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On the Nitration of Sulfodehydroabietic Acid

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In a recent paper, Fieser and Campbell¹ state that the nitration of sulfodehydroabietic acid with mixed acids does not yield the expected mononitro derivative, but they obtained instead the dinitrodehydroabietic acid of Johansson^{2a,2b} together with unchanged sulfonic acid. The identification of such a mononitrosulfodehydroabietic acid probably escaped detection by these investigators since the compound is obtained in crystalline form only with difficulties and loss of material, as it separates from ordinary solvents as a gel.

On nitration of sulfodehydroabietic acid, prepared according to Hasselstrom, *et al.*,^{3a,3b} with fuming nitric acid, we have been able to prepare a mononitrosulfodehydroabietic acid almost quantitatively together with minute amounts of a water insoluble material which was not identified, but which apparently contains dinitrodehydroabietic acid. The mononitrosulfodehydroabietic acid thus prepared was not obtained pure, but it was identified through its beautiful, crystalline dimethyl and diethyl esters obtained from the disodium salt of the mononitro compound by the action of dimethyl and diethyl sulfate, respectively, in the usual manner. The mononitrosulfodehydroabietic acid is readily reduced in acid as well as in alkaline solutions to the corresponding monoaminosulfodehydroabietic acid.

This investigation is being continued with the aim of producing physiologically active resin acid derivatives by using the mononitrosulfodehydroabietic acid as starting material.

Experimental

Mononitrosulfodehydroabietic Acid.—To one liter of fuming nitric acid, sp. gr. 1.49–1.50, was added 200 g. of anhydrous sulfodehydroabietic acid^{3b} in portions during thirty minutes of thorough stirring. The temperature was kept at 0–5° during the reaction. After one hour the clear brownish solution was poured with stirring into 5–6 liters of ice and water, and the gelatinous precipitate removed by filtration and washed twice with 5 liters of a 10% common salt solution. It was then dissolved in about 8 liters of boiling water and filtered, leaving minute quantities of insoluble material probably containing dinitrodehydroabietic acid.¹ After neutralization with sodium

hydroxide, the solution was evaporated to dryness leaving 450 g. of the crude sodium salt of mononitrosulfodehydroabietic acid containing approximately 50% of sodium chloride.

Twenty grams of gelatinous mononitrosulfodehydroabietic acid was dissolved in 100 cc. of acetic anhydride and the solution evaporated until small needles of mononitrosulfodehydroabietic acid started to separate; yield, about 2 g. These were recrystallized once from a benzene-ethanol solution and did not melt below 300°. This product was converted into the diethyl ester, as described herein below, yielding the diethyl ester of the mononitrosulfodehydroabietic acid, m. p. 195.5–196° (cor.), which did not lower the melting point when mixed with an authentic sample.

Diethyl Ester of Mononitrosulfodehydroabietic Acid.—Thirty grams of crude disodium mononitrosulfodehydroabietae, dried at 110° for one hour, was refluxed with 150 cc. of diethyl sulfate for fifteen minutes, and after cooling was poured into 600 cc. of ice water and refluxed for one-half hour. After cooling, the precipitate was removed by filtration, boiled with a sodium bicarbonate solution and washed well with water; yield, 15.9 g. It was recrystallized from acetone, the white needles melting sharply at 195.8–196° (cor.).

Anal. Calcd. for $C_{24}H_{32}O_7NS$: C, 59.85; H, 7.33. Found: C, 60.12, 59.95; H, 7.02, 7.14.⁴

Dimethyl Ester of Mononitrosulfodehydroabietic Acid.—This was obtained in the same manner as the diethyl ester from 30 g. of crude sodium salt of mononitrosulfodehydroabietic acid and 140 cc. of dimethyl sulfate; yield, 6.5 g. Recrystallized from acetone, the white needles melted sharply at 244.3–244.7° (cor.).

Anal. Calcd. for $C_{22}H_{24}O_7NS$: C, 58.26; H, 6.89. Found: C, 58.43, 58.21; H, 6.82, 6.76.

Monoaminosulfodehydroabietic Acid.⁵—Thirty grams of crude sodium mononitrosulfodehydroabietae was dissolved in 300 cc. of methanol. To the refluxing solution was added 120 g. of zinc dust, activated with copper sulfate, in portions of 10 g., together with 300 cc. of concentrated hydrochloric acid during a period of twenty-four hours. The excess of methanol was stripped off and after cooling the residue was neutralized with a dilute solution of sodium carbonate. The precipitated zinc salt was removed by filtration, the filtrate made acid with dilute hydrochloric acid and extracted three times with ether; the ether evaporation residue, consisting of minute quantities of a solidifying oil, was not investigated. The aqueous solution, after ether extraction, was evaporated to about 1 liter,

(4) All analyses by Mr. S. Gottlieb, Columbia University, New York City.

(5) Monoaminosulfodehydroabietic acid is obtained more conveniently, and in higher yield, by reduction of the mononitro acid with sodium hyposulfite in alkaline solution. The description of this method will be incorporated in a later communication to THIS JOURNAL.

(1) Fieser and Campbell, THIS JOURNAL, 60, 2631 (1938).

(2) (a) Johansson, *Arkiv, Kemi Min. Geol.*, 6, No. 19 (1917); (b) Fieser and Campbell, THIS JOURNAL, 60, 159 (1938).

(3) (a) Hasselstrom, U. S. Patent 2,121,032 (1938); (b) Hasselstrom and McPherson, THIS JOURNAL, 60, 2340 (1938).

whereupon about 5 g. of crude aminosulfodehydroabiatic acid precipitated in fine microscopic needles slightly brownish in color. These were recrystallized from water. The acid does not melt below 300°.

Anal. Calcd. for $C_{20}H_{23}O_5NS$: C, 60.73; H, 7.39. Found: C, 60.27, 60.49; H, 7.46, 7.46 (the sample contained 0.42% ash).

Summary

1. On nitration with fuming nitric acid the

sulfonate of dehydroabiatic acid gives a mononitrosulfodehydroabiatic acid almost in quantitative yields. This mononitro product is characterized by the preparation of its diethyl and dimethyl esters.

2. The mononitrosulfodehydroabiatic acid is readily reduced by ordinary means to the corresponding monoaminosulfodehydroabiatic acid.

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RECEIVED NOVEMBER 8, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Osage Orange Pigments. V. Isomerization¹

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In a previous publication² from this Laboratory we have shown that the two closely related yellow pigments, osajin and pomiferin, of the fruit of the osage orange (*Machura pomifera* Raf.) are isomerized by mineral acids to high melting isomers and that in each of these the single absorption maximum is shifted slightly toward the region of shorter wave lengths to produce colorless products. It is the purpose of the present communication to examine further the nature of this isomerization.

Pomiferin ($C_{25}H_{24}O_6$) differs from osajin ($C_{25}H_{24}O_5$) by one hydroxyl group and no other significant difference has yet been found. In a recent publication we have made a tentative assignment of a flavone structure for these substances, subject to confirmation by further degradative work. Mr. Mahan of this Laboratory now has found that an isoflavone structure is present, since alkaline treatment of methylated osajin has produced formic (one mole) and homoanisic (*p*-methoxyphenylacetic) acids and similar treatment of methylated pomiferin has yielded formic (one mole) and homoveratric (3,4-dimethoxyphenylacetic) acids. The details of this work will be communicated at a later date. Iso-osajin does not give a coloration with ferric chloride-alcohol but as there is every reason to believe that a phenolic group is still present in this substance, it would appear that we have in hand a not uncommon case of a phenolic group being undetectable by this color test. Otherwise, the isomerized substances exhibit the same reduction and other

color tests as before isomerization, so that the isoflavone nucleus is still present.

Osajin has been shown to possess two hydroxyl groups and pomiferin three. Of these groups, one hydroxyl in both has been shown to be resistant toward acetylation with acetic anhydride and pyridine in the cold. The fully acetylated derivatives are obtainable on acetylation with hot acetic anhydride and sodium acetate. Under tosylation conditions, pomiferin has been shown to form a ditosyl (di-*p*-toluenesulfonate) derivative and osajin a monotosyl substitution product. Under stringent methylation conditions (hot methyl sulfate and alkali in the presence of acetone) the fully substituted methyl ethers are obtained. Under mild conditions of methylation (short treatment with sodium ethylate and methyl sulfate at 0° or, as now reported, on methylation with diazomethane) pomiferin forms a dimethyl ether which can be further methylated to the trimethyl ether under the more stringent conditions and which can be acetylated under the stringent conditions but not by the mild conditions of acetylation. An analogous behavior toward methylation is now reported for osajin.

The partially substituted derivatives of both substances give a strong ferric chloride-alcohol coloration so that the resistant hydroxyl group in each is phenolic (or enolic). Iso-osajin yields a mono-*p*-toluenesulfonate and isopomiferin produces a di-*p*-toluenesulfonate.² It is now shown that under either the mild or stringent conditions, iso-osajin produces a monoacetate and a mono-methyl ether while pomiferin yields a diacetate and a dimethyl ether. These substitution prod-

(1) Preceding publication in this series: M. L. Wolfrom, P. W. Morgan and F. L. Benton, *THIS JOURNAL*, **62**, 1484 (1940).

(2) M. L. Wolfrom, F. L. Benton, A. S. Gregory, W. W. Hess, J. E. Mahan and P. W. Morgan, *ibid.*, **61**, 2832 (1939).