(5) Both labor and cost of materials are reduced. This allows cellobiose to be prepared commercially at a figure which is not prohibitive to those laboratories desiring to use it in public health work.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

HYDROXYNAPHTHOQUINONE STUDIES. VII. THE BROMINATION OF NAPHTHAZARIN

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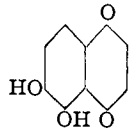
The first study of the bromination of naphthazarin was carried out by one of us and Edwards.[2] The constitution of naphthazarin was regarded at that time as 5,6-dihydroxy-1,4-naphthoquinone but it has now been proved to be 5,8-dihydroxy-1,4-naphthoquinone. Dimroth and Ruck[3]



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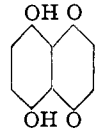


New

have shown that pyroboro-acetate reacts with naphthazarin to form a diboro-acetate. Therefore, the two hydroxyl groups must be para to each other and not ortho, since this reaction occurs between carbonyl and hydroxyl groups ortho to each other. Pfeiffer[4] has shown that tin tetrachloride forms an addition product with loss of one molecule of hydrochloric acid, such a reaction occurring with hydroxyquinones where the carbonyl is ortho to the hydroxyl group. Many formulas in the literature are now affected by this new formula for naphthazarin.

Bromination of Naphthazarin

Naphthazarin takes up a maximum of four atoms of bromine in hot glacial acetic acid solution. Positions 2, 3, 6 and 7 are undoubtedly occupied (Formula II). This tetrabromo naphthazarin gives a diacetyl derivative (III) and a dianilide (IV) on boiling with aniline. In the latter reaction the aniline may have reacted with the bromine atoms of the quinone ring or with those of the phenol ring. The same doubt exists in regard to the relative mobility of the hydrogen atoms of the two rings in naphthazarin. When two chlorine or bromine atoms are taken up, which ring do

[1] This paper is an abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at the University of North Carolina, in June, 1927.

[2] Wheeler and Edwards, THIS JOURNAL, **39**, 2460 (1917).

[3] Dimroth and Ruck, *Ann.*, **446**, 123 (1926).

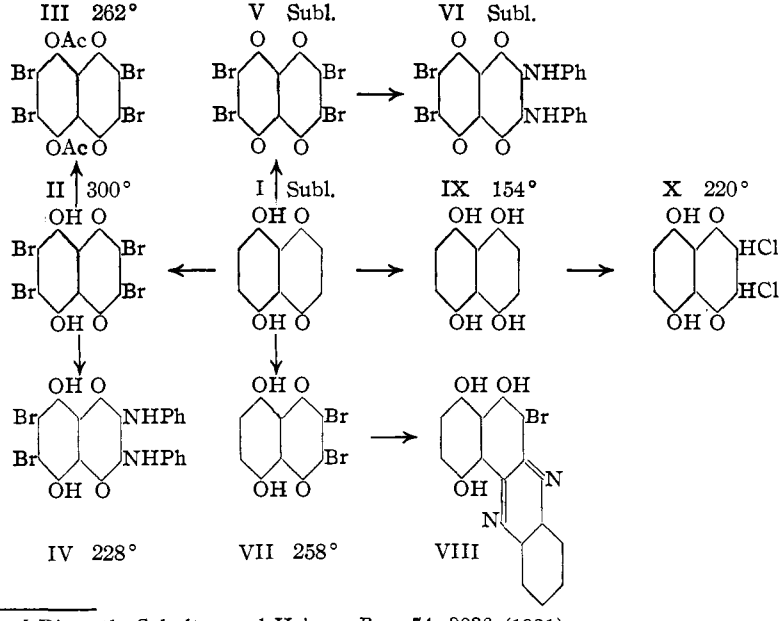
[4] Pfeiffer, *Ber.*, **60**, 111 (1927).

they enter? In all of these cases Positions 2 and 3 in the quinone ring have been regarded as the ones affected. We hope some time to settle this question positively.

If a large excess of bromine is used, naphthazarin takes up four atoms as before but in addition its hydroxyl groups are oxidized, giving a tetrabromoquinone (V). Dimroth, Schultze and Heinze[5] noted that bromine in potassium bromide solution oxidized quinizarin to quinizarin quinone, a reaction analogous to the action of iodine on hydroquinone which yields *p*-quinone. Two atoms of bromine in (V) were replaced by aniline residues, giving (VI).

If two molecules of bromine are used, naphthazarin is converted into a dibromo substitution product (VII), a compound previously made by one of us and Edwards[6] from tetrahydroxynaphthalene. It reacts with *o*-phenylenediamine to form a purplish-blue compound, believed to be a Eurhodol, but we failed to obtain it in a pure state (VIII).

Other reactions included the chlorination of tetrahydroxynaphthalene, which gave naphthazarin dichloride (X), obtained by Zincke and Schmidt[7] from naphthazarin. Napthazarin was boiled with phosphorus trichloride but no new product could be isolated. It was nitrated by three methods but no nitration product was obtained. It was coupled with *p*-chloroaniline but the product could not be purified.



[5] Dimroth, Schultze and Heinze, *Ber.*, **54**, 3036 (1921).

[6] Ref. 2, p. 2647.

[7] Zincke and Schmidt, *Ann.*, **286**, 41 (1895).

Experimental Part

2,3,6,7-Tetrabromonaphthazarin (II).—Five g. (1 mole) of pure sublimed naphthazarin was dissolved in 139 cc. of glacial acetic acid and treated with 15.9 g. of bromine (a little less than four moles). The mixture was boiled under a reflux for eight hours. The product separated on cooling the solution. It was recrystallized from glacial acetic acid, using 35–45 cc. of acid for each gram of product. The crystals are slender, flat, bronze-colored needles, melting at 300°. The compound is insoluble in ether, difficultly soluble in hot alcohol and acetone but easily soluble in hot chloroform, carbon tetrachloride and glacial acetic acid. It is very soluble in toluene. This derivative may also be prepared by allowing the brominating mixture to stand for three weeks at room temperature.

Anal. Subs., 0.1195: AgBr, 0.1772. Calcd. for $C_{10}H_2O_4Br_4$: Br, 63.24. Found: 63.11.

Acetylation yields a diacetate and aniline a dianilide derivative. The bromine is removed by boiling the compound with a 2% hydrochloric acid solution of stannous chloride.

Diacetate (III).—The diacetate was best prepared by first making the sodium salt of the tetrabromonaphthazarin by the ether-sodium carbonate method and then treating the salt with a mixture of equal parts of acetyl chloride and acetic anhydride. Enough of the liquid mixture was used to act as a solvent. It was heated until no further change took place in color, which passed from blood-red to yellow. The product was precipitated with water. It is easily soluble in glacial acetic acid, acetone, chloroform and benzene but difficultly soluble in alcohol and ether. It is best recrystallized from boiling chloroform. It forms light yellow, granular crystals, melting at 262°. It can also be prepared from tetrabromodiquinone by simultaneous reduction and acetylation.

Anal. Subs., 0.1714: AgBr, 0.2185. Calcd. for $C_{10}H_6O_6Br_4$: Br, 54.24. Found: 54.25.

Dianilide (IV).—Two g. (1 mole) of tetrabromonaphthazarin was dissolved in 250 cc. of alcohol and 1 g. of aniline added. The mixture was refluxed for eight hours when, judging from the color of the solution, the reaction was complete. The solution was concentrated to 25 cc. and cooled. The product was recrystallized three times from glacial acetic acid. It consisted of microscopic bronze-colored needles, melting at 251°. There were some red fumes about twenty degrees below the melting point; weight, 2.3 g. It is easily soluble in benzene, alcohol and glacial acetic acid. It dissolves in sodium carbonate solution.

Anal. Subs., 0.1626: AgBr, 0.1200. Calcd. for $C_{22}H_{14}O_4N_2Br_2$: Br, 31.83. Found: 31.41.

2,3,6,7-Tetrabromodiquinone (V).—Five g. of naphthazarin was dissolved in 150 cc. of glacial acetic acid and treated with 30 g. of bromine, nearly double the amount required to make tetrabromonaphthazarin. The mixture was allowed to stand for five weeks at room temperature. At the end of this period a yellow product had settled out. Under the microscope the crystals were found to be yellow platelets, highly refractive and mixed with some red needles. The latter were probably naphthazarin since, on heating the product, red fumes began to appear at 180°. Purification was accomplished by recrystallizing from boiling glacial acetic acid, ethyl acetate or toluene. The quinone is difficultly soluble in glacial acetic acid, acetone, chloroform and benzene; nearly insoluble in alcohol. When recrystallized from acetic acid or ethyl acetate, the color changes from yellow to red and the crystalline form from platelets to microscopic needles. The pure substance sublimes at 275–280°. It is insoluble in sodium carbonate solution. Its preparation can be carried out in hot solution.

Anal. Subs., 0.2538: AgBr, 0.3760. Calcd. for $C_{10}O_4Br_4$: Br, 63.46. Found: 63.04.

The diquinone can be reduced and acetylated in one operation using zinc dust and acetic anhydride, yielding diacetyltetrabromonaphthazarin (III).

Dianilide (VI).—This product was prepared in the same manner as (IV), glacial acetic acid, however, being used as solvent. One g. of the diquinone gave 0.7 g. of product. On recrystallizing from glacial acetic acid, it formed brown needles with a metallic luster, subliming at 220–225°. It is easily soluble in alcohol, benzene and glacial acetic acid, less soluble in ether, nearly insoluble in petroleum ether and insoluble in sodium carbonate solution.

Anal. Subs., 0.3062: AgBr, 0.2288. Calcd. for $C_{22}H_{12}O_4Br_2$: 31.97. Found: 31.78.

2,3-Naphthazarin Dichloride (X).—This compound was obtained by Zincke and Schmidt[7] by chlorinating naphthazarin. We obtained it from tetrahydroxynaphthalene. Two and one-half g. of the latter compound was dissolved in 30 cc. of chloroform and cooled with ice. Dry chlorine was passed in slowly for ten hours. The solution at the end of this time was red, due to a small amount of impurity. The solution was concentrated by blowing off some of the solvent with air. The product was filtered and a small quantity of red crystals was dissolved out on the filter by dropping cold acetone upon the material while the suction was on. The product became pure yellow and melted at 220°.

2,3-Dibromonaphthazarin (VII).—This compound was first made by one of us and Edwards[6] from tetrahydroxynaphthalene. This preparation was made from naphthazarin. One g. (1 mole) of naphthazarin was dissolved in 25 cc. of glacial acetic acid and treated with 1.5 g. of bromine (slightly less than 2 moles). The solution was boiled for four hours. The product, recrystallized from glacial acetic acid, consisted of red leaves of a metallic luster, melting at 258°; weight, 1.3 g. This product will sublime. The reaction may also be carried out at 70°. No anilido derivative could be obtained. An attempt was made to prepare a Eurhodol. A mixture of 1.75 g. of dibromonaphthazarin and 0.60 g. of *o*-phenylenediamine was dissolved in 200 cc. of absolute alcohol and refluxed for eight hours; 1.5 g. of a purplish-blue compound was obtained. It was nearly insoluble in the usual organic solvents. As it dissolved slightly in glacial acetic acid, large amounts of this were used in an attempt to purify the product. It decomposes at about 225°. The substance was not pure, as the content of bromine was 3% low.

Other Reactions

Action of Phosphorus Trichloride.—Two g. of naphthazarin was mixed with 5 g. of dry sodium carbonate and 75 cc. of phosphorus trichloride and refluxed for thirteen hours. The solution became yellow and some yellow substance collected in the condenser. It was poured into sodium carbonate solution. The dirty red precipitate was insoluble in the usual organic solvents. Its sodium hydroxide solution was intensely blue.

Nitration.—Three methods of nitration were tried: (1) a mixture of boric, sulfuric and nitric acids; (2) sulfuric and nitric acids; (3) acetic and nitric acids. The reactions were carried out at 5°. In each case the product was reduced with stannous chloride and diquinol, melting at 154°, obtained.

Coupling with Amines.—*p*-Chloro-aniline was diazotized and coupled

with naphthazarin. The analysis showed a deficiency of 1.4% of chlorine. We were unable to purify the product further.

We hereby wish to thank the Badische Anilin und Soda-Fabrik of Ludwigshaven on the Rhine for a very generous supply of sublimed naphthazarin.

Summary

1. Recent work shows that the hydroxyl groups in naphthazarin are para to each other and not ortho.

2. The following new derivatives of naphthazarin were prepared: 2,3,6,7-tetrabromonaphthazarin, its diacetate and dianilide; 2,3,6,7-tetrabromodiquinone and its dianilide.

3. The known dichloride of naphthazarin was also made from diquinol and likewise the known dibromonaphthazarin.

4. Certain unsuccessful reactions are noted.

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[COMMUNICATION NO. 311 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY]

THE LOWER FATTY ACIDS OF COCONUT OIL

BY E. R. TAYLOR AND H. T. CLARKE

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The analysis of coconut oil has been carried out in a variety of ways, each of which has led to a widely different result. A full discussion of the subject is to be found in the paper of Armstrong, Allan and Moore,[1] in which it was clearly shown by these authors that fractionation of the esters of the acids can yield significant results only when the separation of the various components has been so complete as to yield these in substantially pure form, so that the saponification values of the intermediate fractions may legitimately be employed for the estimation of their composition. These authors conducted their fractionation on the ethyl esters obtained from not more than one kilo of coconut oil, and were unable to detect any acid lower than caprylic acid.

We have carried out a systematic fractionation on approximately 130 kilos of methyl esters obtained from commercial coconut oil[2] by a modification of the method of Haller and Youssoufian.[3] The fractionation was carried out repeatedly and systematically until the total amount of fractions intermediate between those of the pure components amounted to

[1] Armstrong, Allan and Moore, *J. Soc. Chem. Ind.*, **44**, 63T (1925).

[2] This material was stated by its manufacturers (the Procter and Gamble Company) to have been prepared from copra of mixed origin but to be of representative quality.

[3] Haller and Youssoufian, *Compt. rend.*, **143**, 803 (1906).