To the other compound only the oxonium or the chlorohydrin formula can be given; the former seems to be more probable. It is true that the oxonium structure here involves the assumption of hexavalent oxygen, but that such an assumption is legitimate has already been pointed out from previous results.[1] Throughout the whole of this series of investigations, however, no evidence has been obtained of "unsaturated" substances behaving abnormally in taking up more molecules of acid than "saturated" substances, *i. e.*, no addition of acid to ethylene bonds has been observed.

Summary.

The formation and stability of addition compounds of the types aldehyde—acid and ketone—acid have been investigated. From the twenty-four systems examined, eleven compounds have been isolated.

The results obtained are in complete agreement with the view, developed in previous articles, that the reaction is ionic in its nature and that the compounds formed are oxonium salts.

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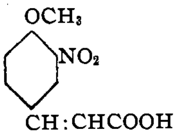
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

3-NITRO-4-HYDROXYCINNAMIC ACID AND ITS METHYL ETHER.

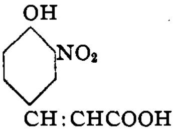
BY TREAT B. JOHNSON AND EDWARD F. KOHMANN.

Received October 28, 1914.

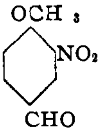
During the progress of an investigation dealing with the chemistry of nitrated protein, which is now being carried on in this laboratory, it became necessary to obtain for purposes of identification the following two acrylic acids, *viz.*, *3-nitro-4-methoxycinnamic* and *3-nitro-4-hydroxycinnamic* acids represented by Formulas I and II, respectively.



(I)



(II)



(III)

These two acids have already been described in the literature by Einhorn and Grabfield.[2] They obtained the acid (I) by application of Perkin's condensation reaction with nitro-anisic aldehyde (III), acetic anhydride and sodium acetate, and assigned to it the m. p. 140°. The corresponding hydroxyacid (II) was prepared by heating this unsaturated acid (I) in an acetic acid solution of hydrobromic acid at 100°. They assigned to this compound a m. p. of 198°.

We have now repeated this work of Einhorn and Grabfield's, and to

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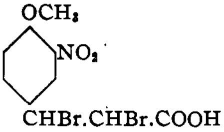
[1] Kendall and Carpenter, *Loc. cit.*

[2] *Ann.*, 243, 362 (1888).

our surprise have obtained two unsaturated acids having entirely different melting points than those given by these investigators. For example, by condensation of nitro-anisic aldehyde with acetic anhydride and sodium acetate, we obtained repeatedly an unsaturated acid corresponding to Formula I, which melted at 247–8° instead of 140°, as observed by Einhorn and Grabfield.[1] We have also obtained this same acid from other sources,[2] but in no case have we obtained a lower modification melting at 140°.

When the methoxy acid (I), melting at 247–248°, was heated with hydrobromic acid in acetic acid solution at 100° it easily underwent complete demethylation giving the unsaturated acid (II), melting at 223°. In this experiment also, which was conducted according to Einhorn and Grabfield's directions, we obtained no evidence of the formation of an acid melting at 198°. Both of the two acids (I) and (II) underwent esterification normally, giving their corresponding ethyl esters melting at 100° and 110–111°, respectively. These two compounds were apparently identical with the two esters described by Einhorn and Grabfield.[1]

Our acid (I) melting at 247–248° differed from Einhorn and Grabfield's acid melting at 140°, in its behavior towards bromine. They state that their acid added bromine easily in ether solution, giving the dibromo-acid (IV).

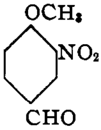


(IV)

Our compound was far less reactive. In fact, no addition of halogen took place when it was subjected to the conditions of their experiment. On the other hand, it added bromine in cold, glacial acetic acid solution, giving the same dibromo-acid (IV) as was obtained by Einhorn and Grabfield. It melted at 178–9°. It is possible that the differences in m. p. of our acids and those obtained by Einhorn and Grabfield are to be explained by the fact that we are dealing here with a new case of stereoisomerism. From the available data, however, we are unable to draw this conclusion. We have never obtained evidence thus far of the formation of isomeric modifications.

Experimental.

3-Nitro-4-methoxybenzaldehyde (Nitroanisic Aldehyde)



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[1] *Loc. cit.*

[2] These observations will be described in a future paper by Mr. Kohmann (T. B. J.).

This aromatic aldehyde has been described in the literature. Einhorn and Grabfield[1] prepared it by nitrating anisic aldehyde below 0° with a calculated amount of nitric acid in presence of concentrated sulfuric acid. They found that it melted at 83.5° and established its structure by the observation that a substituted indigo[2] was not produced by treatment with sodium hydroxide and acetone. Wörner[3] later repeated Einhorn and Grabfield's work and obtained what he supposed was a mononitro derivative melting at 72°. This product gave the same hydrazone as Einhorn and Grabfield's aldehyde melting at 83.5°. Wörner did not make an analysis of his nitro derivative and concludes his description of the compound with the following statement: "So bleibt der Widerspruch in den Beobachtungen des Schmelzpunkts von Metanitroanisaldehyd unaufgeklärt." This work was later repeated by Salway[4] who found that the nitroaldehyde melts at the temperature given by Einhorn and Grabfield.[5]

Einhorn and Grabfield's nitroaldehyde is easily obtained if the experiment is conducted under the following conditions: First, prepare a mixture containing 300 g. of concentrated sulfuric acid and 15 g. of nitric acid (sp. gr. 1.42) and cool to —10°. While holding the temperature of the acid mixture below —10°, then add slowly through a dropping funnel 22.6 g. of anisic aldehyde and then let stand at the same temperature for one hour. On pouring this final solution into one liter of water the aldehyde will separate as a light yellow solid. The yield in one experiment was 18.5 g. and in another 21 g. The compound is easily purified by crystallization from alcohol and melts at 83°.

If the nitration is conducted at a temperature higher than 0° an entirely different result is obtained. Thirty grams of the aldehyde were nitrated with the same proportions of acids but the temperature of reaction was kept between 0° and +3°. On pouring the resulting mixture into water we obtained a nitroaldehyde melting lower. It was apparently contaminated with an impurity. On repeated recrystallization from alcohol the melting point could not be raised above 73°. A mixture of this product and the pure aldehyde, melting at 83°, melted at 69–80°. This substance was apparently the same product as obtained by Wörner. It seems very probable, from what we were able to observe, that this lower melting substance is simply an inseparable mixture of the mononitroaldehyde (melting at 83°) and the dinitroaldehyde[6] (melting at 86°). The analytical values obtained support this conclusion (Kjeldahl):

[1] *Ann.*, **243**, 370 (1888).

[2] Baeyer, *Ber.*, **15**, 2886 (1882).

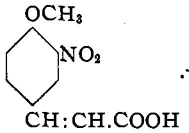
[3] *Ber.*, **29**, 157 (1896).

[4] *J. Chem. Soc.*, **95**, 1164 (1909).

[5] *Loc. cit.*

[6] Wörner, *Loc. cit.*

Calc. for $C_8H_7O_4N$: N, 7.73; $C_8H_6O_6N_2$: N, 12.3; found: N, 8.83, 8.87, 8.84.

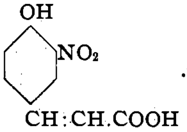


$$\begin{array}{c} OCH_3 \\ \bigcirc\,NO_2 \\ CH{:}CH.COOH \end{array}$$

3-Nitro-4-methoxycinnamic Acid, .—Twenty-one grams of mononitro anisic aldehyde were condensed with sodium acetate (12.6 g.) and 29.4 g. of aceticanhydride by heating for 8 hrs. at 140–150°. After cooling, the resulting mixture was then triturated with dilute aqueous ammonia in order to dissolve the cinnamic acid. On acidifying the alkaline solution with hydrochloric acid the nitro compound separated in the form of yellow crystals. The acid was purified by crystallization from alcohol and separated in long, rectangular prisms or plates, which melted at 247–248°. The acid crystallized from hot water in the form of needles. It is difficultly soluble in hot water, ether and chloroform. The compound did not respond to Millon's test for a phenolic group. A careful examination of all residues and filtrates failed to reveal the presence of any other acid than this modification melting at 247–248°. Einhorn and Grabfield[1] have assigned to this compound a m. p. of 140°. The yield of purified acid was 11 g. Nitrogen determination (Kjeldahl):

Calc. for $C_{10}H_9O_5N$: N, 6.27; found: N, 6.24.

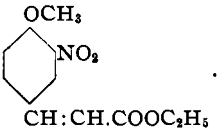
This same acid was also obtained when the crude nitroanisic aldehyde, melting at 73° (above), was used for the condensation.



$$\begin{array}{c} OH \\ \bigcirc\,NO_2 \\ CH{:}CH.COOH \end{array}$$

3-Nitro-4-hydroxycinnamic Acid, .—Attempts to demethylate the above methoxy derivative by heating with hydrochloric acid were unsuccessful. It was heated in acetic acid, saturated at 0° with hydrochloric acid gas, for 4 hrs. at 100° and at 150° for 2 hrs. without any change. Demethylation was finally effected by heating with an acetic acid solution of hydrobromic acid for 3 hrs. at 100°. After concentrating the acid solution and then pouring into water the hydroxy acid separated. This was purified for analysis by recrystallization from alcohol. It separated in the form of yellow needles which melted at 223°. Einhorn and Grabfield[1] state that this acid melts at 198°. Our product gave Millon's test for the phenolic group. Analysis (Kjeldahl):

Calc. for $C_9H_7O_5N$: N, 6.70; found: N, 6.72.



$$\begin{array}{c} OCH_3 \\ \bigcirc\,NO_2 \\ CH{:}CH.COOC_2H_5 \end{array}$$

Ethyl 3-Nitro-4-methoxycinnamate, .—This com-

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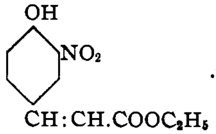
[1] *Loc. cit.*

pound was obtained by esterification of our methoxy cinnamic acid melting at 247–248°. It was obtained as a crystalline solid melting at 96–98°. It was purified for analysis by crystallization from alcohol and finally separated in large glistening prisms which melted at 99–100°. This same melting point was obtained by Einhorn and Grabfield.[1] The yield of purified ester from 1 g. of the acid was 0.7 g. Analysis (Kjeldahl):

Calc. for $C_{12}H_{13}O_5N$: N, 5.57; found: N, 5.50.

Ethyl 3-Nitro-4-hydroxycinnamate,



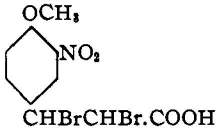
.—Prepared from the corresponding cinnamic acid (melting at 223°) by esterification with ethyl alcohol in presence of sulfuric acid. It was purified by crystallization from alcohol and separated in yellow needles which melted at 110–111°. Einhorn and Grabfield found their ester to melt at 108.5°. Analysis (Kjeldahl):

Calc. for $C_{11}H_{11}O_5N$: N, 5.90; found: N, 5.74.

Methyl 3-Nitro-4-hydroxycinnamate.—This new ester is easily prepared by digesting the corresponding acid in methyl alcohol acidified with sulfuric acid. It crystallizes from alcohol in yellow rosets of fine needles, which melt at 142–144°. The same ester was also obtained by heating the acid in methyl alcohol with an excess of methyl iodide and potassium hydroxide (3 molecular proportions). We obtained no evidence of the formation of methyl *3-nitro-4-methoxycinnamate* under these conditions. The ester responded to Millon's test. Analysis (Kjeldahl):

Calc. for $C_{10}H_9O_5N$: N, 6.27; found: N, 6.18.

3-Nitro-4-methoxyphenyldibromopropionic Acid,



.—Einhorn and Grabfield[1] prepared this acid by the addition of bromine, in ether solution, to their *3-nitro-4-methoxycinnamic* acid melting at 140°. They write as follows: "—— so ist es auffallend, mit welcher Leichtigkeit diese Säure im Stande ist zwei Atome Brom zu fixiren." It has been our experience that our acid melting at 247° adds bromine with difficulty. Attempts to add bromine in ether solution were unsuccessful. The dibrom compound was finally obtained in the following manner: Three grams of the methoxy acid were dissolved in about 250 cc. of glacial acetic acid and the solution cooled to 40°. Two grams of bromine were then added and the solution allowed to stand for 8 days at ordinary temperature. The acetic acid was then removed by distillation in a vacuum at 50° and

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[1] *Loc. cit.*

the addition product dissolved in alcohol and this solution evaporated to remove the alcohol. After this treatment a thick syrup was obtained. This was then dissolved in a little acetic acid and water added when we obtained 2.5 g. of a slightly gummy product, but well crystallized in the form of needles. The substance showed little tendency to crystallize from the ordinary solvents. It was finally obtained pure by dissolving in ether and then precipitating by dilution with petroleum ether. In this manner the acid was finally freed from gum and obtained in a colorless condition. It melted at 178–179° as observed by Einhorn and Grabfield.[1] Analysis (Kjeldahl):

Calc. for $C_{10}H_9O_5NBr_2$: N, 3.65; found: N, 3.71.

NEW HAVEN, CONN.

ON THE BLUE HYDROCARBON OCCURRING IN SOME ESSENTIAL OILS.

[PRELIMINARY NOTE.]

BY ALFRED E. SHERNDAL.

Received November 7, 1914.

Scattered through the literature of the essential oils are frequent descriptions of blue fractions obtained in the distillation of various oils, the most intensely colored sections distilling between the temperatures, 275° and 300°, or higher. A few oils, such as those of chamomile, wormwood, and cubebs, are notable for their blue or green color before fractionation.

In a few instances where intensely colored fractions have been obtained, the investigators have thought themselves in the possession of a pure substance.[2] In most cases however, they have recognized that the color is due to the presence of some colored substance other than the bodies making up the bulk of the oil, and the usually accepted view has been, that this is an oxygenated substance related to the sesquiterpene alcohols.[3]

Semmler[4] has summarized the literature covering these oils, and remarks that there are two views possible in regard to the blue fractions: either the greater part is colorless, and appears colored owing to the presence of a small amount of an intensely blue substance, or the sections boiling between 275° and 300°, are actually composed principally of a blue compound. That the latter is not the case, however, is evident from a survey of the literature, since the only purification method resorted to is a fractionation out of oils which contain large amounts of sesquiterpenes and sesquiterpene alcohols, with boiling points also ranging from 250°

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[1] *Loc. cit.*

[2] Piesse, "Art of Perfumery," 1879, p. 57.

[3] Bartelt, "Die Terpene und Campherarten," 1908, p. 4.

[4] *Die Aetherischen Öle,* 3, p. 260.