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.
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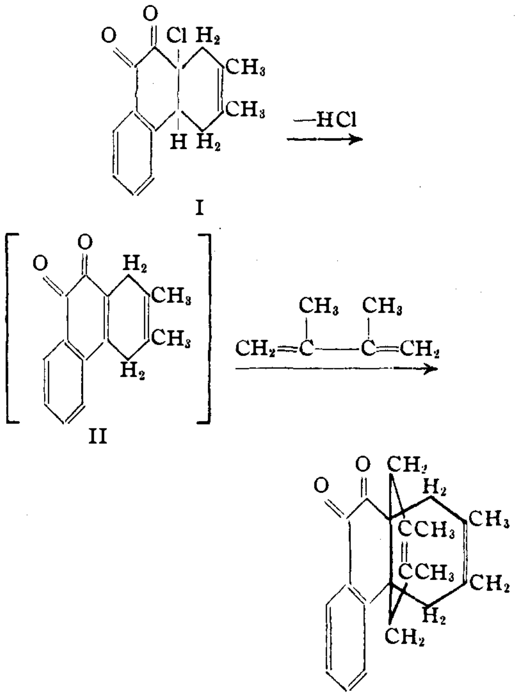
[Contribution from the Chemical Laboratory of Harvard University]

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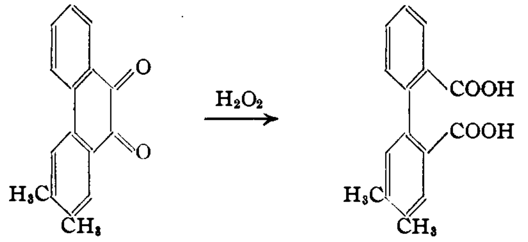
[1] Fieser and Dunn, This Journal, 59, 1016 (1937).

the only product isolated (after exposure to the air) was 2,3-dimethylphenanthrenequinone. Alkaline hydrogen peroxide gave a substance identified as 4,5-dimethyl-2,2′-diphenic acid (V) by comparison of a sample of the acid prepared from 2,3-dimethylphenanthrenequinone by the action of hydrogen peroxide in acetic acid solution.

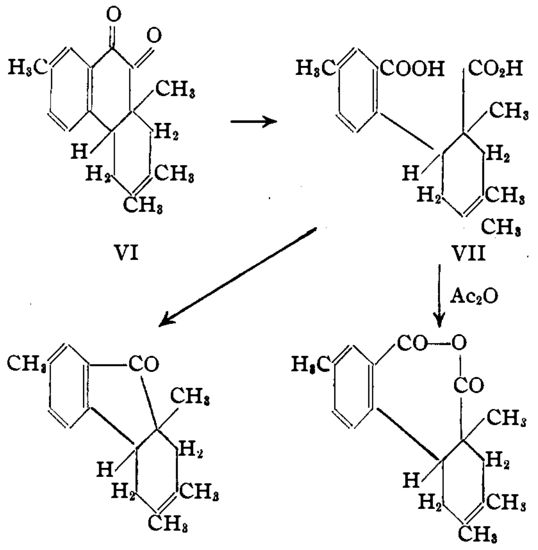


IV V

In all these reactions, and in the Zerewitinoff test, the tetracyclic product seems to lose one molecule of dimethylbutadiene in preference to undergoing other transformations. On attempting to prepare a quinoxaline derivative or a semicarbazone (or acetate), the starting material was recovered unchanged.

Although entirely rigid evidence is not available, the analysis of the new product, the results of titration with perbenzoic acid, and the ready conversion of the substance into 2,3-dimethylphenanthrenequinone all point to the structure III for the compound. Under similar conditions of experiment, an identical product was obtained from 3-bromo-1,2-naphthoquinone. An interesting property of the compound is its ability to exist in the two forms which differ strikingly in appearance. When prepared in the dark and purified with but little exposure to light, the product crystallized in the form of bright yellow prisms. When these were exposed for a short time to direct or diffused sunlight, the yellow color faded and the crystals became very nearly colorless, while retaining the original form. Both modifications have the same melting point.

In the course of the investigation of the tetracyclic diketone III it seemed desirable to determine if any of the peculiarities of this compound are exhibited by the structurally similar addition product VI from 2,6-dimethyl-3,4-naphthoquinone and 2,3-dimethylbutadiene.[2] This is not the case, for the addition compound VI can be distilled in vacuum without loss of dimethylbutadiene; it reacts normally with *o*-phenylenediamine, and yields on catalytic hydrogenation a colorless dihydro derivative possibly similar to that obtained by Smith and Hac[3] from prehnitenequinone-cyclopentadiene. The diketone is cleaved smoothly by alkaline hydrogen peroxide to the dibasic acid VII. The behavior of this tetramethyltetrahydrodiphenic acid on pyrolysis is similar to that of the two perhydrodiphenic acids studied by Vocke.[4] When heated at 300–330°, the acid very slowly loses carbon dioxide and gives a ketone VIII in small yield. The anhydride (IX) can be obtained easily with the use of acetic anhydride, but it does not appear to be formed in the pyrolytic reaction. The behavior of VII therefore accords with the prediction of the Blanc rule and the acid thus differs from those 1,4-dibasic acids derived from steroids in which the acid groups are attached to adjacent rings.



VI VII VIII IX

Experimental Part[5]

1. The Addition Product

2, 3 - Dimethyl - 1, 4, 11, 12 - tetrahydrophenanthrenequinone - 11,12 - endo - 2′,3′ - dimethylbutene - 2′ (III).—A solution of 4 g. of 3-chloro-1,2-naphthoquinone and 16 cc. of 2,3-dimethylbutadiene in 32 cc. of pure chloroform was sealed in a tube and heated in a pan of boiling water with exposure to the sunlight. The red solution became yellow in about forty-five minutes, and after thirty-five to fifty minutes the color changed again to red and this slowly began to fade. After a further period of about two hours the solution had become yellow and acquired a greenish fluorescence. After a total of five hours the tube was cooled, the solution was clarified with Norite, and the sol-

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

[3] L. I. Smith and Hac, THIS JOURNAL, **58**, 229 (1936).

[4] Vocke, *Ann.*, **508**, 1 (1934).

[5] The melting points are uncorrected.

vent was removed on the steam-bath. From a portion of the residual reddish oil seed was obtained with the use of chloroform–petroleum ether by thorough cooling and scratching. A solution of the main product in alcohol slowly deposited crystals on being seeded, and after washing this material free of oil with alcohol and recrystallizing it from alcohol, a pure product was obtained; average yield, 2.4 g. (36%). The compound is very readily soluble in benzene and moderately soluble in alcohol; the solutions ordinarily are colorless but become slightly yellow when exposed to direct sunlight. The solution in glacial acetic acid (readily soluble) becomes yellow on boiling, even without exposure to light. The solutions in alcohol or benzene tend to remain supersaturated, but slowly deposit the compound in the form of large, flat, diamond-shaped prisms which are practically colorless but show a faint tinge of yellow. The melting point is like that of camphor, softening occurring at about 130° with a finely ground sample, and the crystal structure disappearing at 135°. The melt is slightly yellow, but after partial crystallization the sample re-melts at 135°.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.45; H, 7.55. Found: C, 82.43, 82.57; H, 7.56, 7.79.

When the reaction was conducted in the dark, or with but little exposure to light, it was found necessary to continue the heating for sixteen to twenty hours. The reaction product on purification with but little exposure to light crystallized in diamond-shaped prisms similar to those above but having a brilliant yellow color. The melting point was the same as that of the nearly colorless crystals and no depression was observed on mixing the samples. On exposing the yellow prisms to direct sunlight the color faded without change of crystalline form and white crystals, faintly tinged with yellow were obtained. The colorless form seems to be the more stable of the two. A partial reversal occurs when the initially colorless solution of this form in chloroform is exposed to direct sunlight, for the solution acquires a yellowish color and the crystals subsequently deposited are pale yellow.

The compound III was prepared also in a similar manner from 3-bromo-1,2-naphthoquinone and identified by comparison with the above sample. The color changes were less distinct, and heating in the sunlight was conducted discontinuously for a total of thirteen hours; yield 35%.

Titration of III with perbenzoic acid in chloroform solution, conducted by Dr. M. S. Newman, indicated the absorption of 1.7 atoms of oxygen after forty-eight hours and 1.8 atoms after seventy-two hours.

Unsuccessful attempts to prepare derivatives of III and to effect a hydrogenation have been reported above. On heating the compound somewhat above the melting point at 4 mm. pressure, the oil suddenly began to effervesce. When this had ceased, the product was distilled and the glassy distillate was triturated with ether. This gave an orange powder from which pure 2,3-dimethylphenanthrenequinone, m. p. 237–238°, was obtained by crystallization; yield, 72%. A better conversion was obtained by adding 0.25 g. of chromic anhydride in 4 cc. of 90% acetic acid to 0.25 g. of III in 3 cc. of glacial acetic acid. Orange crystals of the quinone soon separated and the total product, collected after adding a little water, amounted to 0.17 g. (91%).

4,5-Dimethyl-2,2′-diphenic Acid (V).—This acid was conveniently prepared by heating a suspension of 1 g. of 2,3-dimethylphenanthrenequinone in 5 cc. of glacial acetic acid with 2 cc. of 30% hydrogen peroxide just below the boiling point until solution was complete and the color had faded to a very pale yellow. On dilution with water, the acid separated as colorless crystals; yield of once recrystallized material, 1 g. (88%). The pure acid separates from dilute acetic acid as clusters of colorless microcrystals, m. p. 203–204°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 70.71; H, 5.49.

The same acid was obtained by warming a mixture of 1 g. of III, 0.7 cc. of 30% hydrogen peroxide solution, 45 cc. of alcohol, and 3 cc. of 10% sodium hydroxide (added in drops) at 50–60° for three hours. The solution was acidified, evaporated to dryness, and the organic material was taken successively into ether, alkali and ether and obtained as clusters of microneedles from ether–petroleum ether (0.75 g.). After repeated crystallization from ether, the product melted at 202–204° and gave no depression with V, above.

2. 2,6-Dimethyl-3,4-naphthoquinone-2,3-Dimethylbutadiene (VI)

The yield in the preparation[2a] of the intermediate 2,6-dimethyl-4-amino-3-naphthol was improved considerably by employing more acid to dissolve the crude amine. The dye from 0.3 mole of the dimethylnaphthol was prepared and reduced exactly as described for the preparation of 1,2-aminonaphthol,[6] and the moist amine was mixed with 800 cc. of water, 45 cc. of concentrated hydrochloric acid, and 0.8 g. of stannous chloride and added to 2.2 liters of boiling water. Solution occurred in forty-five minutes and 200 cc. of concentrated acid was added to the filtrate. The yield of colorless hydrochloride was 62 g. (92%). In conducting the oxidation the amount of acid was increased from 10 cc. to 25 cc.; yield 94%; m. p. (recrystallized), 151–152°.

The addition product VI was obtained in somewhat improved yield (93%) by using 2.9 cc. of dimethylbutadiene and 16 cc. of absolute alcohol per gram of pure quinone, heating the mixture for seventy-five hours at 100°, and crystallizing the product once from dilute methanol.

The quinoxaline derivative, prepared by heating 1 g. of VI and 0.5 g. of *o*-phenylenediamine in 7 cc. of glacial acetic acid on the steam-bath for one hour and crystallizing the product (1.25 g.) from acetic acid, formed yellow plates, m. p. 137–138°.

Anal. Calcd. for $C_{24}H_{24}N_2$: C, 84.66; H, 7.11. Found: C, 84.46; H, 7.44.

A dihydro derivative was obtained by shaking 1 g. of VI dissolved in alcohol and 30 mg. of Adams catalyst with hydrogen, absorption ceasing after five minutes, even when fresh catalyst was added. The product formed colorless needles, m. p. (camphor-like) 131°, from alcohol; yield 0.72 g. The substance dissolves in alcoholic sodium hydroxide solution in the cold to give a pale red solution.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.94; H, 8.21. Found: C, 80.00; H, 8.50.

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(6) Fieser, *Organic Syntheses*, **17**, 9, 68 (1937).

Reduction of VI in alcohol with aqueous hydrosulfite solution gave a colorless product, m. p. 107–108°, which was not further characterized.

2,4,5,4′-Tetramethyl-1,2,3,6-tetrahydro-2,2′-diphenic Acid (VII).—A solution of 2 g. of VI and 1.4 cc. of 30% hydrogen peroxide in 20 cc. of dioxane at 80–90° was treated cautiously with 7 cc. of 10% sodium hydroxide in portions. A vigorous reaction ensued and the yellow color disappeared. Acidified and diluted with 100 cc. of water, the solution slowly deposited needles of good product; yield, 2 g. (92%). The acid is very soluble in dioxane, moderately so in alcohol or ether, very sparingly soluble in benzene. Recrystallization from acetic acid gave small, colorless needles, m. p. 248–249°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.48; H, 7.34. Found: C, 71.43; H, 7.53.

The dimethyl ester, prepared with diazomethane, formed glistening needles, m. p. 88–89°, from dilute methanol.

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.68; H, 7.94. Found: C, 72.66; H, 7.98.

The ester was hydrolyzed completely on being boiled for six hours with 25% potassium hydroxide solution.

The anhydride (VIII) was prepared by refluxing a solution of 0.9 g. of VII in 6 cc. of acetic anhydride for fifteen hours. The solvent was removed in vacuum and the product was crystallized from ligroin, giving 0.45 g. (53%) of nearly pure material. The anhydride forms lustrous, colorless needles from ligroin, m. p. 97–98°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.00; H, 7.09. Found: C, 76.06; H, 7.42.

2,3,7,10-Tetramethyl-1,4,10,11-tetrahydrofluorenone-9-semicarbazone.—The acid VII (0.8 g.) when heated under nitrogen in a bath at 330–33° slowly evolved carbon dioxide. After ten hours the dark residue, which gave no test for anhydride when treated in benzene with aniline, was taken into ether and the solution was extracted with dilute alkali, which gave on acidification 0.65 g. of unchanged acid. The oily residue from the ether was treated in alcohol with semicarbazide solution, heating for three hours on the steam-bath. Some of the semicarbazone crystallized during this period and, after cooling, the total yield was 0.2 g. (22%). The compound forms yellow microcrystals from alcohol; it softens at 244° and melts at 260° with decomposition.

Anal.[7] Calcd. for $C_{18}H_{23}ON_3$: N, 14.14. Found: N, 14.01.

Summary

The product obtained by the addition of 2,3-dimethylbutadiene to 3-chloro-1,2-naphthoquinone loses hydrogen chloride in chloroform solution at 100° and a second molecule of the diene adds to the resulting product giving an interesting compound which probably is a tetracyclic diketone. For comparison with this substance, a further characterization was made of 2,6-dimethyl-1,2-naphthoquinone-2,3-dimethylbutadiene.

[7] By Mrs. G. M. Wellwood.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED MARCH 27, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Application of the Diene Synthesis to Halogenated 1,2- and 3,4-Phenanthrenequinones

BY LOUIS F. FIESER AND J. T. DUNN

Having found that the 3-halo derivatives of β-naphthoquinone react smoothly with dienes and afford products which can be converted easily into 9,10-phenanthrenequinones,[1] we investigated the possibility of utilizing corresponding ortho quinones derived from phenanthrene for the synthesis of compounds of the chrysene and 3,4-benzphenanthrene series.

A suitable starting material derived from 3,4-phenanthrenequinone[2] (I) was obtained very satisfactorily by a process of bromination analogous to that developed by Zincke[3] for the preparation of 3-bromo-1,2-naphthoquinone. Treated with bromine in acetic acid solution, the quinone forms a yellow dibromide from which hydrogen bromide is eliminated by the action of boiling water. That the resulting crimson-red product has the structure of 2-bromo-3,4-phenanthrenequinone is established by the following observations. The Thiele reaction proceeds without disturbance of the halogen atoms and on hydrolysis of the triacetate (V) and oxidation there is obtained a compound having the properties of an hydroxy-*p*-quinone (VI). The bromine atom therefore cannot be located at position 4. Only one other position is available in the quinonoid nucleus, and the behavior of the bromo-3-hydroxy-1,4-phenanthrenequinone under the conditions of a Fischer esterification reaction indicates that the substituent is indeed located at the position (2) in question. Whereas the unsubstituted hydroxyquinone is converted rapidly by the action of meth-

[1] Fieser and Dunn, THIS JOURNAL, **59**, 1016 (1937).

[2] Fieser, *ibid.*, **51**, 940 (1929).

[3] Zincke and Schmidt, *Ber.*, **27**, 733 (1894).