

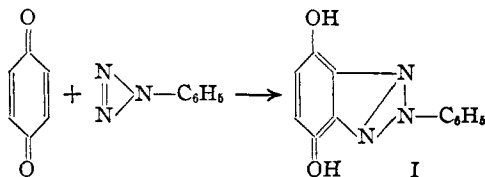
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION OF DIAZOMETHANE AND SOME OF ITS DERIVATIVES TO ALPHA-NAPHTHOQUINONE¹BY LOUIS F. FIESER AND MARY A. PETERS²

RECEIVED JULY 16, 1931

PUBLISHED NOVEMBER 5, 1931

The brilliant discovery by Diels of the addition of unsaturated hydrocarbons to compounds containing an active double bond has given fresh impetus to the study of the addition of unsaturated compounds other than hydrocarbons to quinones. In the field of the unsaturated nitrogen compounds, the observations in this direction are not numerous. Wolff³ added phenylazide to benzoquinone, proved that the addition takes place at the ethylene linkage, and showed that the first reaction product is phenyl benzimidazolo-hydroquinone, I



The only other investigations are those of von Pechmann,⁴ who studied the action of diazomethane. Von Pechmann found that this reagent adds readily to benzoquinone and α -naphthoquinone and he proved that the addition takes place at the quinonoid ethylene linkage and results in the formation of a pyrazole nucleus. There is, however, as will be shown later, reason to question his formulation of the reaction products.

The addition of the substitution products of diazomethane to the quinones is an unexplored field and one which is particularly inviting because of the possibility of utilizing suitable addition products for the preparation of cyclopropane derivatives of quinones and hydroquinones. With this aim in view and with the idea of checking von Pechmann's work we have studied the reaction of α -naphthoquinone with diazomethane, diazoacetic ester and diphenyldiazomethane. Benzoquinone is less suited for the purpose because it ordinarily adds two molecules of reagent and there are two possible modes of addition. Preliminary experiments showed that β -naphthoquinone gives much poorer results than the para isomer.

1. **Diazoacetic Ester.**—This reagent reacts slowly but smoothly with

¹ Third paper in the series, "A Comparison of Heterocyclic Systems with Benzene," *THIS JOURNAL*, **48**, 1097 (1926); **49**, 2604 (1927).

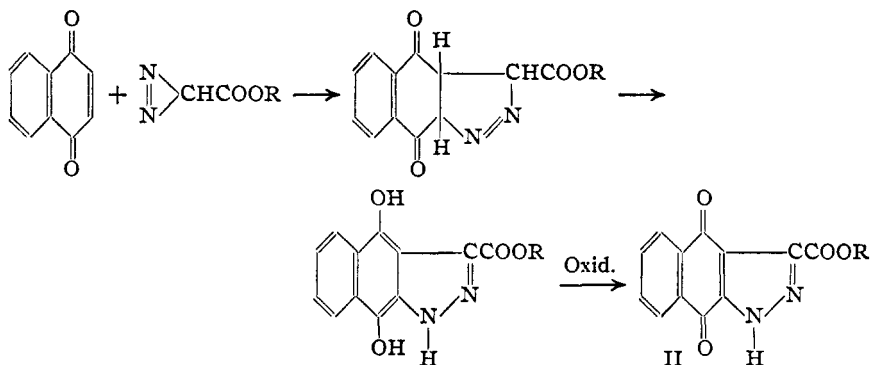
² This paper reports work completed by Mary A. Peters in partial fulfilment of the requirements for the degree of Master of Arts at Radcliffe College.

³ Wolff, *Ann.*, **394**, 68 (1912).

⁴ (a) Von Pechmann, *Ber.*, **28**, 855 (1895); (b) von Pechmann and Seel, *ibid.*, **32**, 2292 (1899).

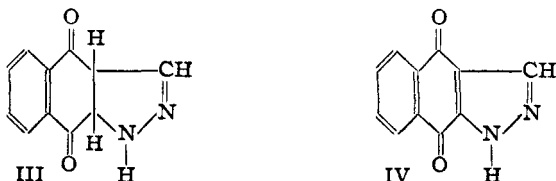
α -naphthoquinone in benzene solution to give two products. One of these (48% yield) is α -naphthohydroquinone. The other, obtained in 47% yield, has the composition of the two reaction products minus two hydrogen atoms. It is a yellow compound which forms a red vat on alkaline reduction, and a fluorescent solution on acid reduction, and which resembles anthraquinone in another highly characteristic property, namely, in its reduction potential. The substance is thus a heterocyclic analog of anthraquinone, in which the heterocyclic ring has aromatic properties, and it may be assigned the formula of 3-carbethoxy-lin.-naphthindazole-4,9-quinone (II, below).

The complete reaction thus consists in the slow addition of diazoacetic ester to α -naphthoquinone, isomerization of an azo-containing ring to a pyrazole nucleus, enolization of the reaction product and finally the oxidation of the dienol by unreacted α -naphthoquinone:



The quinone ester, II, yields a hydroquinone triacetate on reductive acetylation, while on hydrolysis there is formed a free acid which is characterized by being only slightly colored. The precipitated material is colorless and the crystalline product is only a pale buff-yellow. The substance nevertheless vats and forms an oxidation-reduction system of characteristic potential.

2. Diazomethane.—From α -naphthoquinone and diazomethane von Pechmann⁴ obtained in good yield a colorless, high-melting compound. By the oxidation of a similar substance obtained from naphthazarine, he proved the presence in this compound of a pyrazole ring. His analyses agreed well with the formula $\text{C}_{11}\text{H}_8\text{O}_2\text{N}_2$, which represents the sum of the elements of the reactants, and on this basis he formulated the compound as diketonaphthodihydropyrazole, III. The compound was found to be



readily soluble in alkali, and it is this fact which, we believe, is not in accord with von Pechmann's formula. His view that this imino hydrogen should be acidic is hardly warranted. Furthermore, from our results with diazoacetic ester, a compound having the structure of III would be expected to enolize to a hydroquinone type.

In repeating von Pechmann's experiments we observed first the formation in quantitative yield of a yellow intermediate which has the composition, $C_{11}H_8O_2N_2$, assigned by von Pechmann to the final product. It was unstable and on crystallization, or on dissolution in alkali, it changed over into the white substance described by von Pechmann. Our analyses of the white compound, however, indicate the formula $C_{11}H_6O_2N_2$, which has two hydrogen atoms less than his empirical formula. According to our results the yellow substance becomes oxidized to the white compound on crystallization. The true nature of the latter compound remained obscure for a time on account of the total absence of color in any of the samples purified by crystallization.

The compound nevertheless is a quinone! It forms a red vat which is decolorized by air oxidation; it can be reduced easily by means of hydrogen and a catalyst to a hydroquinone with which it forms a stable oxidation-reduction system, having a potential of 0.1545 v. The value is practically identical with that for the anthraquinone-anthrahydroquinone system. From these facts, and from von Pechmann's degradation experiments, we feel justified in assigning to the substance the structure of lin.-naphthindazole-4,9-quinone, IV. Confirmation of this structure is furnished by the fact that alkylation with dimethyl sulfate in alkaline solution yields a monomethyl derivative in which the methyl group must be attached to nitrogen because the quinone group remains intact, as shown by electro-metric titration experiments. The alkali solubility of the original substance is thus attributable to the imino hydrogen atom which, in formula IV, but not in formula III, is flanked by two unsaturated groups.

Final evidence that von Pechmann's compound is lin.-naphthindazole-4,9-quinone was found in the preparation of this substance by the decarboxylation of the 3-carboxy derivative described above. In preparing the compound by this method we made the interesting observation that the sublimed material is faintly, but distinctly, yellow. The quinone thus does not always lack the property which is so characteristic of the class to which it belongs.

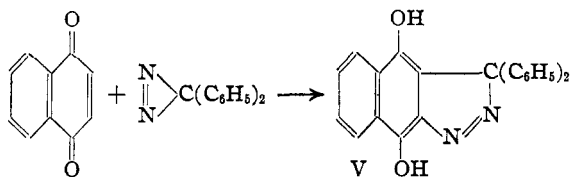
The yellow intermediate product is the hydroquinone of lin.-naphthindazole-4,9-quinone. Like anthrahydroquinone, it is oxidized by the air with great ease, and hence passes into the quinone on crystallization.

The reactions of α -naphthoquinone with diazomethane and with diazoacetic ester both involve isomerization of the primary addition product to a pyrazole derivative and dienolization to a hydroquinone. In the case of

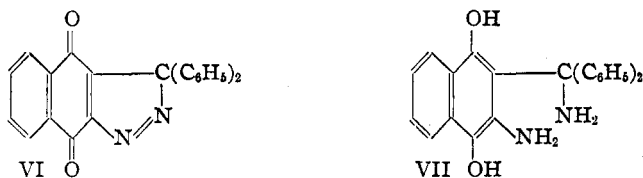
diazomethane the hydroquinone may be isolated, whereas with diazoacetic ester the hydroquinone becomes oxidized quantitatively by unreacted α -naphthoquinone. Since the former hydroquinone is equally capable of being oxidized, it must be concluded that the diazomethane addition is so rapid that no α -naphthoquinone is available for the oxidation. This corresponds with the fact that the reaction is practically instantaneous in the former but not in the latter case.

3. Diphenyldiazomethane.—With each of the reagents mentioned above the primary addition is followed by a shift of the hydrogen from the methane carbon atom to nitrogen, with the subsequent formation of a pyrazole ring. The stable, aromatic character of this ring probably serves to induce the isomerization. In order to produce an addition product in which the azo group would remain intact and from which nitrogen might be eliminated with the closing of a cyclopropane ring, it would seem necessary to replace both of the hydrogen atoms of diazomethane by groups which cannot shift. We thus turned to the diphenyl derivative.

Diphenyldiazomethane reacts vigorously with α -naphthoquinone in benzene solution to give an orange substance having the composition of the sum of the reactants. Since it is found to be a dibasic phenol having the properties of a hydroquinone, it must have the structure of the cyclic azo compound, 2,3-(3,3-diphenyl-pseudopyrazolo-4,5)-1,4-naphthohydroquinone, V. Thus the compound yields a diacetate and a dimethyl ether,



and it may be oxidized by either mercuric oxide or nitrous acid to a quinone, VI.

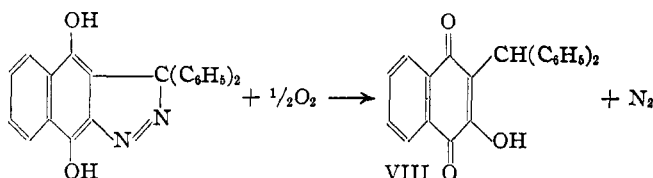


Evidence that the substance contains an azo group is furnished by the result of reduction experiments. Treated with zinc and acetic acid, it takes up four atoms of hydrogen with the formation of a compound having the composition of VII, while on reductive acetylation the diacetate of this compound is produced.

In dilute alcoholic solution the new hydroquinone and its oxidation product form a stable system whose oxidation-reduction potential is

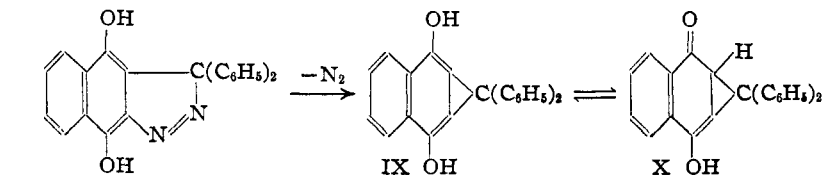
0.5806 v. Comparing this with the value of 0.483 for α -naphthoquinone,⁵ it is seen that the unsaturated azo grouping raises the potential to a considerable extent. This explains why in the above reaction the product isolated is a hydroquinone whereas with diazoacetic ester the product is a quinone. In the latter case the substance produced has a lower potential than the starting material and hence becomes oxidized.

The new azo compound exhibits a striking reaction when the purple alkaline solution of the material is shaken with the air. The color changes through green to a clear red, and on acidification there is precipitated a yellow substance which has been identified as 2-diphenylmethyl-3-hydroxy-1,4-naphthoquinone, VIII.⁶



The reaction is a peculiar one. It appears to involve an oxidation of the hydroquinone nucleus and hydrolysis of the azo grouping with the elimination of nitrogen. The quinone, VI, does not appear to be an intermediate reaction product because it is not affected by alkali. The hydroquinone, V, is likewise indifferent to this reagent alone, for, in the absence of oxygen, the solution is perfectly stable. Thus the two reactions, oxidation and hydrolysis, appear to occur simultaneously. It is possible that the cleavage is brought about by hydrogen peroxide resulting from the air oxidation of the hydroquinone, but we have been unable to secure any evidence for such a mechanism.

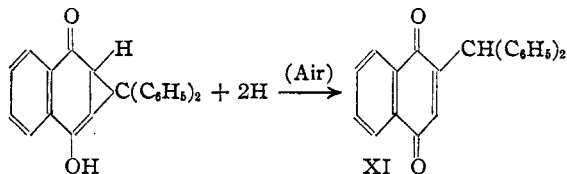
Thermal Decomposition.—While the nitrogen in the azo compound may be eliminated in this rather novel way, it was of interest to see if the substance could be converted into a cyclopropane derivative, following the more usual type of reaction. This indeed is the case. The azo compound melts at 203° and at that temperature decomposes with the evolution of nitrogen. Of three products isolated from the reaction mixture one was found to be a cyclopropane derivative. The substance, which is bright red in color, has the analysis but not the properties of the product, IX, which



⁵ Conant and Fieser, *THIS JOURNAL*, **46**, 1858 (1924).

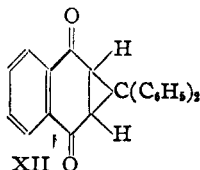
⁶ Fieser, *ibid.*, **48**, 3201 (1926).

might be expected as the result of the simple elimination of nitrogen from the molecule. It forms a monoacetate, and quantitative reaction with the Grignard reagent revealed the presence of one active hydrogen atom and one carbonyl group. Apparently because of the great accumulation of unsaturated groups in IX, the substance has ketonized and is to be represented by formula X. Evidence for this structure was found in the behavior of the substance on reduction. By means of zinc and acetic acid, followed by air oxidation of a hydroquinone first formed, it is converted smoothly into 2-diphenylmethyl-1,4-naphthoquinone, XI,⁷ while on reductive acetylation the hydroquinone diacetate of this substance is produced.



On examining the other products formed in the thermal decomposition of the azo compound it was found that one of these is the quinone, VI, of the azo compound, while the other is 2-diphenylmethyl-1,4-naphthoquinone, XI. This shows that, at the high temperature of the reaction, the decomposition product is partially reduced at the expense of some of the starting material. With the idea that this side-reaction might be avoided by the use of acyl or alkyl derivatives of the hydroquinone, several such substances were prepared and investigated, but none of them behaved as well as the parent substance.

From the behavior of the new cyclopropane derivative it seems improbable that a stable compound, in which the ethylene linkage of α -naphthoquinone is replaced by a cyclopropane ring, can exist. Through a second ketonization, the red decomposition product (X) should yield the quinone of formula XII, but the substance shows no tendency to undergo such a ketonization.

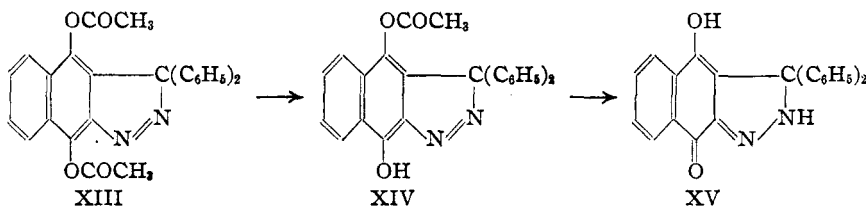


Hydrolysis Product of the Cyclic Azo Compound (V).—An interesting compound was discovered when the diacetate (XIII, below) of 2,3-(3,3-diphenyl-pseudopyrazolo-4,5)-1,4-naphthohydroquinone was hydrolyzed with alcoholic alkali. A substance was produced having the composition

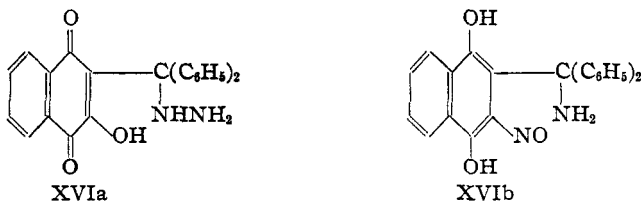
⁷ Möhlau and Klopfer, *Ber.*, **32**, 2146 (1899).

of the unacetylated hydroquinone plus the elements of water. The material, which is either orange or fiery red, dissolves in cold alkali with an intense blue coloration; but, on attempting to determine the number of hydroxyl groups by acetylation, it was found that the material is reconverted into the original diacetate, XIII. The compound has the properties of a quinone, for it takes up two hydrogen atoms on reduction with titanous chloride, and it was found to have a reduction potential of 0.2422 v.

While we have not yet completely solved the problem presented by this compound, we believe that a clue to the mode of its formation is furnished by the fact that the hydrolysis of the diacetate proceeds in normal fashion, and gives the original hydroquinone, when a large quantity of alkali is employed. The new compound is formed on hydrolysis with a small amount of alkali, and this suggests that a monoacetate is responsible for the abnormal reaction. It is reasonable to suppose that hydrolysis would attack first the acetyl nearest to the azo group, because of its unsaturation, and hence that the monoacetate has the structure of XIV.



This might undergo a tautomerization from the hydroxyazo type to a hydrazone structure, which on splitting off the other acetyl group would give XV. Being a quinonimine, this could undergo hydrolysis with rupture of the heterocyclic ring, giving, after rearrangement to the most stable form, the naphthoquinone derivative, XVIa. This formula accounts



satisfactorily for the low reduction potential observed for the new compound, for its quinone-like character, and for the ease with which the material may be converted into the original diacetate. Beyond this there is at present no evidence in support of this structure, and it may be said that the formula here suggested hardly explains the ease with which the substance dissolves in alkali. Another possible formula, and one which is in better accord with the alkali-solubility, is XVIb, or one of its tautomeric forms. This also accords with the other properties of the substance, but it

is not clear why such a compound should not be formed from the original hydroquinone as well as from its diacetate. We hope to investigate the matter more fully in the course of further researches in this field.

4. Benzoquinone and Diphenyldiazomethane.—These substances react readily in benzene solution to give in nearly quantitative yield a compound which forms excellent yellow crystals, and which obviously is the lower benzologue of the compound from α -naphthoquinone.⁸ The compound, however, is less interesting. It is not affected by oxygen in an alkaline solution, the hydrolysis of the diacetate follows a normal course, and no good products could be obtained on thermal decomposition. A remarkable observation may be recorded in connection with the acyl derivatives of the substance. While the dimethyl ether is yellow like the original azo compound itself, the monobenzoate and the diacetate are very nearly colorless.

We are indebted to Mr. Charles L. Bickel and to Mr. Morris N. Young for carrying out several of the analyses (micro and semi-micro) reported in this paper.

Experimental Part

1. Addition of Diazoacetic Ester.—To a solution of 10 g. of α -naphthoquinone in benzene at room temperature a solution of 4 g. of diazoacetic ester in ether was added. The solution was warmed gently at first, boiled for one-half hour, and allowed to stand overnight. By this time the solution had become dark red and the reaction product was deposited as a hard crystalline crust. On digesting this material with chloroform, there was a residue consisting of almost pure 1,4-naphthohydroquinone. Crystallized from benzene it formed colorless needles, m. p. 191°, mixed m. p. with an authentic sample, 190°; yield, 4.9 g. (48%). The chloroform extract on evaporation yielded yellow crystals of the heterocyclic quinone; yield, 7.9 g. (47%).

3-Carbethoxy-lin.-naphthindazole-4,9-quinone (II).—The compound crystallizes well from alcohol or benzene, forming tufts of yellow micro-needles melting at 186.5°. It forms a red vat with alkaline hyposulfite solution and a yellow solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_{10}O_4N_2$: C, 62.21; H, 3.73; N, 10.37. Found: C, 62.12; H, 3.72; N, 10.49.

Hydroquinone Triacetate.—This substance, prepared by reductive acetylation in the usual manner, forms highly refractive colorless prisms melting at 179°. It dissolves readily in alcohol or glacial acetic acid and crystallizes best from ether.

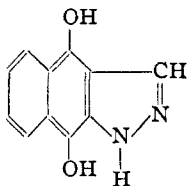
Anal. Calcd. for $C_{20}H_{18}O_7N_2$: C, 60.29; H, 4.56; N, 7.04. Found: C, 60.14, 59.47; H, 5.44, 5.06; N, 6.87, 7.06.

3-Carboxy-lin.-naphthindazole-4,9-quinone.—The ester is hydrolyzed on boiling with alkali and the free acid forms a colorless precipitate on acidification of the yellow solution. On crystallization from alcohol, in which the acid is only moderately soluble, the substance forms small, pale straw-yellow crystals melting at 281°. The alkaline solution is yellow and the vat is red. When the very faintly-colored solution of the

⁸ Staudinger, Anthes and Pfenninger, *Ber.*, **49**, 1928 (1916), noted this reaction several years ago and proposed to study the subject in detail, but their plans evidently have been abandoned.

quinone is shaken with hydrogen and a catalyst, a decidedly yellow and fluorescent solution of the hydroquinone is produced.

Anal. Calcd. for $C_{12}H_6O_4N_2$: C, 59.50; H, 2.50; N, 11.49. Found: C, 59.21; H, 2.83; N, 11.53.



2. Addition of Diazomethane: Lin.-naphthindazole-4,9-hydroquinone.—An ethereal solution of diazomethane from 1.3 cc. of nitrosomethyl urethan was added to a solution of 0.5 g. of α -naphthoquinone in ether. Feathery yellow needles began to separate immediately, and these were collected and quickly dried; yield, 0.58 g. (93%). The substance could not be purified further because, on crystallization, it passed over into the oxidation product described below. The compound remains unmelted at 360° ; it darkens rapidly on storage.

Anal. Calcd. for $C_{11}H_8O_2N_2$: C, 65.98; H, 4.03. Found: C, 66.45, 66.54; H, 4.05, 3.95.

Lin.-naphthindazole-4,9-quinone (IV).—Crystallization of the above hydroquinone from glacial acetic acid gave the white product described by von Pechmann and Seel.^{4b} The material obtained in this way is in the form of a colorless, crystalline powder which, seen under the microscope, consists of very fine, curled needles. Our samples melted at 349° (copper block).

The material sublimes at about the melting point and may be obtained thus in the form of small rectangular plates which are faintly but distinctly yellow. The compound is obtained in this form when it is prepared by the decarboxylation of 3-carboxy-lin.-naphthindazole-4,9-quinone. The reaction is brought about by heating the acid at a temperature slightly above its melting point (281°) with a trace of copper powder. The melt soon solidifies and the decarboxylated quinone then appears as a pale yellow sublimate. The identity of the two samples was established by mixed melting point determination. The compound is sparingly soluble in alcohol or benzene, gives a yellow solution in alkali, forms a red vat, and gives a yellow, fluorescent solution on acid reduction.

Since our first analyses did not agree with those of von Pechmann and Seel, the substance was burned by different operators under a variety of conditions. The results point clearly to the formula $C_{11}H_8O_2N_2$.

| | ANALYSES | | |
|------------------------------|----------|------|-------|
| | C, % | H, % | N, % |
| Semi-micro | 67.18 | 3.46 | |
| burned in oxygen | 67.00 | 3.44 | |
| Semi-micro, burned in air | 66.83 | 3.44 | |
| Micro | 66.77 | 3.47 | 13.98 |
| Von Pechmann and Seel | 66.2 | 3.9 | 14.4 |
| | 66.1 | 3.5 | 14.1 |
| | 65.8 | 3.8 | |
| | 65.8 | 3.8 | |
| Calcd. for $C_{11}H_8O_2N_2$ | 66.65 | 3.05 | 14.14 |
| Calcd. for $C_{11}H_8O_2N_2$ | 65.98 | 4.03 | 14.00 |

1-Methyl-lin.-naphthindazole-4,9-quinone.—This derivative of the quinone was obtained by the action of dimethyl sulfate in alkaline solution. It was crystallized from alcohol and formed long, flat, colorless micro-needles melting at 312° . It is insoluble in alkali.

Anal. Calcd. for $C_{12}H_8O_2N_2$: C, 67.91; H, 3.80. Found: C, 67.87; H, 3.83.

3. **Diphenyldiazomethane and α -Naphthoquinone:** 2,3-(3,3-Diphenyl-pseudo-pyrazolo-4,5)-1,4-naphthohydroquinone (V).—It is essential to use pure α -naphthoquinone for this reaction; impurities appear to catalyze the decomposition of the diazo compound. Satisfactory material was obtained by distilling a dark, commercial product in vacuum, followed by crystallization from ether. The product formed pure yellow prisms melting at 128.5° . The yields obtained in the addition reaction were never good. Some of the quinone was always recovered, even when using a large excess of the other reactant. The best results were obtained by adding to a solution of 1 mol. equivalent of α -naphthoquinone in pure benzene at room temperature a petroleum ether solution of diphenyldiazomethane from 1.4 mol. equivalents of benzophenone hydrazone.⁸ The solution warmed of itself and, when the reaction had subsided, it was heated on the steam-bath for a few hours until there was no increase in the quantity of orange crystals which were slowly deposited. Collected from the hot solution before a dark product had commenced to deposit, this material was nearly pure; yield, 44%.

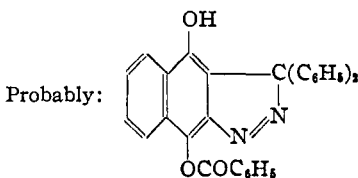
The substance is very soluble in alcohol or glacial acetic acid, sparingly soluble in ligroin, and it crystallizes well from benzene, in which it is moderately soluble. It forms flat, orange-yellow needles melting at 203° . It gives a red-purple solution in alkali or in sodium carbonate, and in the absence of oxygen the solution is stable. Sodium hyposulfite discharges the color, which returns on shaking with air.

Anal. Calcd. for $C_{28}H_{18}O_2N_2$: C, 78.59; H, 4.58; N, 7.95. Found: C, 78.59; H, 4.52; N, 8.36.

Diacetate (XIII).—This was prepared by the action of acetic anhydride on the above hydroquinone, using either sodium acetate or sulfuric acid as catalyst. It crystallized well from alcohol, forming orange, microscopic hexagonal plates melting at 259° and decomposing slowly at that temperature.

Anal. Calcd. for $C_{27}H_{20}O_4N_2$: C, 74.29; H, 4.62. Found: C, 73.96, 74.06; H, 4.80, 4.86.

Monobenzoate.—By the action of benzoyl chloride on the hydroquinone suspended in a solution of two parts of sodium carbonate, the monobenzoate was obtained. It crystallized from alcohol in the form of stout yellow crystals decomposing at about 144° and, according to the analysis, containing one molecule of water.



Anal. Calcd. for $C_{30}H_{20}O_4N_2 \cdot H_2O$: C, 75.92; H, 4.68; N, 5.91. Found: C, 76.14, 76.01; H, 5.36, 5.33; N, 6.31.

The compound gives a red solution in concentrated sulfuric acid and is insoluble in cold alkali. It yields the original hydroquinone, rather than the anomalous hydrolysis product described below, on hydrolysis with alcoholic alkali. Since in the formation of the compound it is probable that it is the more acidic of the two hydroxyls which is acylated, the substance probably has the structure indicated above. That the hydrolysis of this acyl derivative follows the normal course is in accord with the ideas advanced in the theoretical portion of the paper. We would expect to obtain the abnormal reaction with the other possible monobenzoate.

The dibenzoate was obtained either from the monobenzoate or by treating the hydroquinone with benzoyl chloride in the presence of a larger quantity of sodium carbonate (5 parts). Crystallized from benzene-ligroin it formed small pale yellow crystals melting at 215° with decomposition. On hydrolysis it yields the original hydroquinone.

Anal. Calcd. for $C_{37}H_{24}O_4N_2$: C, 79.26; H, 4.32. Found: C, 79.05; H, 4.52.

Dimethyl Ether.—Prepared by the action of dimethyl sulfate and alkali on the hydroquinone in a nitrogen atmosphere, this substance crystallized from methyl alcohol as pale green micro plates, m. p. 192°, dec.

Anal. Calcd. for $C_{23}H_{20}O_2N_2$: C, 78.92; H, 5.42. Found: C, 78.58; H, 5.44.

2,3-(3,3-Diphenyl-pseudopyrazolo-4,5)-1,4-naphthoquinone (VI).—The hydroquinone was oxidized either by shaking a benzene solution of the material with mercuric oxide for several hours or by adding an excess of sodium nitrite solution to a solution of the hydroquinone in glacial acetic acid. The latter method is the simpler and gives a quantitative yield. On diluting the acetic acid solution the quinone separates as a yellow crystalline powder. The substance is readily soluble in benzene or glacial acetic acid, moderately soluble in alcohol. From the latter solvent it forms yellow needles melting at 231°.

Anal. Calcd. for $C_{23}H_{14}O_2N_2$: C, 78.81; H, 4.03. Found: C, 78.77; H, 4.25.

The quinone displays an interesting reaction with alcoholic alkali. When a little alkali is added to a suspension of the quinone in boiling alcohol, the yellow material dissolves at once to give a colorless solution. On diluting this with water and acidifying, a colorless substance is precipitated. On crystallization, this reverts to the quinone.

Reduction of the Azo Compound, V.—A solution of the material in glacial acetic acid was boiled with zinc dust until it was only faintly yellow. Filtered from the zinc and diluted with dilute hydrochloric acid, the solution deposited a nearly colorless product. This crystallized from glacial acetic acid in the form of slightly buff-colored rosetts melting at 255° with decomposition. The substance is not soluble in sodium hydroxide solution but dissolves in alcoholic alkali. Analyses indicated the composition of 2-(α -amino- α , α -diphenylmethyl)-3-amino-1,4-dihydroxynaphthalene, VII.

Anal. Calcd. for $C_{23}H_{20}O_2N_2$: C, 77.50; H, 5.66. Found: C, 77.63, 77.46; H, 5.38, 5.40.

The diacetate of this compound was prepared by direct acetylation or by the reductive acetylation of the hydroquinone. It does not crystallize well, forming only a pale yellow crystalline powder, m. p. 142°, dec. It dissolves readily in the usual solvents.

Anal. Calcd. for $C_{27}H_{24}O_4N_2$: C, 73.61; H, 5.49. Found: C, 73.94, 73.72; H, 5.61, 5.52.

Alkaline Oxidation of the Azo Compound, V.—One gram of the substance was dissolved in the requisite amount of hot alcohol and the solution was treated with 2 cc. of 6 N alkali and shaken with air for fifteen minutes. The color changed from red-purple, through green, to red. Acidified and concentrated, the solution deposited yellow micro-crystals which, after crystallization from benzene, melted at 188°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.15; H, 4.74. Found: C, 80.57, 80.65; H, 4.92, 4.84.

The product was identified as 2-diphenylmethyl-3-hydroxy-1,4-naphthoquinone by direct comparison with a sample previously prepared by one of us.⁶

Thermal Decomposition of the Azo Compound, V.—The material, in 1-g. portions, was heated in a Wood's metal bath at 205–210° for five to ten minutes, when the evolution of nitrogen, which took place vigorously at first, had ceased. This gave a glassy brown solid which dissolved completely in benzene. On suitable concentration of the solution the red compound (X) described below crystallized; m. p. 274°; yield 0.2 g. The next product, obtained by evaporating further and adding ligroin, melted at 229° and was identified as the pseudopyrazolo-quinone, VI. From the mother liquor there was isolated a small quantity of 2-diphenylmethyl-1,4-naphthoquinone, m. p. 189°.

2,3-[Diphenylmethylene]-1-hydroxy-4-keto-3,4-dihydronaphthalene (X).—This compound crystallizes well from either alcohol or benzene, forming long, fiery red needles melting at 274°. The solutions in concentrated sulfuric acid and in alkali are red and purple, respectively. The substance is also soluble in sodium carbonate solution.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 84.76; H, 4.70.

A determination of the consumption of Grignard reagent by the compound at 100°, kindly carried out for us by Dr. E. M. Nygaard, showed that 1 mole of substance liberated 1.24 moles of gas and consumed a total of 2.00 moles of reagent. This indicates a slight enolization by the Grignard reagent.

The acetate, prepared with sodium acetate as the catalyst, formed small yellow needles from alcohol, m. p. 245°.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.94; H, 4.95. Found: C, 82.34, 82.34; H, 4.78, 4.80.

Reduction.—When the red cyclopropane derivative was heated for a short time with glacial acetic acid and zinc, the solution became decolorized, due to the formation of 2-diphenylmethyl-1,4-naphthohydroquinone. On working up the product this became oxidized to the quinone, which was identified by comparison with a sample prepared according to Möhlau and Klopfer.⁷ In order to obtain a better compound for analysis, we added acetic anhydride to the reduced solution and thus prepared 2-diphenylmethyl-1,4-naphthohydroquinone diacetate. This formed small, colorless crystals from glacial acetic acid, m. p. 220°. The same substance was obtained from the synthetic quinone.

Anal. Calcd. for $C_{27}H_{22}O_4$: C, 79.00; H, 5.41. Found: C, 78.98; H, 5.46.

Hydrolysis Product of the Cyclic Azo Compound, V.—The hydrolysis of the diacetate (XIII) of this substance proceeded in normal fashion when a hot, alcoholic solution of 1 g. of the material was treated quickly with 5 cc. of 6 *N* sodium hydroxide. The solution at once acquired the purple color characteristic of the azo compound.

The abnormal hydrolysis product, XVI (?), was obtained by using a smaller quantity of alkali (3 cc.) and adding it by drops in the course of about one hour. The solution became green at first and then slowly changed to blue. On acidifying and diluting the blue solution, a red substance was precipitated in good yield (0.8 g., m. p. 265°). The compound is very readily soluble in alcohol or glacial acetic acid, and only moderately soluble in benzene. It usually crystallizes as small, bright red needles, but some samples were initially orange. These, however, changed on standing or on gentle heating into the red modification. The substance melts with decomposition at 268–269°.

Anal. Calcd. for $C_{23}H_{18}O_3N_2$: C, 74.57; H, 4.90; N, 7.92. Found: C, 74.25; H, 4.97; N, 8.06, 7.92.

The compound evidently has the composition of the original azo derivative plus the elements of water. By the action of acetic anhydride it is both acetylated and dehydrated, for it yields the diacetate, XIII, from which it was prepared.

The substance dissolves readily in cold alkali or soda solution to give a deep blue solution which is not affected on exposure to the air for several hours. An acidic group was not revealed in a quantitative test with the Grignard reagent, but this seemed to be due to the fact that the compound remained undissolved in the solvent employed.

4. Benzoquinone and Diphenyldiazomethane: 2,3-(3,3-Diphenyl-pseudo-pyrazolo-4,5)-hydroquinone.—The reactants combine in vigorous reaction in benzene solution and yellow crystals of the product begin to separate at once; yield, 93%. The compound forms yellow plates from benzene, m. p. 210°, dec. The solution in concentrated sulfuric acid is red; the alkaline solution is likewise red, and it is stable to

the air. Neither this substance nor any of its derivatives listed below gives good products on thermal decomposition.

Anal. Calcd. for $C_{15}H_{14}O_2N_2$: C, 75.47; H, 4.67; N, 9.27. Found: C, 76.02; H, 4.70; N, 9.50.

The diacetate crystallizes from benzene-ligroin as small, perfectly colorless prisms, m. p. 181° , dec. When particularly large crystals were grown, they were found to be very faintly yellow. Solutions of the material are colorless with a marked blue fluorescence. The solution in concentrated sulfuric acid is red.

Anal. Calcd. for $C_{23}H_{18}O_4N_2$: C, 71.48; H, 4.70. Found: C, 71.72; H, 4.79.

The monobenzoate forms silvery plates from alcohol; m. p. 192° , dec.

Anal. Calcd. for $C_{26}H_{18}O_3N_2$: C, 76.82; H, 4.47. Found: C, 76.73, 77.00; H, 4.56, 4.62.

The dimethyl ether crystallizes from alcohol or glacial acetic acid as very pale yellow, stout needles melting at 196.5° .

Anal. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.33; H, 5.49. Found: C, 76.14; H, 5.89.

E. m. f. Measurements.—The potentials of the quinones and hydroquinones which have been described were determined, wherever possible, in both acid and neutral solutions, with the results given in the table. Lack of solubility prevented a study of compounds Nos. 1, 2, 3 and 7 in the neutral buffer, while the potential of No. 6 was so high that no titrating agent suitable for an acid solution was available. Measurements with the first five compounds were carried out by hydrogenating a solution of the quinone and titrating the hydroquinone solution with an oxidizing agent. The last two compounds were available in the form of their hydroquinones. These compounds, which contain the azo group, could not be titrated with a reducing agent. In every case reported the potentials were sharply defined and steady, and the titration curves conformed accurately to the theoretical requirements.

REDUCTION POTENTIALS AT 25°

Solvents: B, 70% Alcohol, 0.5 *N* in HCl and 0.2 *N* in LiCl. C, 37% Alcohol, 0.047 *M* in KH_2PO_4 and 0.047 *M* in Na_2HPO_4 .

| No. | System, named as oxidant | Solvent | Titrated with | — E_0 , v.— | | | | E_0 (av.), v. |
|-----|---|---------|----------------|---------------|--------|--------|--------|-----------------|
| 1 | Anthraquinone | B | $C_6Br_4O_2^a$ | 0.1537 | 0.1540 | 0.1542 | 0.1540 | |
| 2 | Lin.-naphthindazole-4,9-quinone, IV | B | $C_6Br_4O_2$ | .1548 | .1544 | .1541 | .1545 | |
| 3 | 1-Methyl derivative | B | $C_6Br_4O_2$ | .1602 | | | .1602 | |
| 4 | 3-Carbethoxyl derivative | B | $C_6Br_4O_2$ | .2818 | .2815 | .2821 | .2818 | |
| | | C | $K_3Mo(CN)_8$ | .4435 | .4430 | .4438 | .4434 | |
| 5 | 3-Carboxyl derivative | B | $C_6Br_4O_2$ | .2765 | | | .2765 | |
| | | C | $K_3Mo(CN)_8$ | .2656 | .2650 | .2653 | .2653 | |
| 6 | 2,3-(3,3-Diphenyl-pseudo-pyrazolo-4,5)-quinone | C | $K_3Mo(CN)_8$ | .8242 | .8246 | .8252 | .8246 | |
| 7 | 2,3-(3,3-Diphenyl-pseudo-pyrazolo-4,5)-1,4-naphthoquinone, VI | B | $C_6Br_4O_2$ | .5808 | .5804 | .5806 | .5806 | |
| 8 | Anomalous hydrolysis product, XVI? | B | $TiCl_3$ | .2422 | .2424 | .2422 | .2422 | |

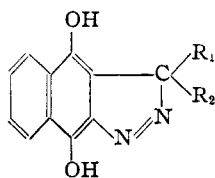
^a Tetrabromo-*o*-benzoquinone.

The potential of No. 1, which is the heterocyclic analog of anthraquinone, corresponded so closely with the value for this quinone reported by Conant and Fieser⁵ that

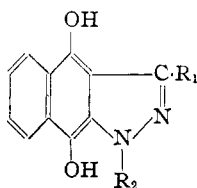
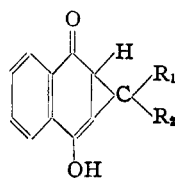
we checked their result (0.155 ± 0.002 v.) by the present, more reliable method of titration. The replacement of a benzene ring by a pyrazole nucleus has no more influence on the potential in the anthraquinone than in the naphthoquinone⁹ series. The potentials of the derivatives, Nos. 3-5 are about what would be expected, except that the pronounced increase in the potential of the carbethoxy compound in neutral solution suggests a possible isomerization of the substance.

Summary

Diazomethane and its mono- and di-substitution products add to α -naphthoquinone to give substances of the type of I.



I

II ($R_2 = H$)III ($R_1, R_2 = C_6H_5$)

If the diazomethane has a methane hydrogen atom, the substance at once isomerizes to a pyrazole derivative, II. Diazomethane itself adds so rapidly that the reaction stops at this point; diazoacetic ester reacts more slowly and the product, having a low potential, becomes oxidized to a quinone by the starting material.

With substitution of phenyl groups for both of the hydrogen atoms of diazomethane, the reaction stops with the formation of I. This, on thermal decomposition, yields a cyclopropane derivative, III.

The formula assigned by earlier investigators to the diazomethane reaction product has been shown to be erroneous.

The cyclic azo compound, I ($R_1R_2 = C_6H_5$), displays some interesting and unusual reactions.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

⁹ Fieser, THIS JOURNAL, **48**, 1097 (1926).