[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

CONDENSATION OF ORTHO-AMINOPHENOL AND OXALIC ACID. PRELIMINARY COMMUNICATION[1]

BY ARTHUR A. LEVINE AND LESTER WEHMHOFF

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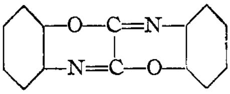
In an investigation undertaken in this Laboratory it was desirable to prepare a number of substituted oxanilides of the general formula $XC_6H_4NHOCCOHNC_6H_4X$. These substances were prepared by fusing the substituted amine with the required quantity of oxalic acid and in each case the desired product was obtained. If *o*-aminophenol and oxalic acid were used, *o*-hydroxy-oxanilide was not obtained but another substance was formed melting at 271–272°. This new condensation product possesses a deep red color and will be designated as the "red condensation product."

o-Aminophenol condenses readily with monocarboxylic acids, giving benzoxazoles or β-substituted benzoxazoles depending on the acid used.[2] Kehrmann and Bener[3] have shown that oxalic acid reacts with *o*-aminophenol hydrochloride dissolved in molten benzoic acid, giving a product melting at 260° to which is ascribed the formula



Discussion

The red condensation product is formed on heating a mixture of two moles of *o*-aminophenol with one mole of anhydrous oxalic acid at 180–200° for thirty minutes. Two moles of water are evolved in the reaction and a small quantity of carbon dioxide (0.04 mole) due probably to partial decomposition of some oxalic acid. If the reaction was carried out at 130–140°, a small quantity of *o*-hydroxy-oxanilide was formed together with large amounts of the red product. At the higher temperature oxanilide could not be found in the reaction product.

Analysis of the red condensation product gave on calculation the same formula as for *o*-hydroxy-oxanilide ($C_{14}H_{12}O_4N_2$). Though certain reactions indicate that the molecular weight must be doubled, a direct determination of this has not been possible, as every effort failed to give concordant results due to the slight solubility in the solvents tried.

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[1] Abstracted from a thesis by L. H. Wehmhoff presented to the Graduate Faculty of the State College of Washington in partial fulfilment of the requirements for the degree of Master of Science.

[2] Ladenburg, *Ber.*, **9**, 1524 (1876); **10**, 1124 (1877).

[3] Kehrmann and Bener, *Helv. Chim. Acta*, **8**, 16 (1925).

If the red condensation product is heated a few degrees above its melting point decomposition occurs, giving carbon dioxide equivalent to one free carboxyl group and a tarry substance which could not be purified. On heating it to a higher temperature the red product decomposes completely into carbon dioxide, water, *o*-aminophenol and an unidentified substance melting above 300°.

With an alcoholic solution of sodium hydroxide, the red product forms a crystalline sodium salt. Analysis of this compound indicates that two atoms of sodium have entered the molecule. The sodium salt on treatment with dimethyl sulfate and an additional quantity of sodium hydroxide gives a crystalline substance containing three methyl groups.

The compound reacts with one molecule of aniline with the elimination of a molecule of water and the formation of a new substance. It gives an acetyl derivative by the action of acetic anhydride or acetyl chloride, which gradually decomposes on recrystallization from benzyl alcohol and yields the diacetate of *o*-hydroxy-oxanilide.

The red condensation product is not affected by acids but it is readily decomposed by alkalies. Toward oxidizing and reducing agents in an acid medium it is stable. Alkaline reducing agents such as zinc dust and sodium hydroxide convert it into a colorless, unstable reduction product which has not yet been obtained in a pure state.

Experimental

Numerous experiments were performed in order to determine the most suitable conditions for the formation of the red product. In some of these trials the relative quantities of *o*-aminophenol and oxalic acid were varied and in others the temperature at which the reaction was carried out. The following procedure has been found to be the most suitable.

One mole of oxalic acid and two moles of *o*-aminophenol were intimately mixed and transferred to an Erlenmeyer flask. This was immersed in an oil-bath and maintained at 180–200° for about one-half hour. The grayish red reaction product was pulverized and washed with dilute hydrochloric acid and water. The impure product (yield, quantitative) melted at 250–260°. It was crystallized first from nitrobenzene and subsequently from benzyl alcohol until a pure substance melting at 271–272° was obtained.

Anal. Subs., 0.2320, 0.3490: CO_2, 0.5270, 0.7934; H_2O, 0.0918, 0.1377. Subs., 0.4676, 0.2854: 33.05, 20.25 cc. of 0.1053 *N* acid. Calcd. for $C_{28}H_{24}O_8N_4$: C, 61.74; H, 4.44; N, 10.29. Found: C, 61.97, 62.02; H, 4.43, 4.42; N, 10.42, 10.46.

Properties of the Red Product.—It crystallizes in small, red plates from dimethylaniline, nitrobenzene and benzyl alcohol. It is insoluble in most solvents. It dissolves in concentrated sulfuric acid, from which it reprecipitates unaltered on addition of water. Concentrated and dilute alkalies on heating decompose it. On acidifying an alkaline solution that has been heated, carbon dioxide is evolved and a tarry substance is formed.

Determination of the Carbon Dioxide Evolved on Heating the Red Product to 280°.—A weighed quantity was heated in an Erlenmeyer flask immersed in an oil-bath maintained at a temperature of 280° for one hour. The flask was connected with a U-tube containing concentrated sulfuric acid and this to a weighed potash bulb. A slow current of air was passed through the apparatus.

Anal. Subs., 2.6420, 2.0300: CO_2, 0.2077, 0.1700. Calcd. for one carboxyl in $C_{28}H_{24}O_8H_4$: 8.09. Found: 7.86, 8.37.

Heating the substance to 320° decomposes it completely into carbon dioxide, water, *o*-aminophenol and an unidentified substance melting above 300°.

The Sodium Salt of the Red Condensation Product.—This is formed on carefully warming the red product with an excess of 0.5 *N* alcoholic solution of sodium hydroxide. Long, needle-like crystals formed. These were recrystallized five times from 80% alcohol containing a small quantity of sodium hydroxide. The amount of sodium was determined by treating a weighed quantity with sulfuric acid and oxidizing the organic matter with nitric acid. Though somewhat high values were obtained. the results indicate that two atoms of sodium had reacted.

Anal. Subs., 0.2807, 0.7638: Na_2SO_4, 0.0775, 0.2026. Calcd. for $C_{28}H_{22}O_8H_4Na_2$: Na, 7.82. Found: Na, 8.94, 8.59.

The corresponding potassium salt was also prepared but was found to be even more difficult to crystallize. Both the sodium and potassium salt decompose readily on heating in aqueous or alcoholic solutions.

The Aniline Derivatives of the Red Product.—Ten grams of the red product were refluxed for one hour with 50 cc. of aniline. The resulting solution deposited well-formed crystals on standing. These were recrystallized from dimethylaniline and subsequently from nitrobenzene. The purified compound melts at 250°.

Anal. Subs., 0.2425, 0.1960: CO_2, 0.5850, 0.4724; H_2O, 0.1048, 0.0879. Subs., 0.4237, 0.2766: 31.18, 20.58 cc. of 0.1053 *N* acid. Calcd. for $C_{34}H_{29}O_7N_5$: C, 65.88; H, 4.72; N, 11.30. Found: C, 65.81, 65.75; H, 4.80, 4.98; N, 10.85, 10.97.

From this it follows that one mole of aniline has reacted with one mole of the original product. The aniline derivative is difficultly soluble in most organic solvents, though readily soluble in benzyl alcohol, nitrobenzene, aniline and dimethylaniline. It is not soluble in concentrated acids or alkalies.

Methyl Ester of the Red Condensation Product.—This was prepared by dissolving 10 g. of the product in 150 cc. of 2 *N* sodium hydroxide and adding 30 cc. of dimethyl sulfate in small portions with constant shaking. After about one-half of the dimethyl sulfate had been added, a crystalline precipitate formed. When all of the dimethyl sulfate had been added, the reaction mixture was heated on the water-bath for one hour. The product was recrystallized from benzyl alcohol until a constant melting point of 246–247° was attained.

Anal. Subs., 0.2245, 0.2832: CO_2, 0.5216, 0.6562; H_2O, 0.1118, 0.1351. Subs., 0.2240: 13.66 cc. of 0.1053 *N* acid. Calcd. for $C_{31}H_{30}O_8N_4$: C, 63.45; H, 5.33; N, 9.38. Found: C, 63.36, 63.20; H, 5.53, 5.36; N, 9.00.

The Acetyl Derivative.—Ten grams of the red condensation product was refluxed for four hours with 200 cc. of acetic anhydride. The acetic anhydride was distilled leaving a residue of about 50 cc. in the flask. This solidified on standing for a short time. The resulting product was transferred to a suction funnel and washed with about 10 cc. of glacial acetic acid, alcohol and finally with ether. The yield of impure product was 6.7 g. melting at 189°. Recrystallization from glacial acetic acid did not change the melting point. From this solvent it precipitates in well-shaped, red-colored plates, quite soluble in acetic acid, nitrobenzene and benzyl alcohol. Analysis for carbon and hydrogen gave values indicating that the substance was not pure. It was recrystallized from benzyl alcohol giving needle-like crystals lighter in color and melting at 183°. Evidently heating the substance with benzyl alcohol caused decomposition. Subsequent crystallization from the same solvent gave finally a perfectly white product, melting at 194°. This white substance is the diacetate of *o*-hydroxy-oxanilide, identified by analysis and a mixed melting point with a synthetic sample prepared by the method of Meyer and Seeliger.[4] These investigators give 201° as the melting point of the diacetate. This melting point is too high; a purified sample melted at 194° (corr.).

Anal. Subs., 0.2002, 0.1891: CO_2, 0.4461, 0.4203; H_2O, 0.0816, 0.0796. Calcd. for $C_{18}H_{16}O_6N_2$: C, 60.67; H, 4.50. Found: C, 60.77, 60.61; H, 4.52, 4.73.

The red acetate may be decomposed by dissolving in benzyl alcohol and heating for a few minutes. The solution is completely decolorized.

Summary

A new condensation product of *o*-aminophenol and oxalic acid has been isolated and some derivatives of it are described.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

TRIMETHYLACETALDEHYDE AND DIMETHYLETHYLACETALDEHYDE

BY J. B. CONANT, C. N. WEBB AND W. C. MENDUM

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Now that tertiary butyl and tertiary amyl alcohols are available, it becomes possible to prepare trimethylacetaldehyde and dimethylethylacetaldehyde in quantities suitable for synthetic work. These aldehydes promised to be of interest in connection with the study of highly-branched compounds which is being carried on in the Harvard Laboratories. In this paper we shall describe the preparation and behavior of these aldehydes in certain reactions. Although the hope of using these substances as a starting point in the synthesis of other branched compounds now seems dim, the results which have come to light are of some general interest.

The procedure we employed in the preparation of both aldehydes is outlined below

$$R_3COH \xrightarrow{HCl} R_3CCl \longrightarrow R_3CMgCl \xrightarrow{HCHO} R_3CCH_2OH \longrightarrow R_3CCHO + H_2$$

The last step, the dehydrogenation, is the same as that employed by Franke[1] in the most recent synthesis of trimethylacetaldehyde. We followed Bouveault's procedure instead of Franke's, however, and using copper at 250–300° obtained a 64–66% yield of aldehyde from both primary alcohols. The yield from the tertiary alcohol to the primary alcohol in both series was 40–50%, making the over-all yield for the four steps given above 25–33%.

[4] Meyer and Seeliger, *Ber.*, **29**, 2644 (1896).

[1] Franke and Hinterberger, *Monatsh.*, **43**, 657 (1922).