trihydroxyanthraquinone and the other seems to be an aminohydroxyanthraquinone, although its purity has not been established with absolute certainty.

This new trihydroxyanthraquinone is not a mordant dye of importance.

By the method employed the yield of the trihydroxyanthraquinone was about 24% of theory.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE BROMINATION OF *p*-NITROTOLUENE.

BY J. F. BREWSTER.

Received November 15, 1917.

Reid[1] has recently made a study of the reaction between *p*-nitrobenzyl bromide and the alkali salts of several organic acids and phenols in which there is formed, respectively, the corresponding *p*-nitrobenzyl ester or ether. In the case of many of the acids and phenols Reid found that the products were obtained in good yield, were readily purified, and, having sharp melting points, the reaction could be recommended as a method of identification.

Having occasion to use Reid's method, the author set about preparing a supply of the bromide, first by heating *p*-nitrotoluene with bromine in sealed tubes as Reid recommends. Frequent breakage, however, due to the poor quality of tubing then at hand, led to a search for some other way to prepare the bromide.

A much easier and more satisfactory method has been found and although there is very little involved therein that is not well known, it was thought worth while to record the procedure as the product itself is of great usefulness.

The method of bromination consists in adding a carbon tetrachloride solution of the calculated quantity of bromine to a boiling carbon tetrachloride solution of *p*-nitrotoluene, containing iodine as catalyzer, in direct sunlight. The reaction proceeds smoothly and rapidly, the actual bromination can be finished in 30 to 60 minutes, and the product, ready for drying, can be obtained in a total time of two hours or less. The yields are from 60 to 71% of the theoretical.

In attempts by this method to prepare *p*-nitrobenzylidene bromide, the second molecule of bromine reacted readily. However, the yield, after necessary recrystallizations for purification, was very small. The third molecule of bromine did not react.

Experimental.

Ten grams of *p*-nitrotoluene contained in a flat-bottomed flask were

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[1] Reid, E. Emmet, THIS JOURNAL, 39, 124, 304 (1917).

dissolved in 100 cc. carbon tetrachloride and a small crystal of iodine was added. The flask, fitted by ground joint to a reflux condenser, was placed on an electric hot plate in direct sunlight and the contents allowed to boil. 11.7 g. (1 mol) bromine dissolved in 50 cc. carbon tetrachloride were introduced in small quantities at a time by means of a separatory funnel whose stem was sealed into the side of the lower part of the condenser tube. Rapid evolution of hydrogen bromide began at once. This was absorbed by water contained in Folin bulbs fitted to the upper end of the condenser.[1] When all the bromine had been used up the flask was detached after cooling and the carbon tetrachloride distilled off. On cooling, the oily residue at the botton of the flask crystallized in a solid mass. This was dissolved by boiling in 95% alcohol and filtered. The filtrate was rapidly cooled and allowed to stand a short time at 0°. The fine crystals were filtered by suction and dried in the air overnight. The yield was 11.2 grams, or 71% of the theoretical. Melting point 99–100°, uncorrected.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR. XII.[2] TETRACHLOROPHTHALOXIME AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND CHARLOTTE H. MILLER.

Received November 16, 1917.

The study of phthalic acid derivatives resulting from replacement in various positions in the molecule and the effects thereby on color has been continued. The present paper considers certain derivatives of tetrachlorophthalic anhydride obtained after one oxygen atom has been replaced by the NOH radical. The reaction is brought about readily by treating tetrachlorophthalic anhydride with an aqueous solution of hydroxylamine. The particular interest in the resulting oxime lies in the proximity effects taking place between the hydroxyl group and the nucleus. This effect becomes very marked on salt formation when it is evidenced to the eye by a vivid red color.

Unhalogenated phthaloxime was found to exist in two modifications, one colorless, and the other canary yellow,[3] but neither Orndorff and

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[1] The apparatus can be simplified by covering the carbon tetrachloride solution in the flask with a little water. This absorbs all hydrogen bromide. If the bromide is introduced by a separatory funnel the tip of whose stem extends down the condenser tube to the point where the vapors condense, there is no loss of bromine whatever and the experiment can be conducted in the open laboratory. The yields by this method are somewhat lower.

[2] THIS JOURNAL, 40, 254 (1918).

[3] Orndorff and Pratt, *Am. Chem. J.*, 47, 90 (1912).