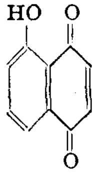
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Addition of Dienes to Halogenated and Hydroxylated Naphthoquinones

BY LOUIS F. FIESER AND J. T. DUNN

The chief purpose of this investigation was to explore further the possibility of synthesizing derivatives of phenanthrene by the addition of dienes to ortho quinones of the naphthalene series. While attempts to utilize β-naphthoquinone itself in the Diels–Alder reaction have not been attended with success, possibly because of the extremely sensitive character of the quinone, it was found[1] that 2,6-dimethyl-3,4-naphthoquinone adds 2,3-dimethylbutadiene very smoothly, a methyl group attached to the active double bond of the quinone effecting a stabilization of this component without offering too great hindrance to the addition. It was thought that other substituted β-naphthoquinones might possess sufficient stability to survive under the conditions required for the addition, possibly even when the substituents are located in the benzenoid ring. 6-Bromo-1,2-naphthoquinone was found in an investigation with Hartwell[2] to be less sensitive than β-naphthoquinone and better adapted to a study of the reactions with diazomethane derivatives, and in a preliminary experiment Dr. Hartwell found that dimethylbutadiene reacts fairly readily with this quinone.[3] With this encouragement, we undertook a study of hydroxylated compounds of a type which would yield polynuclear substances of considerable interest. The condensation of 7-hydroxy-1,2-naphthoquinone with vinylcyclopentene, for example, might afford a 7-hydroxy-1,2-cyclopentenophenanthrene derivative having some features of the oestrone structure. Both 6- and 7-hydroxy-1,2-naphthoquinone were prepared for the purpose in a very satisfactory condition of purity, but the compounds decomposed badly in attempted condensations with the reactive 2,3-dimethylbutadiene and no addition products were isolated.

While the difficulty seemed to be associated chiefly with the tendency of the quinones to undergo decomposition before addition could occur, we thought it worth while to determine whether a hydroxyl group *per se* influences the reaction adversely. In order to establish this point, a few hydroxyl derivatives of α-naphthoquinone were studied under comparable conditions, and it was found that the addition reaction becomes definitely slower with the progressive introduction of hydroxyl groups. Nearly all of the para quinones studied can be condensed satisfactorily with dienes in absolute alcoholic solution at 100° when highly purified products are used, but the time required for complete addition, as indicated fairly accurately by the fading of the original color and by crystallization tests, differs considerably. The addition product of juglone (I) was obtained in 95% yield after heating for twenty minutes, while with naphthazarin (II) a comparable yield (83%) was obtained only after heating for six hours. Naphthopurpurin reacts still more slowly (33% yield in sixty hours), and it was found that addition does not occur to the form which is regarded[4] as the predominant tautomer, IIIa, for water is not eliminated as with 2-hydroxy-1,4-naphthoquinone;[1b] addition occurs rather to the tautomer (IIIb) having an unsubstituted quinonoid nucleus. It is interesting that the acetylation of naphthopurpurin with sulfuric acid as catalyst also proceeds through the form IIIb, for the product is identical with 5,6,8-triacetoxy-1,4-naphthoquinone, prepared[5] from 1,4,5,8-naphthodiquinone by the Thiele reaction. This triacetate



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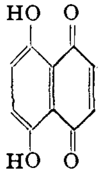

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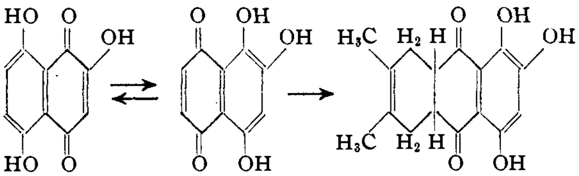

IIIa IIIb IV

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[1] (a) Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934); (b) *Ber.*, **68**, 1747 (1935).

[2] Fieser and Hartwell, THIS JOURNAL, **57**, 1479 (1935).

[3] The crude product (45% yield) apparently suffered oxidation during crystallization from alcohol–benzene and acetic acid, for analysis of the material, m. p. 237–238°, dec., indicated the formula $C_{16}H_{15}O_2Br$ (found: C, 60.8, 60.6; H, 3.90, 3.75).

[4] Fieser, THIS JOURNAL, **50**, 439 (1928).

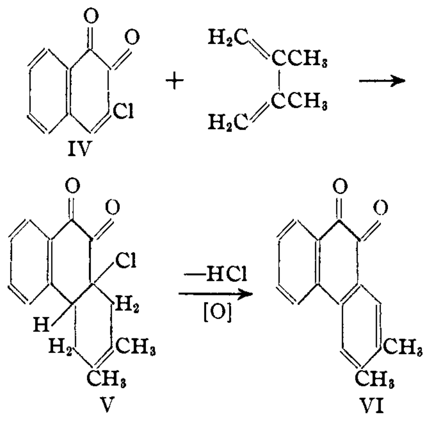
[5] Zahn and Ochwat, *Ann.*, **462**, 72 (1928).

of IIIb adds dimethylbutadiene more slowly (twenty-seven hours) than the diacetate of naphthazarin (three hours).[6] The acetyl derivatives react considerably more rapidly than the corresponding di- and trihydroxyquinones, while juglone appears to add dienes slightly more readily than its acetate. 2-Methyl-8-hydroxy-1,4-naphthoquinone[7] reacts smoothly with dimethylbutadiene, as in comparable cases,[1] and the methyl group merely retards addition.

It is evident from these results that the additive power of a naphthoquinone for dienes is diminished by the presence of hydroxyl groups in the benzenoid nucleus. A lower reactivity of the hydroxylated compounds is manifested also in the Thiele reaction. Dimroth and Roos[8] found it necessary to allow ten days for the completion of the reaction of diacetylnaphthazarin with acetic anhydride–sulfuric acid, and a similar observation concerning acetyljuglone was made in the course of the present work. The marked influence of substituent hydroxyl groups at a considerable distance from the ethylenic linkage involved in the additions is rather surprising. It may be significant that in this series of quinones the additive ability parallels the oxidation–reduction potentials,[4] the compounds of inferior additive propensity being those of low potential.

Since the hydroxylated β-naphthoquinones studied seemed unsuitable for use in the Diels–Alder reaction both because they lack the requisite stability and because of the adverse influence of this type of substituent group, we turned to another line of attack which was suggested by the observation, cited above, that a 3-methyl group stabilizes a 1,2-naphthoquinone and renders it capable of reacting with dienes in very satisfactory fashion. It occurred to us that the same beneficial influence might be exerted by substituents capable of being subsequently eliminated, and we consequently investigated the 3-chloro and 3-bromo derivatives of β-naphthoquinone, and later included the 4-chloro and the 3,4-dichloro compounds in the study. It has been reported already in the patent literature[9] that dienes add to 2-chloro- and 2,3-dichloro-1,4-naphthoquinone, and that hydrogen chloride can be eliminated from the addition products with aromatization of the new ring. We found that the halogenated ortho quinones add dimethylbutadiene very readily in pure chloroform or tetrachloroethane solution, the fading of the color from red to yellow providing a reliable indication of the course of the reaction. To obtain satisfactory results it is essential to prepare the quinones in a state of high purity and to employ pure solvents. Alcohol has a deleterious effect, and even the small quantity present in commercial chloroform brings about extensive decomposition.

3-Chloro-1,2-naphthoquinone reacts with dimethylbutadiene in chloroform solution to an appreciable extent at room temperature, and at 100° the reaction is complete within one hour. A further change occurring under more drastic conditions will be described in another paper. For the isolation of the normal addition product, V, it was necessary to avoid overheating during both the preparation and the recovery of the material. The crude product was obtained as an oil and, once seed was secured, the crystalline substance could be prepared in 70% yield. The pure substance forms pale yellow needles, m. p. 87–88°, but it cannot be preserved for more than a few hours before decomposition sets in. The compound loses hydrogen chloride very readily and the dihydrophenanthrenequinone first formed undergoes oxidation in the air to the phenanthrenequinone VI, or to the quinhydrone. 2,3-Dimethylphenanthrenequinone (VI) can be obtained in excellent yield by the action of alcoholic sodium acetate solution on either the crude or crystalline addition product. With the use of the halogenated quinone, it is thus possible to utilize



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[6] Dieterle, Salomon and Nosseck, *Ber.*, **64**, 2086 (1931), describe the addition of piperylene to diacetylnaphthazarin, the reagents being heated for five hours at 100° in alcoholic solution. The addition of dienes to naphthazarin in benzene solution is reported in the patent literature [see *Chem. Zentr.*, **101**, II, 808 (1930); **102**, I, 2938 (1931)].

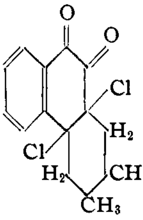
[7] Fieser and Dunn, THIS JOURNAL, **58**, 572 (1936).

[8] Dimroth and Roos, *Ann.*, **456**, 177 (1927).

[9] I. G. Farbenindustrie, English Patent 320,375 (1929) [*Chem. Zentr.*, **101**, II, 808 (1930)].

the Diels–Alder reaction for the synthesis of phenanthrene derivatives in satisfactory yield.

3-Bromo-1,2-naphthoquinone behaves much like the corresponding chloro compound. 4-Chloro-1,2-naphthoquinone is less stable in solution than the 3-isomer, and, as the addition proceeds much more slowly, the compound is not well suited to synthetic uses. The addition product was not isolated but converted in the crude state into VI. The two halogen atoms of 3,4-dichloro-1,2-naphthoquinone seem to hinder the addition to a considerable degree, for the color faded to an appreciable extent only after heating the mixture for three days at 100°. The addition product (VII), isolated as a crystalline solid, is much more stable than the monochloro compound V, probably because the hydrogen atoms adjacent to the halogens are not located on bridge carbon atoms. The substance is attacked only slowly by dilute alcoholic alkali at the boiling point.



VII

Experimental Part[10]

1. Preparation of Hydroxynaphthoquinones

6-Hydroxy-1,2-naphthoquinone[11] was prepared by the method of Dimroth and Kerkovius,[12] the average yield (pure) from 2,6-dihydroxynaphthalene being 31.5%. Reduction of the benzeneazo compound with sodium hydrosulfite gave less satisfactory results. It was found advantageous to use a small amount of stannous chloride as an antioxidant in the crystallization of both the starting material and 1-amino-2,6-dihydroxynaphthalene hydrochloride. The quinone formed bronze-red leaflets from dilute acetone, dec. about 165°. Attempts to isolate products of the reaction of the substance with 2,3-dimethylbutadiene and with diazomethane were unsuccessful, the quinone undergoing extensive decomposition. An acetyl derivative could not be obtained with the use of sodium acetate or in pyridine solution; in the presence of sulfuric acid catalyst, the quinone undergoes the Thiele reaction.[12]

7-Hydroxy-1,2-naphthoquinone was prepared from 2,7-dihydroxynaphthalene by the standard procedure described by one of us,[13] using sulfanilic acid rather than aniline[12] as the coupling component, and reducing the dye with sodium hydrosulfite. For the preparation of 2,7-dihydroxynaphthalene, technical "naphthalene-2,7-disulfonic acid" (220 g.) was crystallized with calcium chloride (equivalent to 55 g. of anhydrous material) from water (250 cc.), and after a further crystallization using Norite the dried, colorless calcium salt (134 g.) was fused with 500 g. of potassium hydroxide and 10 cc. of water, initially at 200° and finally at 300°. The slightly cooled melt was ladled into ice and hydrochloric acid, the material was brought into solution at the boiling point, using sufficient acid to decompose any calcium bisulfite and, after decolorizing with Norite and cooling, the product separated as large colorless needles in 66% yield, based on the purified calcium salt. To obtain 7-hydroxy-1,2-naphthoquinone satisfactorily it is essential to use pure, colorless, 1-amino-2,7-dihydroxynaphthalene hydrochloride (recrystallized in the presence of stannous chloride), to add the ferric chloride to the solution of this substance all at once with efficient mixing, and to collect the product rapidly as soon as the crystals separate. The quinone, obtained as dark red microcrystals, melting at 203–204°, dec., in 30% yield from the dihydroxy compound, could not be recrystallized without undergoing decomposition. The behavior in attempted reactions was like that of the isomer.

Juglone.—We attempted without success to convert 1,5-dihydroxynaphthalene into the 4-amine through the *p*-sulfobenzeneazo compound, and eventually adopted the oxidation method of Willstätter and Wheeler.[14] The 1,5-dihydroxynaphthalene was conveniently precipitated from alcohol with water, washed, and added to the dichromate mixture in the form of a thin paste. The juglone extracted with petroleum ether was further purified by crystallization from alcohol and the yield of material melting at 153–154° was 15%. **Acetyljuglone** was prepared more satisfactorily than described by Bernthsen and Semper[15] by adding 2 drops of concentrated sulfuric acid to a suspension of 0.25 g. of juglone in 2 cc. of acetic anhydride, stirred in an ice-bath. The solid soon dissolved, and after cautiously decomposing the excess anhydride with water and adding more water at the boiling point, the acetyl compound crystallized as yellow plates (0.3 g., 97%). Recrystallized from alcohol, it formed yellow needles, m. p. 153–154°.

1,2,4,5(or 8)-Tetraacetoxynaphthalene was obtained by suspending 1 g. of powdered juglone in a cold solution of 4 drops of concentrated sulfuric acid in 8 cc. of acetic anhydride and allowing the mixture to stand with occasional shaking for ten days. The quinone dissolved, the color of the solution faded and colorless crystals of the product separated. After treatment with water, the crude product (1.4 g., 68%) was crystallized from alcohol, forming clusters of colorless prisms, m. p. (camphor-like) 154°.

Anal. Calcd. for $C_{18}H_{16}O_8$: C, 59.98; H, 4.48. Found: C, 60.37; H, 4.67.

2,5(or 8)-Dihydroxy-1,4-naphthoquinone was obtained by hydrolyzing the tetraacetate with 25% methyl alcoholic potassium hydroxide, oxygenating the solution, and acidifying an aqueous solution of the red salt which separated. The crystalline precipitate (76% yield) separated from aqueous acetone as clusters of lemon yellow microcrystals,

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[10] The melting points are uncorrected.

[11] Kehrmann, *Ber.*, **40**, 1960 (1907).

[12] Dimroth and Kerkovius, *Ann.*, **399**, 36 (1913).

[13] Fieser, *Org. Syntheses*, **17**, 9, 68 (1937); L. F. Fieser and M. Fieser, THIS JOURNAL, **57**, 491 (1935).

[14] Willstätter and Wheeler, *Ber.*, **47**, 2796 (1914).

[15] Bernthsen and Semper, *ibid.*, **18**, 203 (1885).

dec. about 220°. The properties corresponded to those of the oxidation product of juglone obtained by Mylius.[16]

Naphthazarin was prepared according to Fieser[4] (using 15% fuming acid) in the yield reported, and purified by repeated crystallization from benzene, when it formed beautiful long deep green needles having a metallic reflex. Less pure material is red and gives inferior results in the Diels–Alder reaction. The diacetate, m. p. 195–196°, was prepared with the acetic anhydride (8 cc.)–sulfuric acid (6 drops) mixture,[17] and it was noted that no appreciable addition of the reagent occurred on heating the solution at 80° for ten minutes.

Naphthopurpurin was prepared according to Fieser[4] and crystallized twice from benzene; small, red needles were obtained in 22.5% yield.

5,6,8-Triacetoxy-1,4-naphthoquinone.—1,4,5,8-Naphthodiquinone was prepared as described by Zahn and Ochwat[5] and crystallized from glacial acetic acid–petroleum ether, taking care to avoid overheating and employing no decolorizing carbon (which causes reduction). Pale yellow crystals were obtained in 40% yield. The above triacetate was prepared from the diquinone as described[5] in 56% yield and it formed yellow prisms from alcohol, m. p. 165–166°. The sample became red on storage. An identical product was obtained in 94% yield by the action of acetic anhydride–sulfuric acid on naphthopurpurin at room temperature; the reaction was complete after warming for a few minutes.

2. Preparation of Halo-β-naphthoquinones

3-Chloro-1,2-naphthoquinone was prepared in 56% yield from β-naphthol through 1,1,3,4-tetrachloro-2-ketotetrahydronaphthalene according to Zincke,[18] and the properties were as reported. **3-Bromo-1,2-naphthoquinone,** m. p. 177–178°, was obtained in 67% yield by the bromination of β-naphthoquinone.[19] The crude **3,4-dichloro-1,2-naphthoquinone** prepared according to Zincke and Engelhardt[20] contained a considerable amount of dark, resinous material which can be removed by liberal washing with ether. The yield of pure product, m. p. 183.5–184.5°, was 45%.

As Zincke's method of preparing **4-chloro-1,2-naphthoquinone**[21] seemed unsatisfactory, an adaptation of Fries and Schimmelschmidt's[22] method of preparing the 3-bromo compound was employed. 1,1-Dichloro-2-ketodihydronaphthalene was prepared[22] from β-naphthol in 55% yield, and rearranged[22] to 1,4-dichloro-2-naphthol, the yield of distilled material, m. p. 121–122°, in this step being 63%. A fine suspension of 14 g. of the dichloronaphthol in 70 cc. of glacial acetic acid was stirred at 15° and treated slowly with 7 cc. of concentrated nitric acid, when the material soon dissolved. After brief cooling at 0° the crystalline 1,4-dichloro-1-nitro-2-ketodihydronaphthalene which separated was collected and washed with dilute acetic acid and then with water. The substance was obtained as pale yellow needles which cannot be preserved for long at room temperature without decomposing; yield, 10 g. (59%). This material (10 g.) was warmed cautiously with 25 cc. of benzene until dissolved and the solution was boiled for a short time to eliminate nitrosyl chloride. On adding ligroin and cooling, dull orange-red needles of 4-chloro-1,2-naphthoquinone separated; m. p. 132–136°, dec.; yield 5.9 g. (80%). It was not found possible to purify the quinone further by crystallization, as some decomposition invariably occurred. On attempting to prepare the hydroquinone diacetate for analysis by reductive acetylation with acetic anhydride, zinc dust and sodium acetate, it was found that the halogen atom is replaced by an acetyl group, the product being 1,2,4-triacetoxynaphthalene, m. p. and mixed m. p. 134–135°; yield 60%.

3. Addition of Dienes to the Hydroxynaphthoquinones

The condensation of the para quinones with dienes seemed to proceed better in absolute alcohol than in other solvents. The amount of alcohol used was more than ample to bring the quinone into solution at the boiling point (see Table I), one-tenth this volume of freshly prepared diene[23] was added, and the tube was sealed and heated in a steam bomb at 100°. The progress of the reaction could be followed sometimes by the fading of the color, although the change usually is not great. A more reliable indication can be obtained by removing and cooling the tube, for the addition products of the para quinones crystallize quite readily and in characteristic form. The heating was discontinued as soon as the change seemed to be complete, and the figures given in the third column of the table represent the approximate times required for completion of the reactions under comparable conditions. The yields recorded refer to purified, crystalline material. Naphthopurpurin-dimethylbutadiene was extracted from the crude reaction product with petroleum ether and recrystallized from this solvent; the other addition products were crystallized from alcohol. Traces of impurities in the starting material seem to promote extensive decomposition during the condensation.

5,9,10 - Triacetoxy - 2,3 - dimethyl - 1,4 - dihydroanthracene was obtained in 67% yield by the action of acetic anhydride and fused sodium acetate on juglone-dimethylbutadiene. The compound formed colorless needles, m. p. 197–198°, from alcohol.

Anal. Calcd. for $C_{22}H_{22}O_6$: C, 69.07; H, 5.80. Found: C, 69.46; H, 6.02.

2,3-Dimethyl-5-hydroxyanthraquinone was prepared by the action of alcoholic potassium hydroxide solution on both the above triacetate and on juglone-dimethylbutadiene. A solution of 0.2 g. of the latter compound in 8 cc. of alcohol was warmed with 1 cc. of 10% aqueous potassium hydroxide solution, crystals of a red salt which separated were dissolved by adding water, and the solution was oxygenated and acidified. Crystallization of the product from alcohol gave glistening yellow needles melting at 178.5–179.5°; yield 0.18 g.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.16; H, 4.80. Found: C, 76.37; H, 4.96.

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(16) Mylius, *Ber.*, **18**, 463 (1885).

(17) Thiele and Winter, *Ann.*, **311**, 341 (1900).

(18) Zincke and Kegel, *Ber.*, **21**, 3540 (1888).

(19) Zincke and Schmidt, *ibid.*, **27**, 733 (1894).

(20) Zincke and Engelhardt, *Ann.*, **283**, 341 (1894).

(21) Zincke and Kegel, *Ber.*, **21**, 3378 (1888).

(22) Fries and Schimmelschmidt, *Ann.*, **484**, 245 (1930).

(23) In preparing 2,3-dimethylbutadiene by the catalytic method,[1a] it has been found expedient to control the rate of distillation of pinacol through the reaction tube to 35 cc. per twenty minutes. Under these conditions there is less high-boiling material (pinacolone) requiring re-passage through the tube and the total yield of redistilled product is increased to 75%.

TABLE I

ADDITION PRODUCTS OF 1,4-NAPHTHOQUINONES WITH 2,3-DIMETHYLBUTADIENE

Quinone	Abs. alc. per g. of quinone, cc.	Time of heating hrs.	Yield, %	Product	M. p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Juglone	22	0.33	95	Faintly yellow needles	141–142	74.97	75.05	6.30	6.59
Acetyljuglone	24	0.5	94	Colorless needles	126–128	72.43	72.77	6.10	6.26
Naphthazarin[24]	55	6	83	Salmon-pink plates	195, dec.	70.56	70.73	5.93	6.18
Diacetylnaphthazarin[24]	88	3	92	Nearly colorless plates	175, dec.	67.38	67.58	5.66	5.93
Naphthopurpurin	44	60	33	Red-brown microcrystals	255, dec.	66.65	66.90	5.60	5.29
5,6,8-Triacetoxy-1,4-naphthoquinone	75	27	70	Pale brown needles	186, dec.	63.74	63.55	5.35	5.87
2-Methyl-8-hydroxy-1,4-naphthoquinone	20	19	84	Colorless blades	78–79.5, dec.	75.53	75.57	6.71	6.59
WITH BUTADIENE									
Juglone	50	0.5	94	Pale yellow needles	124–125	73.99	74.21	5.31	5.60

4. Addition Products of Halogenated β-Naphthoquinones

3 - Chloro - 1,2 - naphthoquinone - 2,3 - dimethylbutadiene.—A mixture of 4 g. of the quinone, 8 cc. of the diene, and 40 cc. of purified chloroform (shaken with concentrated sulfuric acid, washed with water, dried, distilled) was sealed in a tube and heated in a steam-bath with exclusion of light. The tube was shaken vigorously until all solid material had dissolved, for it is generally found that solid particles of a quinone tend to suffer decomposition and initiate the destruction of material in solution. The red color of the solution soon began to fade and in forty-five to fifty minutes changed to yellow. After one hour the solution was cooled, shaken with Norite for ten minutes at room temperature, and the solvent was distilled from the filtered solution in vacuum, keeping the temperature below 60°. The resulting viscous yellow oil could be preserved for some time as such or in ethereal solution without decomposing. Crystalline material eventually was obtained by cooling an ethereal solution in a bath of solid carbon dioxide and adding petroleum ether, and with seed available the crystalline compound was obtained easily. Recrystallized from ether–petroleum ether, the substance formed glistening, lemon yellow needles, m. p. 87–88°; yield, 4 g. (70%).

Anal.[24] Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.92; H, 5.51. Found: C, 69.61; H, 5.37.

A sample of the pure material kept in a vacuum desiccator at 10° showed signs of decomposition within three hours and soon changed to a greenish black amorphous mass. When shaken with air in suspension in either alcohol or ether, this soon changed to an orange powder; on crystallization from glacial acetic acid orange plates of 2,3-dimethylphenanthrenequinone were obtained in 87% yield. The quinone was identified by mixed melting point determination, using for comparison a sample prepared previously in this Laboratory.[25] Both samples melted at 237–238° (242–243°, corr.[26]). When the oily addition product was heated for a few minutes on the steam-bath at reduced pressure, hydrogen chloride was eliminated suddenly and the dark residue yielded the above quinone when digested with solvents. 2,3-Dimethylphenanthrenequinone was obtained in theoretical yield when the oily or crystalline addition product was warmed with alcoholic sodium acetate solution.

3-Bromo-1,2-naphthoquinone.—The reaction with dimethylbutadiene was conducted exactly as above, except that the heating was continued for two hours, and a solution of the oily addition product in 2–3 cc. of glacial acetic acid was treated with a solution of 1 g. of chromic anhydride in 6 cc. of 80% acetic acid. The solution became warm and, on cooling, 2,3-dimethylphenanthrenequinone crystallized in a nearly pure condition; yield, 0.38 g. (76%).

4-Chloro-1,2-naphthoquinone.—Under the conditions specified for the isomer, the addition of dimethylbutadiene proceeded only slowly; the red color faded slowly and then the solution began to darken. Heating was discontinued after seventy-two hours and the crude reddish oil obtained on removing the solvent was taken into ether–petroleum ether. Attempts to obtain crystals of the addition product were unsuccessful, but the solution on standing slowly deposited orange material from which pure 2,3-dimethylphenanthrenequinone was obtained on recrystallization in 15% yield.

3,4 - Dichloro - 1,2 - naphthoquinone - 2,3 - dimethylbutadiene, prepared by heating 3 g. of the quinone, 6 cc. of the diene, and 30 cc. of pure chloroform at 100° for sixty hours, was obtained crystalline from ether–petroleum ether and recrystallized from this solvent pair; yield 1 g. (24%). The compound formed large, pale yellow prisms melting at 130.5–131.5°.

Anal. Calcd. for $C_{16}H_{14}O_2Cl_2$: C, 62.14; H, 4.57. Found: C, 61.82; H, 4.79.

The dichloro compound is not appreciably attacked by short boiling in an alcoholic solution of sodium acetate; boiling 10% alcoholic potassium hydroxide slowly produces a yellow coloration and gives a resinous product.

Summary

Hydroxylation of the benzenoid ring of α-naphthoquinone results in a decrease in the velocity of addition of dienes; similarly substituted β-naphthoquinone derivatives, like the parent compound, are not suitable for use in the diene synthesis.

3-Chloro- and 3-bromo-1,2-naphthoquinone add

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[24] Analyses by Mrs. G. M. Wellwood.

[25] Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935).

[26] Determined by Dr. Hershberg with his special apparatus [Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936)]. We are at a loss to account for the lower corrected melting point determined for the earlier sample[25] by applying a stem correction and observed independently by another worker.

2,3-dimethylbutadiene readily and the addition products can be converted smoothly into phenanthrenequinones. Halogen substitution at the 4-position is less favorable to the Diels-Alder reaction.

Converse Memorial Laboratory
Cambridge, Mass. Received March 27, 1937

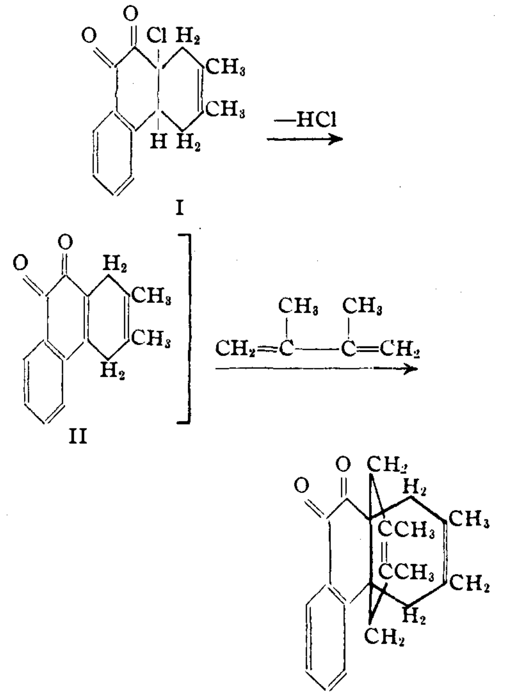
[Contribution from the Chemical Laboratory of Harvard University]

A Further Reaction Product from 3-Chloro-1,2-naphthoquinone and Dimethylbutadiene

By Louis F. Fieser and J. T. Dunn

In studying the reaction between 3-chloro-1,2-naphthoquinone and 2,3-dimethylbutadiene in chloroform solution at 100°,[1] it was observed that the initially red solution fades to yellow as addition proceeds and that the formation of the halogen-containing addition product (I, below) is complete in slightly less than one hour. When the heating is continued much beyond this point the solution slowly acquires a red color, and this second change occurs particularly rapidly when the hot reaction tube is exposed to direct sunlight. In the presence of excess diene, the red color again fades to yellow and when the changes are finally complete the solution exhibits a greenish fluorescence. The reaction product, isolated from this solution in 36% yield in a nicely crystalline condition, is free from halogen and has the composition of the chloroquinone plus two molecules of dimethylbutadiene, less the elements of hydrogen chloride.

The only plausible interpretation of these observations which we have been able to construct is that the yellow addition product I first loses hydrogen chloride from adjacent, bridge carbon atoms, and that the dihydrophenanthrenequinone II adds a second molecule of the diene at the reactive ethylenic linkage thus established, giving a tetracyclic diketone of the structure III. It is assumed that the dihydrophenanthrenequinone II, being a substituted β-naphthoquinone derivative, is responsible for the transient red color of the solution, and if this explanation is correct the influence of light is to catalyze the formation of this substance from I by the elimination of hydrogen chloride.



I

II

III

Attempts to characterize the unusual reaction product regarded as III were disappointing, as were attempts to establish the structure by degradation. In nearly all reactions tried the first change seemed to consist in a reversal of the Diels-Alder reaction, for the only transformation products isolated were derived from the dihydrophenanthrenequinone II. Perbenzoic acid titration alone gave a positive result, for this indicated the presence of two reactive double bonds, as required for the formula III. When heated somewhat above the melting point (135°), the product decomposed with effervescence and left a dark green residue which underwent air-oxidation in contact with solvents and afforded pure 2,3-dimethylphenanthrenequinone in good yield. This quinone was obtained also on heating the supposed tetracyclic compound in glacial acetic acid solution for twelve hours and, more rapidly and in nearly quantitative yield, by the action of chromic acid on the compound in the same solvent. The tetracyclic product did not absorb hydrogen readily in the presence of Adams catalyst, and

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[1] Fieser and Dunn, This Journal, 59, 1016 (1937).