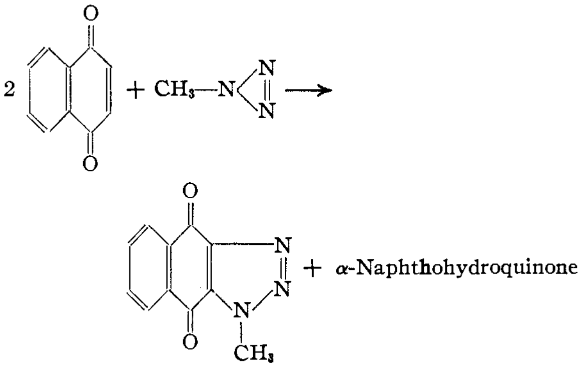
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Diazomethane Derivatives and of Azides on Alpha and Beta Naphthoquinones

BY LOUIS F. FIESER AND JONATHAN L. HARTWELL

It is known from the investigations of Wolff[1] and from previous work in this Laboratory[2] that phenylazide,[1] diazomethane,[2] diazoacetic ester,[2] and diphenyldiazomethane[2] add readily to the quinonoid double bond of α-naphthoquinone, and an additional example has been found in the course of the present work:

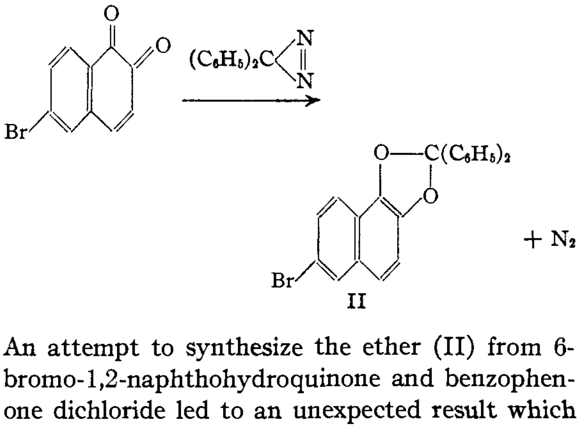


I

The product of the reaction with methyl azide, I, is identical with the 1-methyl-*lin*-naphthotriazole-8,9-quinone prepared recently by Fries, Walter and Schilling[3] by another method. The normal oxidation–reduction potential of this isolog of anthraquinone in 50% alcohol, 0.1 N in hydrochloric acid, at 25° was found to be 0.235 v., a value not far from that for the corresponding 1-phenyl derivative (E_0 = 0.256 v.).[4]

One object of our investigation was to determine the manner in which these same addenda react with a typical ortho quinone having an ethylenic linkage available for addition. The only previous experiments in this direction have been with diazomethane and β-naphthoquinone,[2,5] but only resinous products were obtained. Thinking that the poor results might be associated in some measure with the unusual sensitivity of this particular quinone, we decided to study one of the more stable derivatives. Since 6-bromo-1,2-naphthoquinone,[6] unlike the parent substance, does not decompose in organic solvents and can be obtained in a completely pure condition by recrystallization, it seemed well suited to the purpose. In benzene solution the quinone reacts with diazomethane, either in an absolute ethereal solution or in the presence of methyl alcohol, to give a light yellow, alkali-insoluble powder melting at 190–200°, but we were unable to obtain from this any crystalline products. The results with diazoacetic ester were no better, for under a variety of conditions only starting material could be recovered, and even after heating the reagents for eighteen hours at 100° in xylene there was no evidence of an addition reaction. Phenyl azide, acting on 6-bromo-1,2-naphthoquinone without solvent at 66° for nine hours, converted the quinone into a black powder which was identified as the dinaphthyldiquinhydrone. β-Naphthoquinone behaved in the same way, and methyl azide (in benzene at 105°) also served only to catalyze the self-addition of these two ortho quinones.

It can be inferred from these negative results that the double bond in the ortho quinone nucleus has little additive power for this type of reagent. More convincing evidence on this point was found in studying the reaction of 6-bromo-1,2-naphthoquinone with diphenyldiazomethane in benzene solution at room temperature. There was produced in nearly quantitative yields a colorless, nitrogen-free compound having the properties of the diphenylmethylene ether of the corresponding hydroquinone (II), indicating that the reaction had taken the course



II

An attempt to synthesize the ether (II) from 6-bromo-1,2-naphthohydroquinone and benzophenone dichloride led to an unexpected result which

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[1] Wolff, *Ann.*, **394**, 68 (1912); **399**, 274, 287 (1913).

[2] Fieser and Peters, THIS JOURNAL, **53**, 4080 (1931).

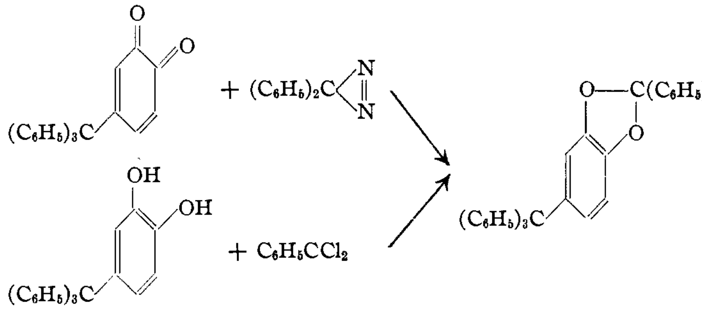
[3] Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

[4] Fieser and Ames, THIS JOURNAL, **49**, 2604 (1927).

[5] Von Pechmann and Seel, *Ber.*, **32**, 2292 (1899).

[6] Fries and Schimmelschmidt, *Ann.*, **484**, 245 (1930).

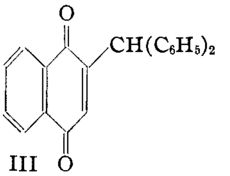
will be described in a later paper, but a complete proof of the course of the reaction was established in the case of another ortho quinone as follows

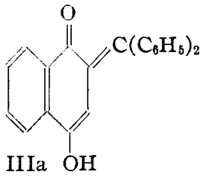


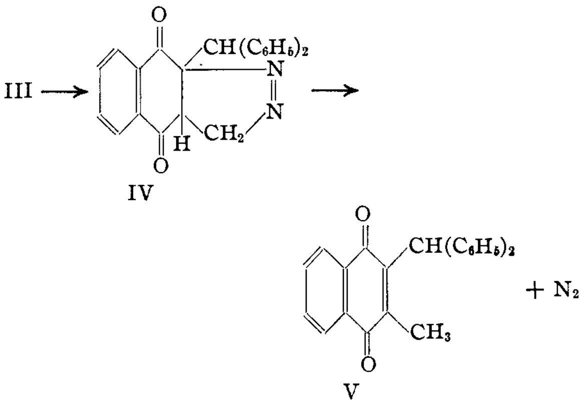
The first of these reactions was markedly catalyzed by ethyl alcohol.

The formation of a methylene ether from an ortho quinone and a diazoalkane has been observed before in the case of phenanthrenequinone,[7] but it is rather surprising that such a reagent should attack the diketone system when a reactive ethylenic linkage is also available. It will be recalled that β-naphthoquinone is nitrated exclusively in the 3-position, and that a high degree of reactivity at the end of the conjugated system (C_4) is manifested in a number of different reactions. Diene addition at the 3,4-double linkage occurs even when a blocking methyl group is situated at C_3.[8] The diazo compounds and the azides seem to be reagents of a special type in that they add to a quinonoid linkage only when it is flanked by two carbonyl groups. Even when such addition is hindered, as by the presence of a 2-methyl group in a 1,4-naphthoquinone, a reaction occurs with diazomethane with the result that a methylene group is inserted between two molecules of the quinone at the C_3 and C_3' positions.[8,9] It is consistent with the above results that a 3-methyl-1,2-naphthoquinone remains unchanged under similar conditions.

In order to gain a further insight into the action of diazomethane on alkylated quinones, a study was made of the readily available 2-diphenylmethyl-1,4-naphthoquinone.[10] One interesting point was to determine if this substance, III, is capable of existing in the tautomeric form IIIa, and this question was soon answered in the negative. Instead of forming a methyl ether, the compound gives with diazomethane in nearly quantitative yield the colorless pyrazoline IV. This substance loses nitrogen smoothly at the melting point and yields a compound having the composition and properties of 2-diphenylmethyl-3-methyl-1,4-naphthoquinone, V. Analogies from the aliphatic series for both the formation and the pyrolysis of the pyrazoline are available in the work of von Auwers,[11] and the reaction series finds a close parallel in the conversion of aldehydes by means of diazomethane into methyl ketones.[12]


III


IIIa



The 2-methyl-1,4-naphthoquinone previously investigated[8] may also form in the first phase of the reaction a pyrazoline similar to IV, but this appears to be unstable at the reaction temperature (100°). That a methyl homolog similar to V is not formed when the unstable pyrazoline loses nitrogen may be because the initial reaction of the quinone with diazomethane in this case proceeds so slowly that unchanged quinone is always available for combination with the intermediate free radical before the latter can isomerize to a stable form. According to this analysis,

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(7) Alessandri, *Atti accad. Lincei*, **22**, I, 517 (1913); Biltz and Paetzold, *Ann.*, **433**, 64 (1923).

(8) Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934).

(9) The negative result reported by Macbeth and Winzor, *J. Chem. Soc.*, 334 (1935), doubtless refers to an experiment conducted at room temperature; the experiment of Fieser and Seligman was conducted at 100°.

(10) Möhlau, *Ber.*, **31**, 2351 (1898); Möhlau and Klopfer, *ibid.*, **32**, 2146 (1899).

(11) Von Auwers, *et al.*, *Ann.*, **470**, 284 (1929); **496**, 27, 252 (1932); *Ber.*, **66**, 1198 (1933).

(12) Meyer, *Monatsh.*, **26**, 1295 (1905); Arndt and Eistert, *Ber.*, **61**, 1118 (1928).

the essential difference in the behavior of the 2-methyl and the 2-diphenylmethyl derivatives of α-naphthoquinone is that the latter reacts so much more readily with diazomethane than the former that a pyrazoline can be produced at a temperature at which it is stable.

Experimental Part

1-Methyl-*lin*-naphthotriazole-8,9-quinone (I).—An ethereal solution of methyl azide prepared from 2.5 g. of sodium azide by the method of Dimroth and Wislicenus[13] was added to a solution of 1 g. of α-naphthoquinone in 25 cc. of benzene and 5 cc. of absolute alcohol. Since there was little reaction at room temperature, the solution was heated in a sealed tube at 105° for twenty hours. On cooling, 0.65 g. (48%) of crystalline material, m. p. 248–250°, separated. Recrystallized from benzene, the substance formed very faintly yellow needles, m. p. 248–250°. The compound was identical with a sample prepared (by E. L. Martin) by the literature method.[3]

Anal. Calcd. for $C_{11}H_7O_2N_3$: C, 62.0; H, 3.31. Found: C, 62.1, 62.1; H, 3.78, 3.04.

The mother liquor on evaporation yielded a large crop of 1,4-naphthohydroquinone.

Preparation of 6-Bromo-1,2-naphthoquinone.—Using the standard methods,[14] 1,6-dibromo-2-naphthol was prepared in 80% yield (the reported yield is miscalculated) and reduced to 6-bromo-2-naphthol in 94% yield. This product contained a small amount of alkali-insoluble material, m. p. 82°, which was identified as the ethyl ether. For comparison with the literature method,[6] 6-bromo-1,2-naphthoquinone was prepared from 6-bromo-2-naphthol through the 1-*p*-sulfobenzeneazo dye, and the 1-amino compound, but the yield was poor (40%) and the process not well adapted to large-scale operation. The only intermediate or derivative isolated was **1-amino-6-bromo-2-naphthol diacetate;** prisms, m. p. 120–121° (calcd. for $C_{14}H_{12}O_3NBr$: C, 52.2; H, 3.76. Found: C, 52.0, 52.1; H, 3.82, 3.89).

The method of Fries and Schimmelschmidt[6] was much more satisfactory. On preparing the nitro ketone on a large scale (from 300 g. of 1,6-dibromo-2-naphthol) it was found convenient to use only half the quantity of acetic acid specified in the literature; yield, 69%. For conversion to the quinone the nitro ketone should be completely dry; yield, 52%. The quinone was obtained as large, transparent, orange prisms from benzene.

Reaction with Phenyl Azide.—When finely powdered 6-bromo-1,2-naphthoquinone was heated at 66° with phenyl azide for twenty hours, the material slowly went into solution. On adding ether, a sparingly soluble, black powder was precipitated. It was identified as a dinaphthyldiquinhydrone by conversion on reductive acetylation into **6,6′-dibromo-1,2,1′,2′-tetraacetoxy-4,4′-dinaphthyl,** which formed fibrous colorless needles, m. p. 226–226.5°, from alcohol–benzene.

Anal. Calcd. for $C_{28}H_{20}O_8Br_2$: C, 52.2; H, 3.13. Found: C, 52.6; H, 3.25.

The same compound was obtained as the sole product of the reductive acetylation of 6-bromo-1,2-naphthoquinone.

From β-naphthoquinone (2 g.) and phenyl azide (4 g.) we likewise obtained only dinaphthyldiquinhydrone (1.5 g.), identified by conversion to the tetraacetoxydinaphthyl, m. p. 164–165°. Similar results were obtained with methyl azide.

Diphenylmethane Ether of 6-Bromo-1,2-dihydroxynaphthalene.—A petroleum ether solution of diphenyldiazomethane prepared from 5.8 g. of benzophenone was added to a solution at room temperature of 5 g. of 6-bromo-1,2-naphthoquinone in 600 cc. of pure benzene. After fifteen hours the orange-yellow solution on concentration yielded 7.8 g. (92%) of slightly colored but nearly pure product. The color was removed easily by a single crystallization from glacial acetic acid in the presence of a trace of zinc dust, or by repeated crystallization from benzene. The ether forms large colorless prisms melting at 150.5–151°.

Anal. Calcd. for $C_{23}H_{15}O_2Br$: C, 68.5; H, 3.73; Br, 19.8. Found: C, 68.5; H, 3.90; Br, 20.3

In one experiment (the first) the yield of the ether was only 67% and there was isolated from the dark-red mother liquor a substance which is very soluble in benzene and which forms fiery red needles, m. p. 210–210.5°, from acetic acid (found: C, 70.97; 70.93; H, 4.33, 4.28). Only a small amount of this material was obtained, and we were unable to produce more of the red substance in subsequent runs carried out under a variety of conditions (using pure and crude solvents, adding alcohol or moisture). The yields of ether were nearly quantitative and the mother liquors were never red.

Diphenylmethylene Ether of 4-Triphenylmethylcatechol.—The reaction of diphenyldiazomethane (in petroleum ether) with 4-triphenylmethyl-1,2-benzoquinone[15] (in chloroform) at room temperature was markedly catalyzed by 95% alcohol. Without alcohol no change occurred on standing overnight; after adding alcohol (10 cc. for 3 g. of quinone) crystals of the reaction product began to separate in one hour. The ether, which is sparingly soluble in glacial acetic acid and readily soluble in chloroform, was obtained in 76% yield. It crystallizes from dioxane as very fine, colorless needles, m. p. 258–259°. Micro- and semimicroanalyses gave irregularly low results for carbon, but the structure was established by synthesis from 4-triphenylmethylcatechol (2 g.) and benzophenone dichloride (3.4 g.), heated for seventeen hours on the steam-bath. A solution of the viscous mass in benzene deposited on cooling a crystalline product (64% yield) melting at 257–258° and showing no depression when mixed with the above sample of the ether.

Addition of Diazomethane to 2-Diphenylmethyl-1,4-naphthoquinone.—On adding a solution of diazomethane (from 4 g. of nitrosomethylurethan) in 65 cc. of dry ether to a solution of 4 g. of the quinone in 85 cc. of benzene, colorless crystals began to separate in about one minute and in ten minutes the liquid was filled with crystals. After one hour the total yield, including a second crop, amounted to 4 g. (89%). The compound is sparingly soluble in ether or benzene and crystallizes from alcohol-benzene as colorless needles melting at 167–168° with gas

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(13) Dimroth and Wislicenus, *Ber.*, **38**, 1573 (1905).

(14) Franzen and Stäuble, *J. prakt. Chem.*, **103**, 368 (1922).

(15) Zincke and Wugk, *Ann.*, **363**, 284 (1908).

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.

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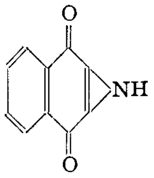
The Reaction of Hydrazoic Acid with the Naphthoquinones

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.



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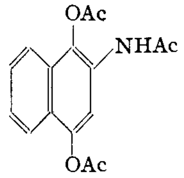

II

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).