

All of the above preparations melted at 88°. The substance is quite stable in the air at room temperature, but loses iodine when warmed, and more gradually when spread out in the air, at the same time becoming lighter in color. In a stoppered bottle it remains unchanged indefinitely. It is very soluble in most organic solvents, the iodine giving the brown or violet color characteristic for the solvent.

Three out of four of the preparations showed an excess of total over external iodine as will be seen from the analyses. The difference represents iodine in the form of iodide. The iodine in this form is, however, a very small fraction of the total, and a periodide formula would require high multiples of cumarin and external iodine. Considering the fact that the crystals could not be purified by washing, it is probable that some iodide from the mother liquor remains as an impurity. Such admixture of iodide would tend to retain also an excess of external iodine. This may account for the variations in the iodine determinations on the different samples. Moreover, in one preparation, the figures for external and total iodine are identical. The simplest formula for an iodide of cumarin with an iodine content approaching these results is (C₉H₆O₂)₂I, or more probably (C₉H₆O₂)₄I₂, where the calculated value is 30.5%.

When sodium chloride was substituted for potassium iodide in the preparation of the substance, the cumarin and iodine crystallized separately. When, however, potassium bromide was used, black crystals with a violet luster were obtained. These had an external iodine content of 31.7%.

AMES, IOWA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

RESEARCHES ON THE ACTION OF SULFURIC ACID ON CERTAIN NITROCARBOCYCLIC COMPOUNDS. I. THE ACTION ON NITROBENZENE.

BY M. L. CROSSLEY AND C. B. OGILVIE.

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Introduction.

As a result of an attempt to condense β -aminoanthraquinone and certain dicarboxylic acids of the acyclic series, in the presence of nitrobenzene, by means of sulfuric acid, we find that, at a temperature of about 175°, a vigorous reaction takes place, with the production of a purplish black product which, at first glance, appears to be chiefly carbon. Investigation proves that concentrated sulfuric acid dissolves it, forming a dark greenish blue solution. The product is reduced by alkaline hydro-sulfite to a brown solution which produces a fast heliotrope color on cotton. The reaction appears to be quite general for nitrocarbocyclic compounds and is not influenced by the acyclic acid. In every case this is recovered

unchanged. The reaction-product appears to be an individual compound but, owing to its insolubility in most organic solvents, the purity has not yet been established with certainty. It contains an NH_2 group, for it diazotizes and gives azo compounds.

The diazotization of the product led us to suppose that the reaction had not taken place through the amino group and suggested the possibility of substituting anthraquinone and finally anthracene for the amino compound. The reaction in each case was similar to that obtained with aminoanthraquinone. The resulting products were similar but not identical. That from the aminoanthraquinone gave a brown vat which dyed cotton heliotrope. That from the anthraquinone reduced under similar conditions to a brown vat which dyed cotton a steel-gray black. Anthracene gave a product which dyed cotton grayish brown. The product from anthracene did not reduce as readily as the other two products.

In general properties the three products are similar. They are practically insoluble in all organic solvents other than nitrobenzene, pyridine, quinoline, and a 10% solution of trimethylamine, in which they are slightly soluble. Pyridine appears to be the best solvent for them but they separate from it in amorphous form. The anthracene product from pyridine analyses for $\text{C}_{46}\text{H}_{29}\text{O}_5\text{SN}_2$. The pyridine solutions show a beautiful brown-red fluorescence. A similar fluorescent solution is obtained by treating the products with concentrated ammonium hydroxide. Concentrated sodium hydroxide gives with them, however, brown solutions which do not fluoresce. Hot alkali and acids seem to change the substances, for the products recovered from these solvents are not identical with the original.

By a process of elimination we soon found that nitrobenzene would give the reaction. The main product looked like carbon but was completely soluble in concentrated sodium hydroxide. It reduced to a vat dye which dyed cotton grayish black. In general the substance is similar to those already mentioned but it is not identical. Many other nitrocarbocyclic compounds have been found to give the reaction. From the nitrobenzene reaction a mixture of two substances is obtained. One of these we have proven to be identical with *p*-aminophenol-*o*-sulfonic acid described by Post,¹ Schmitt,² Brunner and Kramer,³ Brunner and Vuilleumier,⁴ Eckert,⁵ and others.⁶ The chief purpose of this paper is to consider the reaction with nitrobenzene.

It is quite possible that many of the reported cases of carbonization of

¹ *Ann.*, 205, 49-62 (1880).

² *J. prakt. Chem.*, [2] 8, 7.

³ *Ber.*, 17, 1867 (1884).

⁴ *Chem. Zentr.*, [2] 1908, 587.

⁵ *Monatsh. Chem.*, 34, 1957-64 (1914).

⁶ *Ber.*, 28, 2351; 27, 1638 (1895); *Ann.*, 309, 236 (1899).

nitrocarbocyclic compounds¹ are, in reality, reactions similar to that herein described. Every black product obtained in reactions with organic substances is not carbon. Most of the familiar organic reactions are conducted at moderate temperatures. The possibilities at higher temperatures are unlimited and invite careful investigation.

Experimental Part.

The Reaction.—In a round two-liter flask connected with a Liebig condenser, a mixture of 164 g. of nitrobenzene and 144 g. of concentrated sulfuric acid was heated slowly to 195°. At this temperature small bubbles began to form around the edges of the surface of the mixture. The sand bath was removed and wet towels applied to the neck of the flask. In spite of all precautions the reaction increased in vigor and was controlled only with great difficulty. Dense fumes of nitrobenzene and sulfur dioxide were evolved. By removing the sand bath in time the reaction can be controlled so that the contents of the flask do not rise in the condenser. The reaction-mixture is, at first, dark brown but during the course of the reaction it changes to a beautiful red-purple product which finally changes to black. By increasing the temperature rapidly it can be raised to 220° without the slightest sign of the reaction but on cooling the contents of the flask to 185° an energetic reaction starts and the temperature again rises about 50°. Below 170° no reaction takes place. By increasing the proportion of acid, the reaction becomes uncontrollable.

The Reaction-Product.—When cold the product was removed from the flask and washed on a Büchner funnel with water until free of sulfuric acid. It was then washed with ether to remove the last traces of adhering nitrobenzene, the ether extract being allowed to flow into the acid filtrate which contained the bulk of the unchanged nitrobenzene. From the ether extract the nitrobenzene was finally recovered. The average amount obtained was 83 g., or more than half of that taken from the experiment. The reaction-product was powdered and then boiled hard with several portions of distilled water, about six liters in all being used. It was filtered and dried over a water bath. The average quantity obtained in several experiments was 52 g.

This black product is a melanin-like substance whose particles show, after the most thorough grinding, definite cleavage planes when viewed under the microscope. It is practically insoluble in most organic solvents. In nitrobenzene, pyridine, quinoline, and trimethylamine, it is slightly soluble. The pyridine, quinoline, and trimethylamine solutions are reddish purple and manifest a beautiful red-brown fluorescence. It does not crystallize from any of these solvents. From nitrobenzene it separates in the amorphous form. With cold concentrated sulfuric acid, it gives an indigo-blue solution which changes to a brown color when heated.

¹ THIS JOURNAL, 36, 1247 (1914); *Ber.*, 40, 432 (1907).

On diluting the cold sulfuric solution with water, it is again precipitated. It dissolves completely when boiled with a concentrated solution of sodium hydroxide, giving a brown solution which reduces with sodium hydro-sulfite to a brown vat in which cotton is dyed a steel-gray black. This is not fast to boiling alkali. If the reduction is done below 70° , cotton dyes in the vat produced a purplish black. By neutralizing a sodium hydroxide solution of the black product with sulfuric acid, a substance which appears to be different from the original material is obtained. The black product is slightly soluble in ammonium hydroxide. Its solution in this solvent has a reddish purple color which changes to blue on heating. By boiling the product several hours with alcohol, a dark red solution showing brown-red fluorescence is obtained. This on evaporation gives a small amount of a brick-red powder which resembles azoresorufin.¹ The difficulty in ascertaining the purity of these substances makes it impossible at the present time to determine their constitution. The investigation of them will continue in this laboratory.

***p*-Aminophenol-*o*-sulfonic Acid.**—The cold and the hot water washings from the main product were evaporated separately and several fractions of a gray crystalline substance were obtained. On recrystallization, all the fractions proved to be the same substance. It is capable of crystallizing in several different forms. By securing a very concentrated solution and cooling it quickly under running water, radiating tufts of very fine, long, transparent needles formed. By allowing the same solution to cool slowly, hexagonal plates with beveled edges were obtained. From a less concentrated solution, thin, transparent, small plates separated. By slower crystallization from the latter solution were obtained large, wedge-shaped crystals. By long and tedious experimentation the conditions were discovered under which all the several forms could be converted into the form of the silky needle crystals. From 83 g. of nitrobenzene 12 g. of the phenol were obtained.

Calc. for $C_6H_7O_3NS$: S, 16.93. Found: S, 16.99.

The substance is practically insoluble in most organic solvents. It dissolves with difficulty in boiling water. It has no melting point. An ammoniacal solution of it reduces cold silver, mercury, and copper salts. With barium chloride the ammoniacal solution, from which the excess of ammonia has been driven off, gives a barium salt which crystallizes in radiating tufts of brown needles. A neutral solution of the substance gives a violet color with ferric chloride. When the substance is heated in a dry tube it decomposes, giving a violet-red sublimate and evolving ammonia. By heating the substance with concentrated sulfuric acid, the black product is obtained. It is interesting in this connection to call

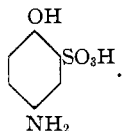
¹ *Ber.*, 17, 1867 (1884).

attention to the fact that Gortner¹ has shown the probable relation between melanin and aminophenols. The neutral solution of the substance darkens in the air and on long standing gives a substance which is very soluble in water and which gives a green salt with sodium hydroxide. The green color disappears after a few minutes but reappears again when the solution is shaken. The substance giving the remarkable color changes is present in a very unstable form and so far we have not succeeded in isolating it from solution. With phosphorus pentachloride the aminophenol sulfonic acid gives a chloride which with aniline forms an anilide melting at 98°. It also gives bromanil when treated with bromine. By heating the aminophenol sulfonic acid with concentrated hydrochloric acid to 170° it is converted into *p*-aminophenol. By boiling it with ferric chloride it is oxidized to quinone.

p-Aminophenol-*o*-sulfoanilide.—A very small quantity of the sulfonic acid was warmed on a sand bath with phosphorus pentachloride. A brown oily product formed. When the hydrochloric acid was completely evolved, pure aniline was added. A brown gummy mass resulted. This was boiled with dilute hydrochloric acid and the liquid portion decanted off. The remaining solid was washed with water and dissolved in alcohol. It was filtered. The filtrate was diluted with distilled water and a white amorphous substance separated. This was filtered and dried. It melted at 98°.

Bromanil.—A small portion of the sulfonic acid was suspended in a few cc. of glacial acetic acid and treated with a solution of bromine in glacial acetic acid. On standing a few hours a yellow substance separated. This was filtered and washed with dilute acetic acid. It sublimed at about 220° and melted at about 300°. These properties agree with the description of bromanil, C₆Br₃O₂.²

All the evidence from the behavior of the sulfonic acid proves it to be identical with *p*-aminophenol-*o*-sulfonic acid,



Summary.

At a temperature above 170° concentrated sulfuric acid converts nitrobenzene into a mixture of a black, alkali-soluble, amorphous substance which resembles melanin and *p*-aminophenol-*o*-sulfonic acid. The reactions seem to be general for nitrocarbocyclic compounds.

When β -aminoanthraquinone, anthraquinone, and anthracene are separately added to the mixture of nitrobenzene and sulfuric acid, reac-

¹ *J. Biol. Chem.*, 10, 89.

² Beilstein, Vol. 3, p. 337.

tion-products are obtained which are similar but not identical with the product obtained in the reaction with nitrobenzene alone. These substances appear to take part in the reaction. No aminophenolsulfonic acid is obtained.

The black products reduce in each case to form vat dyes from which cotton is dyed. The product from nitrobenzene dyes cotton a steel-gray. That from the aminoanthraquinone gives a brown vat oxidizing on cotton to a heliotrope. The anthraquinone product dyes cotton steel-gray. The product obtained with anthracene is less readily reduced than the others mentioned and dyes cotton brown. None of these dyes are fast to boiling alkalis.

The average yield of *p*-aminophenol-*o*-sulfonic obtained was about 10% of the theory.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

A HYDRATE OF ANTHRAQUINONE 2,7-SODIUM SULFONATE.

By M. L. CROSSLEY.

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In a previous communication,¹ the author has shown that in the separation of the sodium salt of the mono- β -sulfonic acid of anthraquinone and the salts of the 2,6- and 2,7-disulfonic acids, in mild acid solution, a salmon-pink substance of very striking properties is obtained. It is a very sensitive indicator and is unlike any anthraquinone sulfonate thus far described. Its chemical activity is very marked. It forms unstable products with ethyl alcohol, chloroform, and toluene.

The natural assumption, in view of the dissimilarity of the substance to other anthraquinone compounds, was that it was formed from some impurity in the anthraquinone. The evidence against this view, at the very outset, was strong. In the first place, the yield was 9 g. from 50 g. of anthraquinone. In the second place, the product was not obtained by other methods of separating the acids. Chemically pure anthraquinone from two sources was crystallized several times from glacial acetic acid and then from benzene, but it still gave the salmon-pink compound. Analysis of the compound showed that it contained at least 14 carbon, 2 sulfur, and 2 sodium atoms.

Calc. for $C_{14}H_8O_8S_2Na_2$: C, 39.07%; H, 1.86%; O, 33.50%; S, 14.88%; Na, 10.69%. Found: C, 39.17; H, 1.93; O, 33.32; S, 14.85; Na, 10.73.

The substance gives the anthranol test. When fused with potassium hydroxide it gives 1,2,7-trihydroxyanthraquinone. It is clear from this evidence that the anthraquinone nucleus is present in the substance. It is also certain that there are two sulfonic groups in the 2,7-positions

¹ THIS JOURNAL, 37, 2178 (1915).