hydrochloride of the above base were obtained. This salt crystallized from dilute hydrochloric acid as clusters of slender needles, which melted at 180° to a colorless oil.

Calc. for $C_{16}H_{20}ONCl$: N, 4.78. Found: N, 4.73, 4.49.

In order to obtain the free base the hydrochloride was decomposed by ammonia and the amine extracted with ether. After drying the ether solution over sodium sulfate the solvent was then evaporated, when the amine was obtained as a solid. It crystallized from 95% alcohol in the form of needles and melted at 99–100° to a clear oil. It was dried for analysis over concentrated sulfuric acid.

Calc. for $C_{16}H_{19}O_2N$: N, 4.34. Found: N, 4.5, 4.6.

Part of the Schiff base underwent hydrolysis during the above operation and we recovered 1.2 g. of the hydrochloride of phenylethylamine.

NEW HAVEN, CONN.

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

A NEW CASE OF TAUTOMERISM: 1,4,5,6-TETRAHYDROXYNAPHTHALENE.[1]

BY A. S. WHEELER AND V. C. EDWARDS.

Received December 20, 1915.

Zincke and Schmidt[2] reduced 5,6-dihydroxy-α-naphthoquinone (naphthazarine) with stannous chloride, obtaining a yellow compound, melting at 154°, which they designated 1,4,5,6-tetraoxynaphthalin. Its phenolic character was indicated by the easy preparation of a tetracetyl derivative, colorless prisms melting at 277–9° with decomposition, and also by the fact that its solutions show a strong greenish fluorescence. A peculiar behavior of the solutions was noted in that they soon turn red if exposed to the air and deposit red crystals, which melt at the same temperature as the yellow compound, 154°. The deep color is retained after recrystallization. Heating and the presence of oxidizing agents hasten the change from yellow to red, but ultimate analysis indicates no change in composition and the two forms yield the same derivatives. The authors attributed the color to the presence of a highly colored oxidation product in slight amount. This peculiarity and the results obtained by Willstätter and Wheeler[3] on the hydrojuglones led to the study of this phenol.

The Badische Anilin u. Soda-Fabrik, Ludwigshafen am Rhein, gener-

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[1] This paper forms Part I of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of North Carolina by V. C. Edwards. Part II on The Bromination of 1,4,5,6-Tetrahydroxynaphthalene will appear later.

[2] *Ann.*, **286**, 27 (1895).

[3] *Ber.*, **47**, 2796 (1914).

ously supplied the naphthazarine required for this research and we take this opportunity to express to them our sincere gratitude.

Willstätter and Wheeler reduced juglone and obtained α-hydrojuglone, a trihydroxynaphthalene of grayish green color, which readily passed on melting into the ketone form, a yellow compound, which had been regarded by Mylius[1] as another trihydroxynaphthalene, a theory which involves the migration of an hydroxyl group. The discovery of the ketone character of the β-hydrojuglone suggested the possibility that the tetrahydroxynaphthalene might also exist in two forms and our study of the compound shows that this is the case. We treated the tetrahydroxynaphthalene with the important ketone reagents, hydroxylamine, semicarbazine, phenylsemicarbazine, and several others not so often used. No oxime could be otained, only a black amorphous product. The phenols of the naphthalene series are very sensitive to alkalies and our study shows that hydroxylamine is too basic. Semicarbazine, which is less basic, gave a crystalline product mixed with some amorphous material which, however, we were unable to remove. Phenylsemicarbazine, containing the added negative phenyl group, gave readily a pure crystalline phenylsemicarbazone. Other ketone reagents containing negative groups, as *p*-bromophenylsemicarbazine, *p*-nitrophenylsemicarbazine, benzhydrazine and *p*-nitrobenzhydrazine gave equally fine yellow crystalline products which were readily obtained in pure condition.

If we regard the hydrogens which were introduced by the reduction of naphthazarine as the more mobile ones, then there is the possibility of the presence of two ketone groups. This idea did not occur to Willstätter and Wheeler in their study of the hydrojuglones. By employing two molecules of phenylsemicarbazine we obtained a compound, the yield of which was 98% of the theoretical for a diphenylsemicarbazone. We have, however, been unable to obtain it perfectly pure. We made numerous attempts to methylate the tetrahydroxynaphthalene. Gummy or amorphous products were obtained with dimethylsulfate and also with diazomethane in ether solution but a chloroform solution gave a crystalline product. Methyl alcohol and sulfuric acid gave a derivative which, though it had no sharp melting point, gave good figures for a monomethyl ether. We were unable to prepared any metallic derivatives of tetrahydroxynaphthalene.

The tautomerism of 1,4,5,6-tetrahydroxynaphthalene differs from that of the hydrojuglones which are very easily obtained pure in the enol and keto forms. We tried many methods of conversion from enol to keto and of keto to enol forms but nothing has come under our notice except the yellow compound which melts at 154° and the red melting at the same point. All endeavors to distinguish any difference in behavior of

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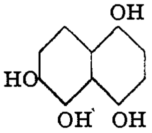
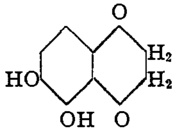
[1] *Ber.*, 18, 478, 2571 (1885).

the yellow and red forms proved unavailing. Of these experiments one was a comparison of the speed of reaction of the two forms in alcoholic solution with phenylsemicarbazine. In both cases the carbazone began to appear at the end of six hours and the two reactions gave like yields. The development of the red color is largely prevented by substituting nitrogen for air. A slight amount of stannous chloride will also prevent the assumption of the red color. Single red crystals appear yellow under the microscope. A mass of crystals viewed directly is dark red and so are the solutions. Our conclusion is that the form of tautomerism here is like that of phloroglucinol where we are able to lay the finger upon one form only which reacts readily with both phenol and ketone reagents. Previous investigators have regarded the compound only as a phenol. We may represent the formulas as follows:





Experimental.

Purification of Naphthazarine.—The naphthazarine as obtained from the Badische Anilin u. Soda-Fabrik was not pure and a study of its purification was undertaken by Mr. V. C. Coulter in this laboratory. The purity of the product of each experiment was qualitatively tested by reducing a pinch with stannous chloride and hydrochloric acid. If the product was a clear yellow, it was comparatively pure. If it was greenish or blackish, it indicated an unsatisfactory method of purification. All of the well-known organic solvents and numerous mixtures of these were unavailing. Solution in alkali and reprecipitation with acid also proved unsatisfactory. Sublimation in an atmosphere of carbon dioxide at 230–40° gave a pure product but a small yield. Finally sublimation *in vacuo* in an electrically heated apparatus was resorted to with success. The apparatus of Morey[1] suggested to us the best arrangement. An abandoned base of an old style vacuum pump served perfectly for the bottom piece. A second inverted glass cylinder set within the crystallizing dish reduced the area upon which the naphthazarine condensed. A platinum dish was used to hold the substance. The heating element was made by winding nichrome wire around a plate of asbestos. A vacuum of 2–10 mm. was maintained and a current of 1.5 amperes was required. Each charge of 20 g. was sublimed in about eight hours. The yield of pure naphthazarine was 70% or over.

Reduction of Naphthazarine.—The use of alcohol as employed by Zincke and Schmidt was abandoned when it was found that a purer product

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[1] THIS JOURNAL, 34, 550 (1912).

could be obtained with hydrochloric acid alone. Twenty grams of sublimed naphthazarine were boiled 20 minutes in 5 liters of 12% hydrochloric acid with the addition of 100 g. of stannous chloride. The light yellow solution was filtered hot with suction and allowed to cool down. About 18 g. of tetrahydroxynaphthalene crystallized out in plates or prisms which melted at 153–4°. Recrystallization was unnecessary.

Attempt to Prepare the Oxime.—Two-tenths of a gram of tetrahydroxynaphthalene, 0.075 g. of hydroxylaminehydrochloride and 0.10 g. of barium carbonate were heated with 15 cc. of absolute alcohol for four hours, and then allowed to stand for four days. No crystalline product could be isolated from the black amorphous precipitate or from the solution.

Semicarbazone, $C_{11}H_{11}O_4N_3$.—One gram of tetrahydroxynaphthalene was dissolved in 100 cc. of absolute alcohol and to this was added 0.57 g. of semicarbazine hydrochloride and 0.51 g. of potassium acetate in 3 cc. of water. The solution was kept in a stoppered flask. Crystallization began in four hours and was complete in a day when 1.05 g. of yellow crystals were filtered off. When heated these gave off violet vapors at 170–200°, becoming a soft, black mass. The product, consisting of yellow prisms, was insoluble in water and ligroin and only slightly soluble in other cold solvents. The solubility was only slightly increased in hot solvents. In all cases the microscope revealed a little amorphous material. The three samples analyzed were purified by extracting the impurities so far as possible with large quantities of solvents. I. 1.0 g. was shaken 24 hours with 500 cc. of methyl alcohol. II. 1.1 g. were shaken with 1 liter of ether and then with 500 cc. of methyl alcohol, each 24 hours. III. A portion of II was then shaken with 500 cc. of benzene and finally with 500 cc. of carbon tetrachloride, each 24 hours.

Calc. for $C_{11}H_{11}O_4N_3$: N, 16.85. Found: I, 18.50; II, 17.67; III, 17.01.

Phenylsemicarbazone, $C_{17}H_{15}O_4N_3$.—Two grams of the tetrahydroxynaphthalene were dissolved in 200 cc. of absolute alcohol and mixed with 1.6 g. of phenylsemicarbazine dissolved in 50 cc. of absolute alcohol. The solution was kept in a stoppered flask. In six hours clusters of yellow crystals began to form and after 24 hours 2.7 g. of product were filtered off. It crystallized from absolute alcohol in fan-shaped groups of short, stout needles, which melted at 218° with decomposition, giving off violet vapors.

0.1840 g. subst. gave 0.4128 g. CO_2 and 0.0826 g. H_2O; 0.1570 g. subst. gave 17.54 cc. N_2 (18° and 757.5 mm. over 40% KOH).

Calc. for $C_{17}H_{15}O_4N_3$: C, 62.74; H, 4.65; N, 12.93. Found: C, 62.40; H, 5.12; N, 12.87.

To see if the reaction with phenylsemicarbazine would give any hint as to whether the yellow and red forms of the tetrahydroxynaphthalene represented enol and keto forms, comparative reactions were run both in alcohol and chloroform solutions. In the alcohol solutions the phenylsemicarbazone appeared in six hours and in like amount when the reaction was complete. In the chloroform solutions the results were the same, except that the crystallization began in four hours. Thus no hint was obtained.

The phenylsemicarbazone is easily soluble in acetone, xylene and pyridine, much less soluble in alcohol, chloroform and benzene and insoluble in the other ordinary solvents. It was recrystallized from alcohol or chloroform.

Diphenylsemicarbazone.—In view of the reduction of two quinone oxygens, there should be two labile hydrogen atoms and hence the possibility of a diphenylsemicarbazone. One-half gram (1 mol.) of the tetrahydroxynaphthalene and 0.8 g. (2 mols.) of phenylsemicarbazine were dissolved in 70 cc. of absolute alcohol and set aside in a stoppered flask. Crystallization began in about 3 hours and after 3 days 1.17 g. of product, consisting of yellow prisms, were filtered off. The crystals were very slightly soluble in acetone, ethyl and amyl alcohols and practically insoluble in other organic solvents. Acetone extracted a small quantity of a compound consisting of scales and melting at 120–1°. The insoluble crystals consisted of hexagonal plates which darkened at 280° and at 285–7° a dark liquid condensed on the upper walls of the capillary tube.

0.1621 g. subst. gave 25 cc. N_2 (26° and 752 mm. over 40% KOH). Calc. for $C_{24}H_{22}O_4N_6$: N, 18.34. Found: 17.04.

We were unable to obtain a purer compound. The war shut off our supply of naphthazarine and hence this investigation is temporarily interrupted.

***p*-Bromophenylsemicarbazone,** $C_{17}H_{14}O_4N_3Br$.—Two grams of tetrahydroxynaphthalene, dissolved in 200 cc. of alcohol, were mixed with 2.4 g. of *p*-bromophenylsemicarbazine in 250 cc. of alcohol. In 7 hours no reaction was apparent but in 8 days a product weighing 1.47 g. was obtained. It was insoluble in water and ligroin but soluble in alcohol, ether, benzene, chloroform and carbon tetrachloride. It crystallizes from hot acetone in yellow needles which decompose at 220–3°.

0.0688 g. subst. gave 0.0416 g. AgBr. Calc. for $C_{17}H_{14}O_4N_3Br$: Br, 19.97. Found: 19.54.

***p*-Nitrophenylsemicarbazone,** $C_{16}H_{13}O_5N_3$.—One and one-half grams of tetrahydroxynaphthalene and 1.2 g. of *p*-nitrophenylsemicarbazine were dissolved in 200 cc. of absolute alcohol and set aside in a stoppered flask. After 6 hours crystallization began and after 40 hours 1.23 g. of greenish yellow crystals were filtered off. The product was not readily soluble in alcohol, ether or benzene. It crystallized from hot acetone in yellow needles or prisms which began to decompose at 234° and at about 241° gave off violet vapors.

0.0871 g. subst. gave 9.90 cc. N_2 (17° and 748 mm. over 40% KOH). Calc. for $C_{16}H_{13}O_6N_3$: N, 12.85. Found: 12.98.

Benzhydrazone, $C_{17}H_{14}O_4N_2$.—One-half gram of tetrahydroxynaphthalene in 50 cc. of alcohol was added to 0.4 g. of benzhydrazine in 10 cc. of alcohol. No crystals appeared on the first day but after 4 days 0.51 g. of product was obtained. It was fairly soluble in acetone and alcohol, less so in ether and benzene and insoluble in water. It was purified by dissolving in acetone and pouring the solution into water. The pure substance consisted of beautiful yellow needles which decomposed between 170 and 185°.

0.1087 g. subst. gave 8.85 cc. N_2 (19° and 743.8 mm. over 40% KOH). Calc. for $C_{17}H_{14}O_4N_2$: N, 9.04. Found: 9.17.

***p*-Nitrobenzhydrazone,** $C_{17}H_{13}O_6N_3$.—One-half gram of tetrahydroxynaphthalene and 0.5 g. of *p*-nitrobenzhydrazine were dissolved in 100 cc. of alcohol, warmed for 4 hours and set aside for 2 days. Dark yellow crystals, weighing 0.2 g., were filtered off and from the mother liquor a further quantity was obtained on concentration. These crystallized from acetone in yellow needles which melted at 220–4° with decomposition.

0.0922 g. subst. gave 9.40 cc. N_2 (23° and 744 mm. over 40% KOH). Calc. for $C_{17}H_{13}O_6N_3$: N, 11.83. Found: 11.65.

Action of Dimethylsulfate.—One gram of the tetrahydroxynaphthalene was dissolved in 10% sodium hydroxide and to this was added 2.6 g. of dimethylsulfate. After 40 hours the reaction was examined. The precipitate consisted of dark amorphous material which yielded no crystalline product to any solvent. The reaction was repeated with twice the amount of dimethylsulfate. A few crystals were noted in much amorphous material.

Action of Diazomethane.—Four-tenths of a gram of tetrahydroxynaphthalene were dissolved in ether and treated with a slow current of ether and diazomethane vapors. After an hour some ether solution of diazomethane was added and the mixture was set aside for two days. The solution had become reddish yellow. When it was concentrated *in vacuo* only a black gummy mass was left. A chloroform solution gave better results. 0.2 g. of tetrahydroxynaphthalene was dissolved in dry chloroform and 0.2 g. of diazomethane was passed in slowly. This was practically all absorbed. After a week the chloroform was evaporated off and fan-shaped groups of crystals were obtained but some amorphous material was present. The product weighed 0.18 g. It was almost completely soluble in alcohol or chloroform but was unfortunately lost through an accident. It is hoped to study this reaction again.

Action of Methyl Alcohol in Sulfuric Acid.—1.5 g. of tetrahydroxynaphthalene were dissolved in 500 cc. of absolute methyl alcohol and 15 cc. of conc. sulfuric acid. The mixture was boiled 75 min. under a reflux condenser using a half atmosphere of excess pressure. The reaction mixture was poured into 150 cc. of hot water, boiled and filtered from a slight residue. The reddish filtrate upon cooling gave a large crop of reddish yellow needles which after twice recrystallizing from hot water gradually melted between 115 and 140°.

0.1659 g. subst. gave 0.4976 g. CO_2 and 0.0784 g. H_2O. Calc. for $C_{11}H_{10}O_4$: C, 64.08; H, 4.85. Found: 64.05, 5.32.

The analysis indicates a monomethyl ether but we believe the reaction will bear further study.

Metallic Salts.—Attempts were made to prepare metallic salts of the tetrahydroxynaphthalene. Water and alcohol solutions were used but no salts of barium, lead or silver could be obtained.

CHAPEL HILL, NORTH CAROLINA.

[CONTRIBUTION FROM THE UNIVERSITY OF PITTSBURG, DEPARTMENT OF CHEMICAL ENGINEERING.]

THE PRESENCE OF BENZENE HOMOLOGS IN THE HIGH BOILING DISTILLATES OF PETROLEUM.

BY BENJAMIN T. BROOKS AND IRWIN W. HUMPHREY.

Received December 14, 1915.

In studying the properties of the substances which cause fluorescence in petroleum distillates,[1] the conclusion was drawn that the substances in question were probably related to benzene and the essential facts advanced in support of this hypothesis were the following:

(1) Oils distilled *in vacuo* are much less fluorescent than when distilled slowly at ordinary pressure and accompanied by cracking and formation of relatively large quantities of coke. There is an unmistakable parallelism between the distillation of coal *in vacuo* and at atmospheric pressure and the distillation of oil under similar conditions. In general, destructive distillation of organic material containing little oxygen is conducive to the formation of aromatic hydrocarbons. The coal-tar distillates produced by distillation *in vacuo* are relatively very low in aromatic hydrocarbons and are only very slightly fluorescent.[2]

(2) No fluorescent organic substances are known which belong strictly to the paraffin or naphthene series of hydrocarbons. The vast majority of fluorescent organic compounds, whose constitution is known, possess condensed ring structures such as the derivatives of benzene, naphthalene, anthracene, fluorene, pyrone, acridine, azine, oxazine, thiazine, and the like. The character of the fluorescence of petroleum distillates is affected by such solvents as carbon bisulfide, aniline, nitrobenzene, amyl alcohol,

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[1] Brooks and Bacon, *J. Ind. Eng. Chem.*, **6**, 623 (1914).

[2] A. Pictet, *Ber.*, **46**, 3342 (1913); Jones and Wheeler, *J. Chem. Soc.*, **105**, 2562 (1914); **107**, 1318 (1915).