evolution. The **pyrazoline (formula IV)** is insoluble in alkali and is apparently unaffected by sodium hydrosulfite.

Anal. Calcd. for $C_{24}H_{18}O_2N_2$: C, 78.7; H, 4.95. Found: C, 78.8; H, 4.62.

2-Diphenylmethyl-3-methyl-1,4-naphthoquinone (V).—On heating 4 g. of the pyrazoline, III, in a metal bath, gas was suddenly evolved at 169°, and after raising the temperature to 190° for two minutes the orange residue was cooled and dissolved in ether. On thorough cooling nearly pure crystals of the reaction product were deposited; yield, 3 g. (81%). The quinone was obtained from alcohol–ethyl acetate as bright yellow prisms, m. p. 162–163°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.36. Found: C, 85.2; H, 5.14.

Attempts to prepare the compound from 2-methyl-1,4-naphthoquinone and benzhydrol were unsuccessful. The quinone is easily reduced by zinc dust in glacial acetic acid solution, and the hydroquinone is easily oxidized by the air. The **hydroquinone diacetate** crystallizes from benzene as colorless needles, m. p. 215–217°.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.2; H, 5.70. Found: C, 79.2; H, 5.69.

Summary

The quinonoid ethylenic linkage of ortho quinones is remarkably inert to diazomethanes and to alkyl and aryl azides, although these reagents add easily to para quinones. With diphenyldiazomethane the ortho quinones are converted into methylene ethers rather than into pyrazolines.

2-Diphenylmethyl-1,4-naphthoquinone adds diazomethane with great readiness, and the pyrazoline on losing nitrogen yields the 3-methyl derivative of the starting material.

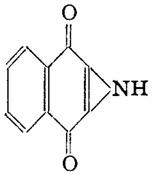
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS
RECEIVED JUNE 3, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

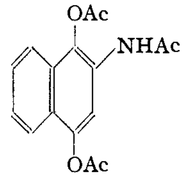
The Reaction of Hydrazoic Acid with the Naphthoquinones

BY LOUIS F. FIESER AND JONATHAN L. HARTWELL

In 1924 Korczynski[1] reported that hydrazoic acid reacts with α-naphthoquinone to give a brown substance of the composition $C_{10}H_5O_2N$, and he suggested for the substance the structure I. β-Naphthoquinone was reported to yield a brown-red product of the same composition. Since the empirical formulas alone are such as to indicate a rather remarkable reaction, it was thought that the problem merited further investigation. On repeating Korczynski's work we obtained in nearly quantitative yields substances corresponding to his descriptions. Reductive acetylation of a compound of the structure of I, it was thought, should cleave the three-membered ring, and indeed the expected triacetate II actually was obtained. This triacetate, however, is the normal product of the reductive acetylation of 2-amino-1,4-naphthoquinone, and it was noticed that the melting point of the latter compound is only a few degrees higher than that of the brown reaction product from α-naphthoquinone and hydrazoic acid. The correspondence of the product from β-naphthoquinone with 4-amino-1,2-naphthoquinone was equally striking, and, when the two substances were recrystallized by the rather special methods required for the proper handling of the amino-naphthoquinones,[2] samples of bright orange-red needles and of bright red needles were obtained which were identical in every way with 2-amino-1,4-naphthoquinone and 4-amino-1,2-naphthoquinone, respectively. Korczynski's samples were impure and the analyses were in error.



I



II

The conversion of the naphthoquinones into their amino derivatives by the action of hydrazoic acid is capable of various interpretations, but only one mechanism appears to us to be plausible. Since hydrazoic acid adds to benzoquinone to give azidohydroquinone,[3] a similar addition probably occurs in the present case as well. In such a compound, III (hypothetical) for example, opportunity exists for intramolecular oxidation–reduction. The hydroquinone grouping is capable of oxidation, while the ordinary azido group is

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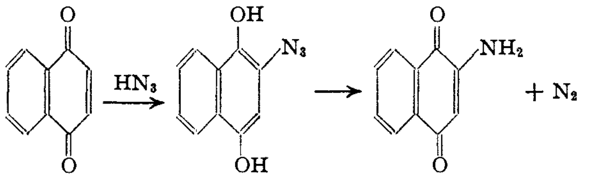
[1] Korczynski, *Bull. soc. chim.*, [4] **35**, 1186 (1924).

[2] Fieser and Fieser, THIS JOURNAL, **56**, 1565 (1934).

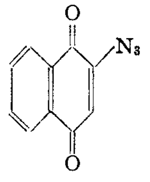
[3] Oliveri-Mandalà and Calderaro, *Gazz. chim. ital.*, **45**, I, 311 (1915); Oliveri-Mandalà, *ibid.*, **45**, II, 120 (1915).



III IV

easily reduced with the liberation of nitrogen. The transference of the hydroquinone hydrogen atoms to the oxidizing group would lead to the formation of the aminoquinone, IV. The difference in the end-result with the benzo- and naphthoquinones is easily accounted for on this basis. It may be assumed that the oxidizing power of the azido group is approximately the same in each case, but it is certain that the naphthohydroquinone would be a more potent reducing agent (lower oxido-reduction potential) than the substituted benzohydroquinone. Azidobenzohydroquinone is sufficiently stable to be isolated because the reducing group of the molecule is not sufficiently potent to interact with the reducible azido group; with the compound of the naphthalene series the potential is at a more effective level and interaction occurs.

Attempts to test this mechanism experimentally met with little success. The reaction with hydrazoic acid proceeds rapidly even at 5°, and we were unable to isolate the azidonaphthohydroquinone, III, on varying the conditions. We sought to prepare it by the careful reduction of the azidonaphthoquinone V, which was easily obtained from 2-chloro-1,4-naphthoquinone and sodium azide, but the azido group appeared to be reduced as easily as the quinonoid nucleus. It was thought that the addition of hydrazoic acid to a quinone of potential between that of benzoquinone and that of β-naphthoquinone might yield an azidohydroquinone sufficiently stable to be isolated, but capable of being transformed into the aminoquinone without exploding. *p*-Xyloquinone, however, failed to react, while toluquinone and *ar*-tetrahydro-α-naphthoquinone behaved like benzoquinone.



V

Since the reaction with hydrazoic acid provides a very convenient means of obtaining the amino derivatives of the two naphthoquinones, the limits of the reaction were briefly investigated. With 2-methyl-1,4-naphthoquinone and 4-methyl-1,2-naphthoquinone there was no reaction, showing that the methyl group in each case effectively blocks the addition. The behavior of 3-bromo-1,2-naphthoquinone was interesting, for on treatment with sodium azide in either alcohol or glacial acetic acid the substance was converted into 3-bromo-4-amino-1,2-naphthoquinone. The bromine atom offers little hindrance to the addition of hydrazoic acid, which in the alcoholic solution must come from the hydrolysis of the metal salt, and this addition takes precedence over the other possible reaction, namely, the replacement of halogen by the azido group.

Experimental Part

The Preparation of Aminonaphthoquinones.—A solution of 5 g. of α-naphthoquinone in 50 cc. of glacial acetic acid at 40° was treated with a solution of 3.4 g. of sodium azide in 10 cc. of water. Gas was evolved, the solution became dark brown in color, and after one and one-half hours the brown, crystalline material which had separated was collected and washed; yield, 4.7 g. (87%). The substance melted at 202–204°, and when crystallized from alcohol with decolorizing charcoal it formed clear orange-red needles melting at 204–205°. There was no depression of the melting point on admixture with authentic samples of 2-amino-1,4-naphthoquinone melting at the same temperature, and the material gave the color test[2] characteristic of this compound. Reductive acetylation gave the triacetate of 2-amino-1,4-naphthohydroquinone (m. p. 223–224°), identified by comparison with a sample, m. p. 224–225°, prepared from authentic 2-amino-1,4-naphthoquinone (calcd. for $C_{16}H_{15}O_5N$: C, 63.8; H, 5.02. Found: C, 63.7; H, 4.77). This compound was prepared and analyzed by Kehrmann,[4] but an error apparently was made in reporting a melting point of 259–260°.

The reaction with a very pure sample of β-naphthoquinone[5] proceeded in the same way and gave a quantitative yield of brown-red 4-amino-1,2-naphthoquinone. The quinone crystallizes poorly from organic solvents and usually decomposes when heated in solvents other than water. When the reaction product was crystallized from water it formed beautiful deep red needles which blacken with decomposition at about 270°. In these properties, and in being soluble in strong alkali and in dilute hydrochloric acid, the substance corresponded exactly with an authentic sample. The hydroquinone triacetate, m. p. 194–195° was identified by mixed melting point determinations.

3-Bromo-1,2-naphthoquinone, treated with sodium azide in acetic acid solution, gave 3-bromo-4-amino-1,2-naphthoquinone[6] in 72% yield, while the yield was 47% when the reagents were brought together in a boiling alcoholic solution. Crystallized from pyridine, the substance melted at 263° with decomposition (literature, 265°), and the identity was confirmed by hydrolysis with hydrochloric acid to give 2-bromo-3-hydroxy-1,4-naphthoquinone, m. p. 196–197° (compare 196.5°).[6]

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[4] Kehrmann, *Ber.*, **27**, 3341, 3344 (1894).

[5] Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

[6] Zincke and Gerland, *Ber.*, **20**, 1514 (1887).

2-Azido-1,4-naphthoquinone.—An aqueous solution of 2.2 g. of sodium azide was added to a suspension of 5 g. of 2-chloro-1,4-naphthoquinone in 65 cc. of boiling alcohol. The chloro compound soon dissolved and after two minutes the solution was cooled and the orange crystals which separated were collected and washed with alcohol and then with water (90% yield). Crystallized from alcohol, the substance formed yellow prisms melting at 118° with the evolution of gas. Analysis was not attempted.

Nitrogen was evolved when the quinone was treated under various conditions with alkaline hydrosulfite solution, with zinc dust and acetic acid, or with 1,4-naphthohydroquinone, indicating that the azido group is attacked prior to, or along with, the reduction of the quinone group. 2-Amino-1,4-naphthoquinone usually was found as an end-product after air-oxidation, but the reductions were not smooth.

The Reaction of Hydrazoic Acid with other Quinones.—Azidohydroquinone corresponding to the description of Oliveri-Mandalà[3] was obtained in 40% yield by adding an aqueous solution of sodium azide (110% excess) to a solution of quinone in acetic acid (instead of from anhydrous hydrazoic acid in benzene). With only a 15% excess of sodium azide a quinhydrone (black needles) of explosive character was obtained. Treated in the same way with a 57% excess of sodium azide, toluquinone was converted partly into toluquinhydrone, m. p. 96–98°, and partly into an azido-toluhydroquinone. This formed colorless needles from ether–petroleum ether, it turned pink in the sunlight, and exploded when heated. From *ar*-tetrahydro-α-naphthoquinone there was obtained a substance crystallizing as purple-black needles and having the character of a quinhydrone. The substance exploded on being heated, and when shaken with dilute alkali it evolved nitrogen and gave a blue solution.

Summary

Korczynski's account of the reaction of hydrazoic acid with α- and β-naphthoquinone is in error, for the reaction products, obtainable in excellent yields, are 2-amino-1,4-naphthoquinone and 4-amino-1,2-naphthoquinone. It is believed that hydrazoic acid adds to the conjugated system of the quinones and that the azidonaphthohydroquinones at once suffer intramolecular oxidation–reduction with the liberation of nitrogen and formation of the aminoquinones.

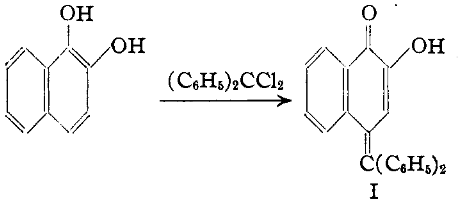
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 6, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Tautomerism between Diphenylmethyl-β-naphthoquinone and Hydroxy-α-naphthofuchsone

BY LOUIS F. FIESER AND JONATHAN L. HARTWELL

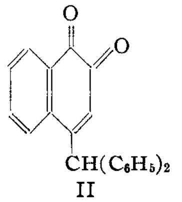
On treating 1,2-dihydroxynaphthalene with benzophenone dichloride in the expectation of obtaining a colorless, inert diphenylmethylene ether, there was produced instead an orange-red, alkali-soluble compound, $C_{23}H_{16}O_2$. In view of the ease with which monohydric phenols and naphthols are converted into fuchsones and naphthofuchsones by the same reagent, the reaction can be formulated as follows



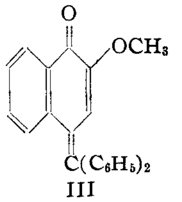
I

The color, acidity and composition of the compound all correspond well with its formulation as 2-hydroxy-1,4-naphthofuchsone-1 (I). Such a substance is unknown in the benzene series, for catechol reacts with benzophenone dichloride to give the diphenylmethylene ether.[1] The greater reactivity of the α-position of naphthalene probably is responsible for the nuclear substitution observed in the present case.

While there is no doubt about the nature of the reaction, it is a more subtle problem to determine whether the substance exists wholly or chiefly in the naphthofuchsone form I or in the tautomeric form of 4-diphenylmethyl-1,2-naphthoquinone, II. The solubility of the substance in alkali speaks for the naphthofuchsone structure, and it has been found also that the compound forms an acetate and that it is converted into the methyl ether III by the action of diazomethane.



II



III

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[1] Sachs and Thonet, *Ber.*, **37**, 3328 (1904).