

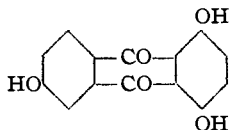
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

1,4,6-TRIHIDROXYANTHRAQUINONE.

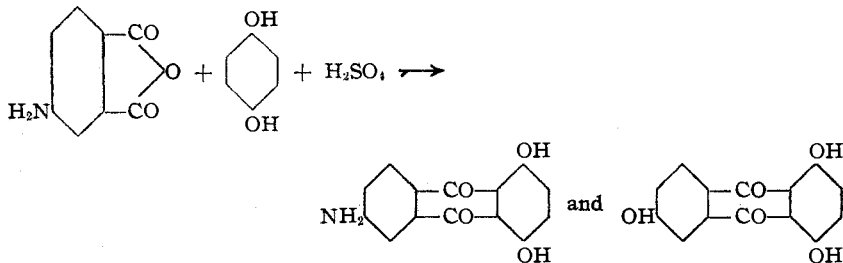
By M. L. CROSSLEY.

Received November 14, 1917.

Of the several possible trihydroxyanthraquinones, seven isomers, the 1,2,3-, 1,2,4-, 1,2,5-, 1,2,6-, 1,2,7-, 1,2,8-, and 1,4,8-, have been discovered and studied prior to this synthesis. The purpose of this research was to prepare 6-amino-1,4-dihydroxyanthraquinone by condensing 4-aminophthalic anhydride with hydroquinone. The result of the condensation was a mixture of two substances whose sodium salts differ in color and solubility. The more soluble of the two is blue-violet and the other is red-brown. On acidification of the blue-violet sodium salt a product is obtained which when purified analyzes for $C_{14}H_8O_5$. It is a reddish brown powder which is slightly soluble in boiling water, giving a solution which is yellowish red. It does not crystallize from its water solution. It is quite soluble in glacial acetic acid, ethyl alcohol, methyl alcohol, ether, chloroform, and nitrobenzene. It is sparingly soluble in benzene. It is best purified by precipitating it with water from a glacial acetic acid solution and subsequently crystallizing from nitrobenzene. It dissolves readily in alkalis giving blue-violet salts which are quite soluble in water. It is not important as a mordant dye. It gives the anthranol and picrate tests for the anthraquinone molecule. The behavior of the substance and the synthesis prove the compound to be 1,4,6-trihydroxyanthraquinone



The aminophthalic anhydride and hydroquinone condense to give the aminodihydroxyanthraquinone, a part of which is converted into the trihydroxyanthraquinone



The less soluble sodium salt obtained from the reaction mixture contains nitrogen and appears to be the sodium derivative of aminodihydroxyanthraquinone. Its water solution is reddish brown. By neutralizing the alkaline solution a dark blackish product is precipitated. This is

not very soluble in organic solvents and does not crystallize. Its nitrogen content agrees with that calculated for $C_{14}H_9O_4N$.

Experimental Part.

4-Aminophthalic Anhydride.—Phthalic anhydride was nitrated as described by Bogert and Boroschek¹ and the resulting 3- and 4-nitro acids were roughly separated by crystallization from water and then the crude 4-nitrophthalic acid was converted into the corresponding methylphthalate by the method of Bogert and Renshaw.² The 4-nitrodimethylphthalate was then reduced to the corresponding amino compound by the method of Baeyer.³ The ester was saponified by boiling it with an alcohol solution of sodium ethylate and the sodium salt was subsequently decomposed with hydrochloric acid to give the 4-aminophthalic acid. This acid was then dehydrated by the method of Bogert and Renshaw⁴ and a fair yield of the anhydride thus obtained.

1,4,6-Trihydroxyanthraquinone.—A mixture of 5 g. of 4-aminophthalic anhydride, 3 g. of hydroquinone, and 40 g. of concentrated sulfuric acid was heated in a round flask in an oil bath at 170° for two hours. The temperature was raised to 190° and maintained at this point for one hour. The reaction product was then poured into water and the mixture stirred thoroughly. It was filtered on a Buechner funnel and washed with water until free from acid. It was extracted with a cold 10% solution of sodium hydroxide and a violet-blue solution obtained. This was acidified with hydrochloric acid. A reddish brown substance separated from the acid solution. It was filtered and washed with water until free of acid. The product was then dissolved in glacial acetic acid and again reprecipitated by dilution with water. It was filtered and then crystallized from nitrobenzene. It is nitrogen-free and does not melt below 300° . The yield of the pure product was 1.9 g.

Calc. for $C_{14}H_9O_5$: C, 65.62; H, 3.13; O, 31.25. Found: C, 64.84; H, 3.00; O, 32.16.

The residue left from the extraction with sodium hydroxide was boiled with sodium hydroxide and gave a dark brown solution from which a blackish substance containing nitrogen was precipitated by acid. This product was not obtained in a pure condition but its properties suggest that it is an aminohydroxyanthraquinone. It gives positive tests for amino, hydroxyl, and anthraquinone groups.

Conclusions.

By the condensation of 4-aminophthalic anhydride with hydroquinone a mixture of two substances is obtained. One of these proves to be 1,4,6-

¹ THIS JOURNAL, 23, 740 (1905).

² *Ibid.*, 28, 617 (1906).

³ *Ber.*, 10, 125, 1079 (1877).

⁴ *Loc. cit.*

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.

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Reid¹ 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

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