

those given for the corresponding acids of Kurokawa origin, showing that the respective acids are isomers.

It is well known that Kurokawa and Niitsu oils have rather high specific gravities and have very dissimilar properties from those of Nishiyama oil. The identification of the naphthenic acids of low specific gravities in Nishiyama oil and of the isomers of high specific gravities in Kurokawa oil is of great interest in view of the geological formation of these petroleums. It seems probable that Kurokawa and Niitsu petroleums have been subjected to volcanic action and that consequently the isomeric change of naphthenic acids has occurred through the possible influence of heat and pressure.

Summary

A mixture of pure naphthenic acids was obtained from the waste lye produced in the refining of a "neutral oil" distillate (33.2 Bé.) from Echigo-Nishiyama oil and the corresponding free naphthenic acids, namely, dodecanaphthenic, tridecanaphthenic, tetradecanaphthenic and pentadecanaphthenic and their methyl esters have been isolated. It is noted that the specific gravities of the acids are much lower than those given for the corresponding acids of Akita-Kurokawa origin, indicating that the respective acids are isomers.

It is also pointed out that the presence of these isomers of the naphthenic acids is of great interest in view of the geological formation of petroleums.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

THE PREPARATION AND PROPERTIES OF 1-BENZOYLAMINO-2-METHYLANTHRAQUINONE¹

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RECEIVED MAY 27, 1925

PUBLISHED SEPTEMBER 5, 1925

The amino-anthraquinones have received considerable attention because they serve as the starting point in the synthesis of many anthraquinone derivatives, some of which are valuable vat dyes. It is known that the replacement of an amino hydrogen atom by an aliphyl or aryl group causes greater depth of color, but none of the compounds so formed has affinity for textile fibers. On the other hand, the introduction of an acyl group is accompanied by a decrease in the depth of color, and the product may be a vat dye.²

Very little work has been done with the substitution products of the methylamino-anthraquinones. Roemer and Link prepared the mono-

¹ This paper incorporates a thesis presented to the Faculty of the University of Florida by J. Lowry Bray in partial fulfilment of the requirements for the degree of Master of Science.

² Barnett, "Anthracene and Anthraquinone," D. Van Nostrand Co., 1921, p. 8.

acetyl derivative of 1-amino-2-methylantraquinone, presumably by treating the amine with acetyl chloride.³ Their product was hydrolyzed by boiling hydrochloric acid. Similarly, 1-diacetylamino-2-methylantraquinone has been made by heating a mixture of the amine and acetic anhydride.⁴

The preparation of the benzoyl derivative of 1-amino-2-methylantraquinone was undertaken in order to study the influence of the methyl group in the nucleus on the color and tinctorial properties by comparison with 1-benzoyl-amino-antraquinone, a technically important vat dye, known in the trade as Algol Yellow W G.

Experimental Part

2-Methylantraquinone was obtained by the well-known phthalic acid synthesis; m. p., 177°.⁵

1-Nitro-2-methylantraquinone is best prepared by adding powdered potassium nitrate to a solution of methylantraquinone in concd. sulfuric acid; m. p., 268.5–269.5°.⁶

1-Amino-2-methylantraquinone.—Numerous methods for reducing nitro-antraquinones to the amines are to be found in the literature. The method using sodium sulfide as the reducing agent was found to give the most satisfactory results.⁷ The substance melts at 202°.

1-Benzoylamino-2-methylantraquinone.—Ten g. of 1-amino-2-methylantraquinone and 4.4 g. of anhydrous sodium carbonate were suspended in a mixture of 5 g. of benzoyl chloride and 100 g. of toluene. The mixture was heated under a reflux condenser for about ten hours. The benzoyl derivative dissolved in the hot toluene forming a light brown solution. The sodium carbonate was removed by filtration. After most of the toluene had evaporated the benzoyl derivative separated in the form of small, yellow crystals. By crystallization from glacial acetic acid solution, the pure benzoyl derivative was obtained as brilliant yellow needles; m. p., 200–202° (uncorr.); yield, 4.4 g., or 30.8%.

Properties of 1-Benzoylamino-2-methylantraquinone

This compound dissolves with difficulty in ethyl alcohol, chloroform, benzene and acetone. It dissolves readily in hot glacial acetic acid. It differs from the acetyl derivative prepared by Roemer and Link in that it is not appreciably hydrolyzed by hydrochloric acid. Concd. sulfuric acid

³ Roemer and Link, *Ber.*, **16**, 699 (1883).

⁴ Badische Anilin- und Soda-Fabrik, Ger. pat. 212,204. *Chem. Zentr.*, [II] **80**, 667 (1909).

⁵ Friedel and Crafts, *Ann. chim. phys.*, [6] **14**, 446 (1888). Limpricht, *Ann.*, **299**, 300 (1898). Limpricht and Wiegand, *Ann.*, **311**, 181 (1900). Heller and Schülke, *Ber.*, **41**, 3627 (1908).

⁶ Boettger and Peterson, *Ann.*, **166**, 147 (1873). Roemer, *Ber.*, **15**, 1786 (1882). Graebe and Blumenfeld, *Ber.*, **30**, 1118 (1897).

⁷ Ref. 2, p. 192.

readily hydrolyzes it to the amine. When the compound is warmed with sulfuric acid and ethyl alcohol, ethyl benzoate is evolved.

From a hydrosulfite vat it colors cotton and artificial silk a brilliant lemon-yellow, but it shows much less affinity for textile fibres than 1-benzoylamino-anthraquinone, which produces an intense golden yellow.

All efforts to analyze 1-benzoylamino-2-methylanthraquinone by the Dumas combustion method for nitrogen failed. The compound decomposes only at a high temperature, and then does so with almost explosive violence. It was successfully analyzed by the Kjeldahl method, using copper sulfate as a catalyst.

Anal. Subs., 1.9369, 2.3541: 18.00, 21.65 cc. of 0.31036 *N* NaOH. Calcd. for $C_{22}H_{16}O_3N$: N, 4.11. Found: 4.04, 4.00.

Use of 1-Benzoylamino-2-methylanthraquinone as a Vat Dye

The vat was prepared by adding 4 g. of sodium hydrosulfite and 5 cc. of a solution of potassium hydroxide (30 g. per 100 g. of water) to 50 cc. of water; 0.2 g. of 1-benzoylamino-2-methylanthraquinone was added, and the mixture was warmed until the dye had dissolved. A sample of artificial silk (or cotton) weighing 10 g. was then placed in the bath, and the temperature was raised gradually to about 75°. The sample assumed a red-brown color which changed to a lemon-yellow on exposure to the air.

Summary

1. The preparation of 1-benzoylamino-2-methylanthraquinone has been described.

2. Its properties have been compared with those of 1-benzoylamino-anthraquinone.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]
TRIPHENYLMETHYL. XXXIV. 2,5-, 2,4-, AND 3,4-DIMETHOXY-TRIPHENYLMETHYLS

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RECEIVED JUNE 1, 1925

PUBLISHED SEPTEMBER 5, 1925

Introduction

It is now well established that a comparatively slight variation in the composition of the aryl groups in hexa-arylethanes may exert a notable influence on the extent of the spontaneous dissociation of these ethanes in solution into free triarylmethyl radicals. It has been found that a methoxyl in the *ortho* position of one of the phenyl groups in triphenylmethyl augments to the extent of 32% the degree to which the free radical exists

¹ The material here presented is from a dissertation submitted by G. C. Forrester to the Faculty of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1923.