slowly turned yellow, the melting point falling to 92–93°. The yellow samples upon analysis appeared to have lost iodine.

Anal. Calcd. for $C_{12}H_8OI_2$: I, 57.86. Found: I, 55.10.

The 3,5-diiodo-4-hydroxybiphenyl set free from a sample of this ammonium salt gave white needles which readily decomposed.

(b) Seventeen grams of 4-hydroxybiphenyl was dissolved in 40 ml. of glacial acetic acid. To this mixture, 45 g. of iodine monochloride dissolved in 25 ml. of glacial acetic acid was added dropwise over a period of one-half hour. The mixture was then refluxed on a steam-bath for two hours. Hydrogen chloride gas was liberated freely during the reaction. After this treatment the mixture was cooled to room temperature and poured into a large volume of ice-water. A pale yellow solid and an oily, brown substance separated. Solid sodium bisulfite was added to the mixture in order to remove the iodine to some extent. The water soluble constituents of the mixture were decanted and the remaining portion extracted with carbon tetrachloride. The carbon tetrachloride solution was washed with sodium bisulfite solution which removed the remaining iodine and was then washed with water and dried over anhydrous sodium sulfate.

After the solution had dried, its volume was reduced to one-fourth the original volume by distillation under reduced pressure. Addition of petroleum ether to the remaining solution caused 21 g. of a white precipitate to separate. After dissolving the precipitate in chloroform and precipitating it from solution by the addition of petroleum ether several times and finally recrystallization from the mixed solvent of one-third chloroform and two-thirds petroleum ether (b. p. 30–35°), the yield was reduced to 4.8 g. The pure white solid melted at 86–87°.

Anal. Calcd. for $C_{12}H_8OI_2$: I, 60.15. Found: I, 60.07.

Benzoylation of 3,5-Diiodo-4-hydroxybiphenyl.—The procedure used to prepare 3,5-diiodo-4-benzoxybiphenyl was the same as given above for the preparation of 3-iodo-4-benzoxydiphenyl. The product was recrystallized from ethanol. The resulting white needles melted at 159–160°.

Anal. Calcd. for $C_{19}H_{12}O_2I_2$: I, 48.24. Found: I, 47.80.

Attempted Triiodination of 4-Hydroxybiphenyl.—Several attempts were made to prepare this compound in the manner described above for the mono- and diiodination of 4-hydroxybiphenyl by varying the solvent, the time of reaction and external heat applied. In each attempt, however, isolation of the desired product was unsuccessful.

Summary

4-Hydroxybiphenyl has been mono- and diiodinated forming 3-iodo-4-hydroxybiphenyl and 3,5-diiodo-4-hydroxybiphenyl, respectively. They were identified by analysis and analogy to the chlorination and bromination products of 4-hydroxybiphenyl.

Attempts to triiodinate 4-hydroxybiphenyl were unsuccessful.

The benzoate derivatives of the above mono- and diiodo-hydroxybiphenyls have been prepared. The mononitro derivative of 3-iodo-4-hydroxybiphenyl also has been obtained.

NORMAN, OKLAHOMA
AUSTIN, TEXAS
RECEIVED OCTOBER 1, 1943

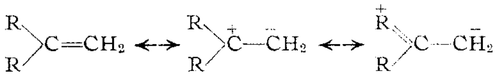
[CONTRIBUTION FROM THE MARIAN EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

The Condensation of Naphthoquinones with Polar Ethylenes

BY MARSHALL GATES

In 1939 Wizinger and Coenen[1] showed that a carbon–carbon bond could be established by displacement of chlorine from polynitro aromatic chlorides using as displacing agents certain unsymmetrically substituted ethylenes.

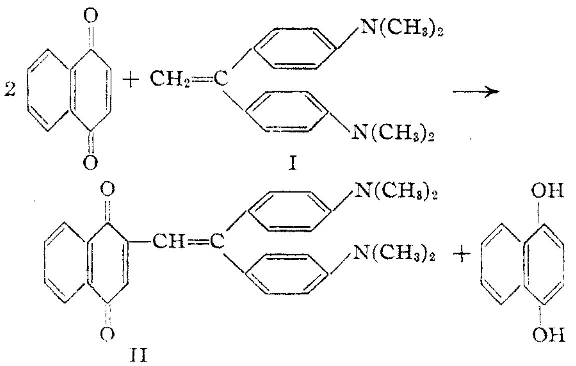
The ethylenes involved were of the type whose members readily form halochromic salts and show reactions with other types of electron acceptors.[2] Their reactions indicate large contributions from forms in which the ethylenic link is polarized



$$\mathrm{R_2C{=}CH_2} \longleftrightarrow \mathrm{R_2\overset{+}{C}{-}\overset{-}{C}H_2} \longleftrightarrow \mathrm{\overset{+}{R}(R)C{-}\overset{-}{C}H_2}$$

Since many of the reactions of quinones involve the addition of a molecule with an unshared electron pair to the conjugated system of the quinone, it might be expected that a carbon–carbon bond could be established by the action of a polar ethylene of the above-mentioned type acting as an electron donor on a quinone acting as an electron accepting center. This expectation was fully realized and a number of condensations of this type were found to take place with ease.

To provide a trial free from the complicating side reactions which might be expected of benzoquinone, the action of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene (I) on α-naphthoquinone was studied. On mixing these two reagents in benzene, acetone or dioxane, an intense deep purple color is produced immediately even at room temperature, and on standing the solution deposits beautiful fine purple needles of 2-(1′,4′-



II

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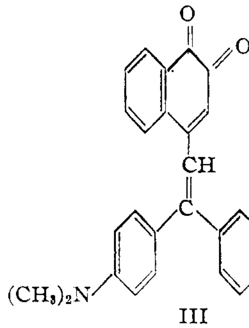
[1] Wizinger and Coenen, *J. prakt. Chem.*, **153**, 127 (1939).

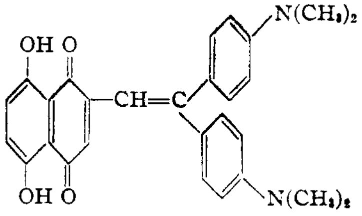
[2] Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

naphthoquinonyl-2')-1,1-bis-(*p*-dimethylaminophenyl)-ethylene (II). The best preparative procedure for this condensation product involves heating two molecular equivalents of quinone with one of ethylene to 70° for twenty-four hours in dioxane. Under these conditions II separates in a directly pure condition in 59% yield, m. p. 271–272.5° (cor.). From the filtrate α-naphthohydroquinone, characterized as its diacetate and by oxidation to the starting quinone, was obtained in 95% yield (crude). The expected reaction course, in which the intermediate hydroquinone of II is oxidized to the quinone at the expense of a molecule of starting quinone, is followed. The sparingly soluble condensation product II was characterized by analysis and by reductive acetylation to a greenish-yellow leucodiacetate.

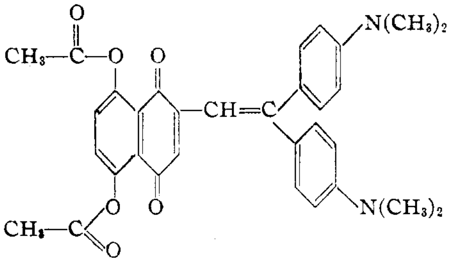
Using freshly prepared β-naphthoquinone, an even more facile condensation afforded 2-(1',2'-naphthoquinonyl-4')-1,1-bis-(*p*-dimethylaminophenyl)-ethylene (III) as deep blue-black needles (indigo blue in solution) in 83.7% yield. It was characterized as its deep red azine and as its canary-yellow leucodiacetate. Other successful condensations using the same ethylene include those with naphthazarin and naphthazarin diacetate, leading to the related condensation products IV and V, respectively.



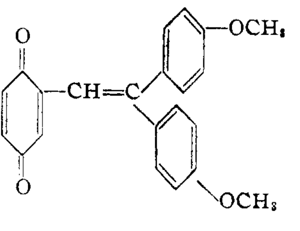
III



IV



V

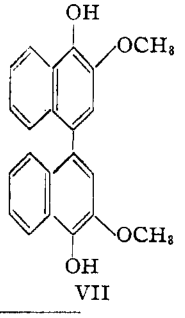


VI

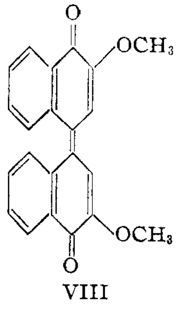
Although poor yields were obtained in the case of the naphthazarin derivatives, purification losses were high and it is believed that the yields of pure material do not reflect the extent of condensation. The condensation product from naphthazarin crystallizes from benzene in beautiful black needles which exhibit a faint deep green surface luster, m. p. 306–308° (uncor.). Naphthazarin diacetate gives V as an amorphous indigo-blue solid, m. p. 261–264°, which can be hydrolyzed to IV with acid. The sparingly soluble 5,8-diacetoxy-1,4-naphthohydroquinone was isolated in 58% yield as the expected by-product.

Condensation of the desired type was not obtained using 2-methyl-1,4-naphthoquinone and I. A compound apparently derived from two moles of quinone and one of ethylene was obtained in low yield but its structure has not been established. The failure of 2-methyl-1,4-naphthoquinone to undergo easy condensation was not entirely unexpected since Fieser and Seligman[3] showed that the presence of a methyl group in the quinonoid ring of 1,4-naphthoquinone materially reduces its ability to undergo 1,4-additions.

Extension of this reaction to the preparation of condensation products of 1,1-dianisylethylene was successful at least in the case of α-naphthoquinone. In keeping with the less highly polar nature of this ethylene, as exhibited by its weaker proton affinity,[1] condensation took place only slowly to give 2-(1',4'-naphthoquinonyl-2')-1,1-dianisylethylene (VI) as fine deep orange-red needles. An attempt to condense 1,1-dianisylethylene with β-naphthoquinone in methanol failed to yield a condensation product containing the ethylene, but in addition to 8% of 2-methoxy-1,4-naphthoquinone, gave rise to 43% of a high melting (275°) hydroquinone, $C_{22}H_{11}O_4$, containing two methoxyl groups. On methylation with dimethyl sulfate this gave the known[4] 3,4,3',4'-tetramethoxy-1,1'-binaphthyl. The hydroquinone can



VII



VIII

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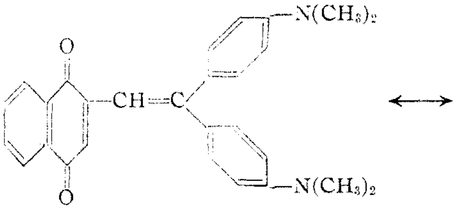
[3] Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934).

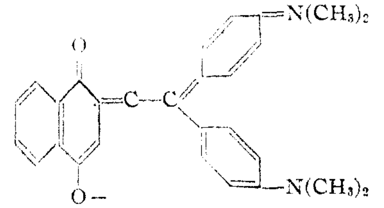
[4] Straus, Bernoully and Mautner, *Ann.*, **444**, 165 (1925).

probably be assigned the structure VII, since oxidation with silver oxide gave the hitherto unknown dimethyl ether of Stenhouse and Groves's[5] "dinaphthyl diquinhydrone" as a deep magenta-colored quinone, m. p. 260–262° (VIII).

The deep purple-black condensation product II derived from α-naphthoquinone and 1,1-bis-(*p*-dimethylaminophenyl)-ethylene dissolves readily in 3 *N* hydrochloric acid to give a bright yellow solution. Dilution of this hydrochloric acid solution with a large volume of water causes the original quinone to separate as a purple-black solid. The bright scarlet 3 *N* hydrochloric acid solution of IV likewise precipitates the original blue-black solid on strong dilution. These observations indicate that condensation of 1,1-bis-(*p*-dimethylaminophenyl)ethylene with α-naphthoquinones results in a considerable decrease in basicity. An explanation of this is provided by a comparison of the structure of the free base with that of the cation formed by proton addition. Conjugation of the ethylene with a quinonoid nucleus increases the number of contributing forms of the free base considerably, and thereby increases the stabilizing resonance of the free base. Two of the possible forms are represented by formulas II and IIa.

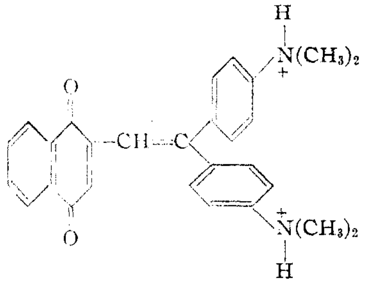


II



II a

On the other hand, this increased resonance is not shown by the cation, in which the electron pairs responsible are tied up by covalent bond formation with the added proton or protons. This results in stabilization of the free base over the cation. The effect is greater in the condensation product than in the original ethylene and thus the condensation product is the weaker base. Formula IX represents a possible structure for the cation.



IX

Related to the above phenomena are the color changes which occur on solution of these condensation products in moderately concentrated solutions of strong acids. Thus the deep purple-black II gives a bright yellow solution, IV gives a brilliant scarlet-red solution, and III (deep indigo blue) gives an orange-brown solution in 3 *N* hydrochloric acid. Since deep color is associated with the high electronic mobility of extensively conjugated systems to which many forms contribute,[6] elimination of part of these contributing forms as shown above should lighten the color.[7] Qualitatively, at least, elimination of this resonance restores the color attributable to the original quinones alone, since α-naphthoquinone is bright yellow, naphthazarin is crimson, and β-naphthoquinone is golden-yellow to brown-yellow. Even the yellow to yellow-green leucodiacetates of II and III show this effect, both dissolving in dilute hydrochloric acid with complete loss of color which is restored by neutralization with bases. It is hoped to investigate these phenomena with the aid of absorption spectroscopy.

Many condensations involving the union of an electron donating group with an accepting center are subject to catalysis by both acids and bases.[8] The available evidence indicates that this is not the case with the condensation under discussion. Indeed, the reaction goes quite readily in aprotic solvents. Thus while preparative convenience dictates another choice of solvent the condensation between α-naphthoquinone and the ethylene I proceeds with ease in benzene. It might be predicted that acidic catalysis, operating by activating the electron accepting center, would fail because the electron donating ethylene is much more strongly basic than the accepting quinone in this case, and would be tied up as its inactive salt. This prediction is verified by the complete failure of the reaction to proceed when glacial acetic acid is used as solvent.

Somewhat similar considerations indicate that basic catalysis is also unlikely. This type of catalysis, ordinarily effective because of proton capture from the electron donating component, cannot activate the donor in this case, since the donor is already basic and tends to gain rather than lose a proton. Experimentally it is found that even with the least basic ethylene examined (1,1-dianisylethylene), condensation with α-naphthoquinone goes with optimum yields when

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(5) Stenhouse and Groves, *J. Chem. Soc.*, **33**, 418 (1878).

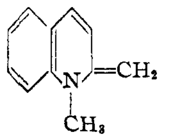
(6) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

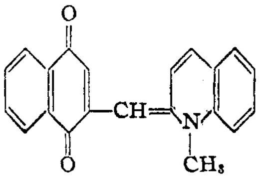
(7) Compare the cases of "reverse halochromism" described by Brooker, Sprague, Smyth and Lewis, THIS JOURNAL, **62**, 1116 (1940).

(8) For examples, see Hauser and co-workers, Abstracts, Ninth National Organic Chemistry Symposium, 1941, p. 84.

no added basic catalyst (dimethylaniline) is present.

It is planned to extend this work to other series of quinones and polar ethylenes, and at least a start has been made in this direction. Thus with the expectation of obtaining XI, α-naphthoquinone has been condensed with N-methyl-2-methylene-1,2-dihydroquinoline (X), although the condensation product has not been fully characterized


X


XI

The relationship of this condensation product to the cyanine dyes is apparent. Other members of this series should be available by this condensation.

An examination of the oxidation-reduction potentials of these condensed quinones should provide interesting data, and such determinations are to be made at the earliest opportunity.

The interruption of this work for the duration of the national emergency has prompted publication of the present incomplete report.

Experimental Part[9,10]

2-(1′,4′-Naphthoquinonyl-2′)-1,1-bis-(*p*-dimethylaminophenyl)-ethylene (II).—A solution of 1.16 g. of α-naphthoquinone in 15 ml. of warm dioxane was added to 0.973 g. of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene[11] dissolved in 15 ml. of the same solvent. A dark purple-red color appeared immediately. The mixture, protected from light, was heated to 70° for twenty-three hours in a flask closed with a rubber stopper, then allowed to cool for four hours. The beautiful blue-black needles which had separated were collected and washed with cold dioxane; yield 906 mg. (59%), of directly pure material, m.p. 270.5–272°. The condensation product is very sparingly soluble in alcohol, acetone and glacial acetic acid, moderately soluble in boiling dioxane with a deep purple-blue color. Its solution in concentrated sulfuric acid is deep red-brown in color. It dissolves in 3 *N* hydrochloric acid to give a bright yellow solution, which on strong dilution with water gives first a greenish-yellow solution which then deposits the original material as a blue-black solid. A small portion was recrystallized twice from dioxane and dried at 78° and 0.1 mm. for analysis, m.p. 272–273.5°.

Anal. Calcd. for $C_{28}H_{26}O_2N_2$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.45; H, 6.04; N, 6.72.[12]

The original dioxane filtrate was diluted with somewhat more than an equal volume of water, then strongly acidified with dilute hydrochloric acid. The dirty brown solution thus obtained was extracted twice with ether, the ether layers washed with dilute hydrochloric acid, saturated brine, decolorized with norite, filtered through anhydrous sodium sulfate, concentrated and diluted with 30–60° petroleum ether to incipient crystallization. On cooling, 437 mg. of impure material, m. p. 175–179° with decomposition, was obtained. A second crop of 119 mg. was obtained from the filtrate; yield 95% (crude). Attempts to recrystallize this material from dilute alcohol in the presence of a little stannous chloride and hydrochloric acid were unsuccessful. Accordingly, 177 mg. was dissolved in 1 ml. of pyridine and treated with 0.5 ml. of acetic anhydride. After standing two hours, the mixture was heated to boiling and poured into water. The precipitated material was taken into ether, washed with dilute alkali several times, then with brine, filtered through anhydrous sulfate, and concentrated nearly to dryness. The residue on crystallization from alcohol afforded 127 mg. of light tan blades, m. p. 128–130°. Recrystallization gave 92 mg., m. p. 129–130°. Korn[13] records 128–130° for the m. p. of 1,4-diacetoxynaphthalene.

The remainder of the material, dissolved in alcohol-acetone, was treated with 1 g. of ferric chloride dissolved in dilute hydrochloric acid. A crop of orange-brown needles separated. These were collected, taken into ether, the ethereal solution treated with norite, filtered, concentrated, and diluted with petroleum ether. A crop of acicular blades separated, 86 mg., m. p. 121.5–125°. After recrystallization from ether, the material melted at 123.5–125.5° and did not depress the melting point of an authentic sample of α-naphthoquinone.

The original orienting experiments on this condensation were carried out using benzene as a solvent. The condensation takes place readily under these conditions but the by-product α-naphthohydroquinone is sparingly soluble in this solvent and contaminates the product. It can also be carried out in refluxing acetone to give good yields. However, the procedure given above yields the best product and is preferred.

The following describes an unsuccessful attempt to carry out the condensation using glacial acetic acid as a solvent. To the brilliant deep blue-green solution of 976 mg. of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene in 6 ml. of glacial acetic acid was added a warm solution of 1.16 g. of α-naphthoquinone in 4 ml. of glacial acetic acid. Another 2 ml. of acid was used to wash in the quinone. The mixture was heated to 70° for sixty-seven hours, then allowed to cool. No crystalline material had deposited after standing for twenty-four hours. The desired product is very sparingly soluble in glacial acetic acid (74 mg. in 100 ml. at room temperature).

2-(1′,4′-Diacetoxynaphthyl-2′)-1,1-bis-(*p*-dimethylaminophenyl)-ethylene.—The condensation product II was reductively acetylated as follows: 502 mg. of II dissolved in 10 ml. of hot pyridine was treated with 0.4 g. of zinc dust and 5 ml. of acetic anhydride. On addition of the acetic anhydride the deep purple-black color changed to a light yellow-tan marked by an intense greenish fluorescence.

After standing ten minutes, the zinc was filtered off and washed with ether, the filtrate diluted with ether, washed three times with water, then three times with dilute alkali, once with water, finally with brine, and filtered through anhydrous sodium sulfate. The yellow solution thus obtained had the same intense greenish fluoresence observed in the reaction mixture. After removal of the ether the residual deep brown viscous oil on triturating under hexane solidified to a brown-yellow solid, 628 mg. (605 theoretical) m. p. 201–211°. In contrast to the starting quinone, this leucodiacetate crystallizes only with difficulty and purification was costly. The crude material (550 mg.), dissolved in the minimal quantity of hot dioxane was treated with a little hot water and allowed to cool. The first crop separated as a glassy crust, 205 mg., m. p. 227–230°, with decomposition. Dilution of the filtrate with alcohol gave 97 mg., m. p. 225–226°, dec. These two crops were combined, dissolved in the minimal quantity of hot dioxane, diluted with an equal volume of hot alcohol and allowed to crystallize. The solution still showed an intense fluorescence. Small compact prisms adhering to the walls of the flask were obtained, 181 mg., m. p. 228–230° with decom-

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[9] All melting points are corrected except those specifically described as uncorrected.

[10] A preliminary condensation was carried out in collaboration with Mrs. Ray Longley.

[11] Pfeiffer and Wizinger, *loc. cit.* One crystallization from alcohol containing a trace of alkali yields an excellent product if the crude ethylene is subjected to preliminary vacuum distillation.

[12] Semimicro Dumas analysis by Miss Gladys Whitridge.

[13] Korn, *Ber.*, **17**, 3025 (1884).

position. Two further crystallizations gave small yellow-tan prisms, m. p. 230–231° with decomposition. The m. p. depends somewhat on the rate of heating. For analysis the material was dried for three hours at 78° and 0.1 mm. It is sparingly soluble in alcohol, fairly soluble in acetone, and readily soluble in dioxane. Its solution in concentrated sulfuric acid is orange-red appearing canary-yellow to greenish-yellow in thin layers. It is soluble with complete loss of color in 3 *N* hydrochloric acid. Neutralization with dilute alkali gives a bright yellow precipitate of the unchanged leucodiacetate.

Anal. Calcd. for $C_{32}H_{32}O_4N_2$: C, 75.56; H, 6.34. Found: C, 75.20; H, 6.23.

2-(1′,2′-Naphthoquinonyl-4′)-1,1-bis-(*p*-dimethylaminophenyl)-ethylene (III).—To 2.32 g. of β-naphthoquinone[14] in 30 ml. of warm methanol was added a solution of 1.95 g. of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene in 50 ml. of warm methanol. An immediate deep blue-green color was produced which on heating to boiling rapidly gave way to a deep indigo blue. At the end of a few minutes the product began to separate as fine violet-black prismatic blades. The reaction mixture was allowed to stand overnight at room temperature, then the product was collected and washed with cold methanol until the filtrate was clear blue with no reddish-purple tinge. After air drying, 2.58 g. (83.7%) of material, m. p. 194–196° was obtained. It is rather sparingly soluble in methanol, fairly soluble in hot acetone and dioxane to give deep indigo blue solutions. Its solution in concentrated sulfuric acid is a deep ultramarine color. It dissolves in 3 *N* hydrochloric acid with a brown color. Dilution has no effect on this color, nor does it cause precipitation of the free base. A small sample was recrystallized twice from acetone-methanol, then dried at 100° and 10^{-4} mm. for one hour, m. p. 199–201°, with gas evolution.

Anal. Calcd. for $C_{28}H_{26}O_2N_2$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.40; H, 6.10; N, 6.81.[15]

2-(1′,2′-Diacetoxynaphthyl-4′)-1,1-bis-(*p*-dimethylaminophenyl)-ethylene.—To 630 mg. of the condensation product III suspended in 5 ml. of acetic anhydride was added 0.4 g. of zinc dust, then 10 ml. of pyridine. The deep blue suspension rapidly gave way to a greenish-yellow fluorescent solution. After standing for fifteen minutes, the zinc dust was filtered off, washed with ether, then twice with hot pyridine, then again with ether. The light yellow filtrate was diluted with water, the yellow ethereal layer was separated, washed three times with water and then extracted twice with dilute hydrochloric acid. The nearly colorless acid layer on neutralization with solid sodium bicarbonate yielded a canary-yellow solid. A third acid extract gave no precipitate on neutralization. After air drying, this precipitate amounted to 738 mg. (97.4%), m.p. 95–102°. The material is sparingly soluble in cold methanol, readily soluble in benzene and chloroform. Its solution in hot acetone on cooling deposits the material as beautiful canary yellow needles, m. p. 92.5–94.5°, but the yield on crystallization is poor. Successive crops afforded a total of 541 mg. (71.5%), m. p. 93–94°. To avoid prohibitive crystallization losses, a mixture of acetone–hexane was used for subsequent purification of an analytical sample. The material is obtained in partially solvated form from mixtures containing acetone. Thus a sample of the above material after two further crystallizations melted at 96–96.8°, but after drying one hour at 78° and 10^{-4} mm., the m. p. was raised to 105.6–106.8°. It is soluble in concentrated sulfuric acid with a deep orange-red color which changes to red-purple on standing. Its solution in 3 *N* hydrochloric acid is colorless. Neutralization precipitates the bright yellow solid.

Anal. Calcd. for $C_{32}H_{32}O_4N_2$: C, 75.56; H, 6.34. Found: C, 75.59; H, 6.64.

Azine of Condensation Product III.—A solution of 619 mg. of III and 168 mg. of *o*-phenylenediamine in 10 ml. of benzene was treated with 1 ml. of glacial acetic acid. On addition of the acetic acid and slight warming, the color changed from the original blue to a deep red-brown. The mixture was heated under reflux for ten minutes, then diluted with an equal volume of hexane and set aside. Collection of the crystallizate afforded 645 mg. (89%) of deep red prismatic needles, m.p. 244–246°, softening from 241°. Three further crystallizations of a small sample from benzene–hexane gave ruby-red blades, m. p. 246–247.5°. The azine is rather sparingly soluble in alcohol and acetone, readily soluble in hot acetic acid, hot dioxane or hot benzene. Its solution in concentrated sulfuric acid is a deep black-purple. It dissolves in 3 *N* hydrochloric acid with an orange color, and does not precipitate even on strong dilution. For analysis the material was dried at 78° and 10^{-4} *mm. for one hour.*

Anal. Calcd. for $C_{34}H_{30}N_4$: C, 82.56; H, 6.11. Found: C, 82.94; H, 6.15.

Condensation of Naphthazarin with 1,1-Bis-(*p*-dimethylaminophenyl)-ethylene (IV).—A solution of 190 mg. of naphthazarin and 133 mg. of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene in 15 ml. of benzene was brought to boiling, then heated for twenty-four hours at 74° in the dark. The resulting deep red-purple solution was concentrated somewhat and set aside to crystallize. The crude material which separated was collected and recrystallized from benzene to give 54 mg. of black needles, m. p. 303–305° (uncor.). Recrystallization from hot benzene (deep blue-purple solution) gave 37 mg. of beautiful black needles with a faint deep green surface reflex, m. p. 306–308° (uncor.). Its solution in concentrated sulfuric acid is a beautiful intense deep purple color. It dissolves in 3 *N* hydrochloric acid with a deep crimson color, and on strong dilution separates out as a blue-black solid. A small amount suspended in alcohol (very sparingly soluble) gives a deep cornflower blue color on treatment with a drop of dilute alkali. The cornflower blue alkali salt thus formed is rather insoluble in water, but has some solubility in alcoholic solutions. The color produced is very similar to that produced when naphthazarin itself is treated with alkali. For analysis the material was dried at 78° and 10^{-4} mm. for one hour.

Anal. Calcd. for $C_{28}H_{26}O_4N_2$: C, 73.99; H, 5.77. Found: C, 74.27; H, 5.40.

A larger run using dioxane as a solvent gave 233 mg. of crude material, m. p. 290–296° (uncor.), starting from 500 mg. of naphthazarin, but attempts to purify this by solution first in dilute alcoholic alkali, then in dilute hydrochloric acid resulted in prohibitive losses, although a small amount of excellent material was obtained.

Condensation of Naphthazarin Diacetate with 1,1-Bis-(*p*-dimethylaminophenyl)-ethylene (V).—A solution of 402 mg. of naphthazarin diacetate[16] in 8 ml. of hot dioxane was treated with 192 mg. of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene in 2 ml. of dioxane and heated to 78° for ninety hours protected from light. The reaction mixture became brown immediately, then gradually darkened to purple-red. Some very small well-formed colorless prisms separated along with some dark purple-red solid. The mixture of solids was filtered off (air dried, 286 mg.) and recrystallized once from dioxane and once from ethyl alcohol to give 133 mg. of colorless prismatic plates of 5,8-diacetoxy-1,4-naphthohydroquinone,[17] m. p. 249–250°. The filtrate was diluted with water and the blue-black solid which precipitated was filtered off. In contrast to the other condensation products described, this material was not easily obtained in crystalline form. From its strongly concentrated dioxane solution only amorphous material separated (88 mg., m. p. 253–257°). Very slow recrystallization of this material yielded amorphous material along with some needles. A further crystallization gave 60 mg. of blue-black amorphous material, m. p. 261–264°. It is very sparingly soluble in alcohol, soluble in acetone, dioxane or benzene. Its solution in sulfuric acid is a beautiful deep purple color. It dissolves in 3 *N* hydrochloric acid to give a bright yellow solution which acquires a

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(14) "Organic Syntheses," **17**, 68 (1937).

(15) Semimicro Dumas analysis by Miss Mathilde Boal.

(16) Thiele and Winter, *Ann.*, **311**, 348 (1900).

(17) Wheeler and Edwards, THIS JOURNAL, **39**, 2465 (1917).

greenish tinge on dilution but fails to precipitate. For analysis the material was dried at 78° and 10^{-4} mm. for two hours.

Anal. Calcd. for $C_{32}H_{30}O_6N_2$: C, 71.36; H, 5.61. Found: C, 71.25; H, 5.23.

The material is readily hydrolyzed to the parent naphthazarin derivative as the following experiment shows.

A solution of 42 mg. of crude condensation product (m. p. 250–255°) in 3 ml. of dilute hydrochloric acid was heated to boiling for five minutes. As the solution was heated, the color changed from yellow-green to deep crimson. The hydrolytic mixture was diluted with water, neutralized with solid sodium bicarbonate, the precipitated blue-black solid was taken into benzene, filtered, concentrated and set aside to crystallize. Beautiful black needles of IV (20 mg.), m. p. 307–308° (uncor.), were obtained.

Condensation of 2-Methyl-1,4-naphthoquinone with 1,1-Bis-(*p*-dimethylaminophenyl)-ethylene.—The reddish purple methanol solution of 645 mg. of 2-methyl-1,4-naphthoquinone and 500 mg. of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene was heated to boiling, then allowed to stand at room temperature. A considerable portion of the ethylene separated on cooling. After standing in the dark without attention for one month, the original color had changed to a deep green and small nodules of dark crystalline material had separated. These were quite insoluble even in the boiling solvent, and on collection appeared greenish gray. The material was taken into dioxane to give a deep purple solution which on crystallization yielded 311 mg. of light tan platelets, m. p. 285–295° (uncor.). Two further crystallizations from dioxane gave 105 mg. of yellow plates which when introduced into a copper melting point block at 290° melted at 298–300° (uncor.) after drying at 78° and 10^{-4} mm. for two hours. The melting point depends on the rate of heating. This material is soluble in dilute hydrochloric acid but is insoluble in alkali even on boiling. Its solution in concentrated sulfuric acid is a bright purple-blue which fades to a paler green-blue on standing. Analytical figures indicate that it is derived from two moles of quinone and one of ethylene. It has not been further characterized.

Anal. Calcd. for $C_{40}H_{40}O_4N_2$: C, 78.40; H, 6.58. Calcd. for $C_{40}H_{38}O_4N_2$: C, 78.66; H, 6.27. Found: C, 78.47; H, 6.57.

2-(1′,4′-Naphthoquinonyl-2′)-1,1-dianisylethylene (VI).—A solution of 500 mg. of α-naphthoquinone and 38 mg. of 1,1-dianisylethylene[2] in 10 ml. of methanol was refluxed for six days, when a small amount of the ethylene remained undissolved. After a day, the mixture had turned a dirty gray-green color and small amounts of bright orange fluffy solid could be discerned. At the end of the refluxing period the reaction mixture was filtered hot, the insoluble material washed thoroughly with hot methanol, then taken into hot benzene. After filtration to remove a small amount of dark green-brown material insoluble in benzene, the filtrate was diluted with hot methanol and allowed to crystallize. Fluffy balls of very fine orange needles separated, 139 mg. (35% based on ethylene utilized), m. p. 209–210°. A second crop of 18 mg., m. p. 208–210° was obtained from the filtrate; total yield 39.4%. Two further crystallizations from benzene–methanol gave 105 mg. of fluffy balls of very fine orange needles, m. p. 211.8–212.3°. The substance is very sparingly soluble in methanol, readily soluble in hot benzene. Its solution in concentrated sulfuric acid is a deep blue to blue-green color. It is not soluble in dilute acids. The sample was dried at 78° and 10^{-5} mm. for two hours for analysis.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09; 2 OCH_3, 15.66. Found: C, 78.85; H, 4.76; OCH_3, 15.59.

The original methanol filtrate on concentration and crystallization yielded 138 mg. of recovered ethylene as tan plates, m. p. 140–141.5°.

Earlier attempts to carry out this preparation in dioxane using anhydrous zinc chloride as a catalyst were unsuccessful, although the reaction was not heated so long as in the example given above.

An effort to speed up the condensation and improve the yield by use of dimethylaniline as a catalyst was likewise unsuccessful, although a small amount of the desired product was obtained. A description of this experiment follows:

A mixture of 500 mg. of α-naphthoquinone, 380 mg. of 1,1-dianisylethylene, 4 drops of dimethylaniline and 25 ml. of methanol was heated in a closed pressure bottle at 78–80° for forty-eight hours. After cooling, the precipitated solid was filtered off and washed with methanol. The insoluble residue amounted to 257 mg. and contained particles of the characteristic orange condensation product. It was taken into boiling benzene, filtered from some dark gray-brown insoluble material (49 mg.) and diluted with an equal volume of hot methanol. The desired condensation product was obtained in poor condition as orange brown fluffs, 37 mg., m. p. 206.5–208°, mixed m. p. with material obtained as above, 207–208.5°.

The filtrate from this crop on concentration and crystallization afforded 100 mg. of felty, fine gray-tan needles, m. p. 136–139°, which after two crystallizations from pure methanol formed nearly colorless plates, m. p. 141–141.5°. A mixed m. p. with the starting ethylene was not depressed.

The original methanol filtrate on concentration and crystallization yielded 226 mg. of nearly black very impure material, m. p. 123–128°, probably largely unchanged ethylene.

Attempted Condensation of β-Naphthoquinone and 1,1-Dianisylethylene.—A solution of 1.00 g. of β-naphthoquinone and 760 mg. of 1,1-dianisylethylene in 30 ml. of methanol was heated to boiling and set aside in the dark. A part of the ethylene separated on cooling. After standing for one month, the solution was again heated to boiling. The ethylene dissolved, but considerable insoluble material remained. This was filtered off, dissolved in boiling dioxane to give a wine-red solution, and crystallized. Compact, red-brown prisms were obtained, 469 mg. (43% crude), m. p. 273–276°. While this material dissolved in boiling dioxane to give a deep wine-red solution, it was noticed that the refluxing solvent washed crystalline material adhering to the flask walls almost colorless. Therefore a small amount of stannous chloride dissolved in hydrochloric acid was added. This caused complete removal of the wine-red color, and after two crystallizations, 355 mg. of very pale pink prisms was obtained, m. p. 277.5–278.8°, becoming brown a degree or so below the melting point. One further recrystallization from dioxane containing stannous chloride and hydrochloric acid gave 313 mg. of nearly colorless material of the same melting point. Its solution in concentrated sulfuric acid was a very deep black to black green color. For analysis one sample was dried two hours at 100° and 10^{-3} mm., and another sample was sublimed at 200° and 10^{-3} mm.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.27; H, 5.24; 2 OCH_3, 17.92. Found: (crystallized sample) C, 76.18; H, 5.41. Found: (sublimed sample) C, 76.37; H, 5.24; OCH_3, 17.41.

Eighty-three mg. of this material was suspended in a small amount of potassium hydroxide solution containing some sodium hydrosulfite. Complete solution did not occur even after further dilution with water, but the hard prisms gave way to a very fine suspension. This suspension was treated with 0.2 ml. of dimethyl sulfate, stoppered, and vigorously shaken. The methylation was repeated, using additional dimethyl sulfate and more alkali. The agglomerated solid material was filtered off, washed with water, then with methanol, and crystallized from methanol. A considerable portion was lost accidentally, but the remainder afforded 27 mg. of small plates, m. p. 145–147°. One further crystallization gave material melting at 146.5–148.5° which showed no depression in melting point when mixed with an authentic sample of 3,4,3′,4′-tetramethoxy-1,1′-binaphthyl[4] prepared by methylating a vatted sample of dinaphthyldiquinhydrone[5] with dimethyl sulfate.

The original methanol filtrate on concentration yielded 428 mg. of unchanged ethylene, m. p. 139–141°, mixed m. p. 140.5–142°. The filtrate from this crystallization on standing deposited 147 mg. (8%) of brick-red material, m. p. 177–180.5°. Recrystallization from methanol with the aid of charcoal gave 109 mg. light yellow needles, m. p. 180.5–181.5° whose mixed m. p. with an authentic sample of 2-methoxy-1,4-naphthoquinone of m. p. 181.2–182° was 180.5–181.7°.

Oxidation of VII.—A suspension of 40 mg. of VII, 200 mg. of silver oxide and some anhydrous magnesium sulfate in dioxane was warmed to facilitate solution. A brilliant deep magenta-purple was produced almost at once. After shaking for thirty minutes the suspension was heated to boiling and filtered. The deep magenta filtrate was concentrated to a small volume and set aside. An amorphous dark precipitate separated which was collected and washed with cold dioxane, yield 17 mg., m. p. 260–262°. When held above its melting point for a few minutes, the beautiful deep red melt fades to a yellow-brown. The material when dry possesses a deep greenish-bronze surface reflex. Its magenta-purple solution in dioxane on standing fades to a brown solution. A small amount in dioxane on treatment with dilute aqueous alkali fades through a tan to a light green-yellow solution. It dissolves in concentrated sulfuric acid with a deep green-black color. For analysis, the material was dried at 78° and 10^{-4} mm. for one hour.

Anal. Calcd. for $C_{22}H_{16}O_4$: C 76.73; H, 4.68; 2 OCH_3, 18.02. Found: C, 76.26; H, 4.79; OCH_3, 16.33.

Summary

1. Condensation reactions between 1,1-bis-(*p*-dimethylaminophenyl)-ethylene and α-naphthoquinone, β-naphthoquinone, naphthazarin, and naphthazarin diacetate as well as a similar condensation between 1,1-dianisylethylene and α-naphthoquinone have been described.

2. These condensations are those expected from a consideration of the electron donating capacity of the ethylene and the electron accepting capacity of the quinones involved. Present evidence indicates that the condensation is not catalyzed by acids or bases.

3. A discussion of certain points of interest in connection with the color and basicity of the condensation products is given.

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RECEIVED SEPTEMBER 7, 1943

[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Structure of the "B" Modification of Starch from Film and Fiber Diffraction Diagrams[1]

BY R. E. RUNDLE, LESTER DAASCH AND DEXTER FRENCH

Introduction.—Of the unit cells proposed for the "A" (cereal) and "B" (tuber) modifications of a starch, those of Bear and French[2] are supported by the best diffraction data, and are altogether the most reasonable thus far proposed. Yet even their data, as they point out, were necessarily confined to those available from powder diagrams. Such data are not wholly adequate for the support of large unit cells for crystals of low symmetry, so that their results are left open to question.

Though the desirability of obtaining film and fiber diffraction diagrams for starch is obvious, attempts to prepare suitable films and fibers have been unsuccessful because whole starch was employed. The chief constituent of whole starch[3] is a highly branched component, amylopectin in Meyer's nomenclature,[4] where interruptions in the starch chains occur approximately every 20 glucose residues. The resulting unbranched portions of the chains are too short to produce satisfactory films or fibers.

Fortunately, it is now possible to isolate the unbranched (amylose) component present in most starches.[5] The unbranched chains in this component are probably in excess of 200 glucose units long,[6] and upon suitable treatment form both films and fibers. The production of these films and fibers and mention of the importance of their optical properties have been reported previously.[7] Recently Whistler and Hilbert have confirmed this property of amylose, finding that the acetate of this component of starch forms films with properties to be expected only for films of long, linear molecules.[8]

The diffraction diagrams from amylose retrograded at room temperature are quite like those from tuber starch granules and retrograded whole starch, so that the amylose component of starch can be used for the study of the crystalline portions of whole starch.

Preparation of the Samples.—A hot solution containing about 5% amylose is allowed to evaporate slowly, and the surface skins are removed carefully from time to time. The skins are allowed to dry on an aluminum sheet or ferrotype. Dry films thus prepared are only a few hundredths of a millimeter thick. The thicker films usually tend to curl or become distorted, but this can be overcome to some extent by doubling them while they are still wet.

Fibers which produce a "B" diffraction diagram are very difficult to prepare, and none that we have produced is of particularly high quality. The chief difficulty lies in the fact that plasticizers which can be used to aid in stretching produce fibers corresponding to new crystalline modifications of starch. These, of course, are of interest in

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[1] Journal Paper No. J-1129 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 639. Supported in part by a grant from the Corn Industries Research Foundation.

[2] R. S. Bear and D. French, THIS JOURNAL, **63**, 2298 (1941).

[3] F. Bates, D. French and R. Rundle, *ibid.*, **65**, 142 (1943).

[4] K. Meyer, "Advances in Colloid Science," Interscience Publishers, Inc., New York, N. Y., 1942, pp. 142–162.

[5] T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942). For an analysis of the component isolated by Schoch, and a discussion of structure, see (3).

[6] J. Foster and R. Hixon, *ibid.*, **65**, 618 (1943).

[7] R. Rundle and D. French, *ibid.*, **65**, 559 (1943).

[8] R. Whistler and G. Hilbert, "The Film-Forming Properties of the Acetates of Fractionated Starch," read before the Division of Sugar Chemistry, Am. Chem. Soc. convention, Detroit, 1943.