of the aldehyde, but no satisfactory analytical figures could be obtained for a product containing two acid residues, in spite of many analyses.

3,4-Methyleneoxybenzalethyl-p-aminobenzoate, $CH_2 : O_2 : C_6H_3CH : NC_6H_4\text{-}CO_2C_2H_5$, is prepared by boiling 1.50 grams piperonal and 1.65 grams ethyl-*p*-aminobenzoate in 10 cc. benzene for six hours. The product crystallizes poorly from benzene so the latter is evaporated off. Out of ligroin the compound crystallizes readily in long, pale yellow, glistening needles which melt at 109° (cor.).

Calculated for $C_{15}H_{15}O_3N$: C, 68.66; H, 5.08
Found: C, 68.96; H, 5.04

3,4-Methyleneoxybenzal-p-anisidine, $CH_2 : O_2 : C_6H_3CH : NC_6H_4OCH_3$. The condensation of piperonal with *p*-anisidine is carried out exactly as that of vanillin with *p*-anisidine. The product crystallizes well from ligroin or benzene. The crystals are very pale yellow needles, which separate in feathery groups. Melting point, 117.5° (cor.).

The experimental work here described was carried out by Mr. L. E. Stacy, Jr., and Mr. L. B. Rhodes and I wish to thank them for their careful work.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE EXPERIMENTAL STATION OF THE E. I. DUPONT DENEMOURS POWDER CO., WILMINGTON, DELAWARE.]

THE FREEZING OF NITROGLYCERINE.

THE HEAT OF TRANSFORMATION OF THE NITROGLYCERINE ISOMERIDES.

BY HAROLD HIBBERT AND G. PRESCOTT FULLER.

Received May 12, 1913.

Introduction.

In a previous communication on "The Preparation, Crystallin Structure and Physical Properties of the Two Forms of Solid Nitroglycerine,"[1] the preparation and some of the physical properties of the two isomeric

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[1] *International Congress of Applied Chemistry, N. Y.* (1912), *Section III-b*, page 37.