[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Diene Reaction between Tetramethyl-*o*-benzoquinone and Cyclopentadiene[1]

BY LEE IRVIN SMITH AND LUCILE R. HAC

The reaction between dienes and quinones constitutes an important method for preparing polynuclear compounds, especially those in which methyl groups are substituted on carbon atoms common to two rings.[2] Moreover, the product to be expected from the diene reaction involving an *o*-quinone would be a cyclic diketone, which could be cleaved to give a dibasic acid, and in this way it should be possible to synthesize very many complicated dibasic acids. The importance of such substances in connection with work in certain fields of natural products is obvious and has already been fully discussed by the workers in these fields.

Fieser and Seligman[3] who used 2,6-dimethyl-3,4-naphthoquinone and 2,3-dimethylbutadiene, were the first to describe the isolation of crystalline products from the reaction between a diene and an *o*-quinone. Previously, Albrecht[4] had reported that β-naphthoquinone did not react with cyclopentadiene, while Alder[5] stated that this quinone did undergo the diene reaction. Fieser and Seligman[3] also found that β-naphthoquinone would undergo the reaction, although the products were not suitable for further study. Thus all work published so far on the reaction between dienes and *o*-quinones has dealt with dinuclear quinones; the work described in this paper constitutes the first study of the reaction between a typical diene and a mononuclear *o*-benzoquinone.

Mononuclear *o*-quinones, except those containing several halogen atoms, are very sensitive substances which often decompose within an hour or two after isolation. Consequently, for successful reactions involving these substances the quinone must be used immediately after isolation, and conditions must be found under which the desired reactions will proceed more rapidly than the decomposition of the quinone.[6] Since prehnitenequinone (tetramethyl-*o*-benzoquinone) has recently been prepared and found to be somewhat more stable than the unsubstituted homolog[7] and because it was desired to use a quinone with methyl groups adjacent to both carbonyl groups, this quinone was selected as the first one to be studied. And because a supply of cyclopentadiene was available, this diene was the one to be used.

Prehnitenequinone and cyclopentadiene reacted readily in alcohol solution at the temperature of the steam-bath, to give a stable, bright yellow crystalline compound which had the composition $C_{15}H_{18}O_2$, formed by the union of one molecule of each of the reactants. This substance was formed in yields of 63–70%, and it was the only addition product formed. All attempts to add two molecules of the diene to one of the quinone were unsuccessful. This was not due to any hindrance caused by the alkyl groups, for the unsubstituted *o*-benzoquinone likewise gave only a mono-addition product with cyclopentadiene. These results support the conclusion of Fieser and Seligman[3] (p. 2692) that alkyl groups do not appear, of themselves, to impose serious limitations on the diene reactions of quinones, although this depends upon the reaction conditions and, at least to some extent, upon the nature of the diene. Thus toluquinone reacts with only one molecule of cyclopentadiene[8] or butadiene.[9] Likewise *o*-benzoquinone and prehnitenequinone react with only one molecule of cyclopentadiene, but *p*-xyloquinone[6,10] reacts with one or two molecules of butadiene or 2,3-dimethylbutadiene, and thymoquinone[3,6] also reacts with 2,3-dimethylbutadiene and with piperylene.

The addition of prehnitenequinone to cyclopentadiene would be expected to give a substance having the structure represented by I, and the composition and properties of the addition prod-

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(1) Abstracted from a thesis by Lucile R. Hac, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1935.

(2) For other methods of synthesizing these substances, see (a) Ruzicka, Koolhaas and Wind, *Helv. Chim. Acta*, **14**, 1154 (1931); (b) Kon, *J. Chem. Soc.*, 1081 (1933); (c) Harper, Kon and Ruzicka, *ibid.*, 124 (1934); (d) Cook, Hewitt, Mayneord and Roe, *ibid.*, 1727 (1934); (e) Clemo and Dickenson, *ibid.*, 735 (1935); (f) Chuang, Ma and Tien, *Ber.*, **68**, 1946 (1935).

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

(4) Albrecht, *Ann.*, **348**, 31 (1906).

(5) From the review in Abderhalden, "Handbuch der biologischen Arbeitsmethoden," Urban and Schwarzenberg, Berlin, 1933, Abt. 1, Teil 2, II, Heft 9, p. 3112.

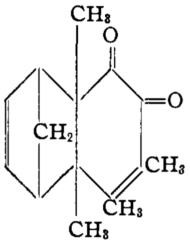
(6) See on this point Fieser and Seligman, *Ber.*, **68**, 1748 (1935); also ref. 3, p. 2695.

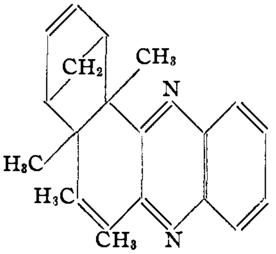
(7) Smith and Hac, THIS JOURNAL, **55**, 477 (1934).

(8) Lauer and Miller, *ibid.*, **57**, 520 (1935).

(9) Chuang and Han, *Ber.*, **68**, 876 (1935).

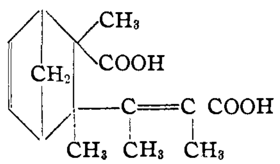
(10) Adler, *Arkiv Kemi, Mineral och Geol.*, **11B**, No. 49, 1 (1935).

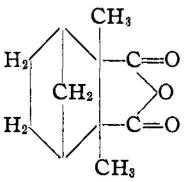

I


III

uct indicated that it had this structure. The substance was a yellow, crystalline solid, m. p. 181–182°, which formed a mono semicarbazone (II) and a colorless phenazine III, the latter formed in quantitative yield.[11] The substance was recovered unchanged after several hours' boiling with acetic anhydride, which indicated the absence of hydroxyl groups. In the Grignard machine[12] two moles of methylmagnesium iodide were consumed, and no gas was liberated. The substance was therefore a diketone.

When cleaved by alkaline hydrogen peroxide, I gave a crystalline dibasic acid (IV) in good yield. It was hoped that this acid could be successfully degraded to IVa, a known substance prepared by Diels, Alder and Naujoks[13] from cyclopentadiene and pyrocinchonic anhydride. The most promising procedure for this degradation appeared to be that used by Fernholtz[14] in his work on stigmasterol. But although the acid IV readily gave a crystalline dibromide (probably VI), ozonolysis of VI, followed by reductive cleavage of the ozonide, led only to resinous products.

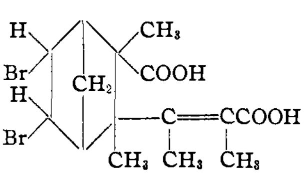

IV

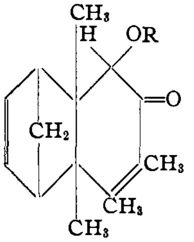

IVa

An attempt was made to convert the addition product into an hydrocarbon (X) in the hope that subsequent dehydrogenation by selenium would lead to a naphthalene derivative.

Reduction of I by Clemmensen's method gave an oil which still contained oxygen and which could not be purified sufficiently to obtain analyses corresponding to any reduction product likely to be produced. Nevertheless, dehydrogenation by selenium was tried upon this impure oil, and upon the addition compound I as well. Both substances gave low yields of very impure products,[15] from which no solid material, nor any solid picrate,[16] could be obtained.

The addition product I could, however, be converted into any one of three crystalline reduction products. A colorless dihydro derivative, VII, was obtained by reduction with zinc and acetic acid. This substance formed a monoacetate (XI) and a mono oxime (XII); in the Grignard machine it consumed two moles of reagent and liberated one mole of gas; oxidation with chromic acid gave the addition product I; and with *o*-phenylenediamine, VII gave the same phenazine, III, as was obtained from I. This behavior is characteristic of compounds containing the group —CHOHCO—; thus, benzoin gives the same quinoxaline as does benzil.[17] The structure VII, with the hydroxyl group in the α-position, was preferred for this dihydro derivative rather than the alternative structure with the hydroxyl group in the β-position, because of the complete absence of any diketone in the product. Substance VII could have been formed by a 1,2-addition of hydrogen to the α-carbonyl group, or a 1,4-addition to the system O=C–C=O, but it seemed that if only the β-carbonyl group were involved, at least some reduction should have occurred 1,4 at the conjugated system C=C–C=O, and so have produced a diketone. This evidence, of course, does not fix definitely the location of the hydroxyl group and for the present, the structures VII, VIII, and their acetates, oximes and semicarbazones must be regarded as provisional in respect to the location of the hydroxyl group, especially since 2,6-dimethyl-3,4-naphthoquinone


VI


VII, R = H. XI, R = Ac

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[11] Clemo and McIlwain, *J. Chem. Soc.*, 1991 (1934), have recently prepared nearly colorless phenazines from cyclic α-diketones derived from cyclohexane.

[12] Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

[13] Diels, Alder and Naujoks, *Ber.*, **62**, 554 (1929).

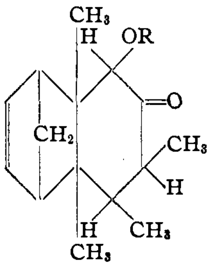
[14] Fernholtz, *Ann.*, **507**, 132 (1933).

[15] Fieser and Seligman (ref. 3, p. 2692) found that the addition product of 2,6-dimethyl-3,4-naphthoquinone and 2,3-dimethylbutadiene underwent a deep-seated decomposition when attempts were made to degrade it with sulfur.

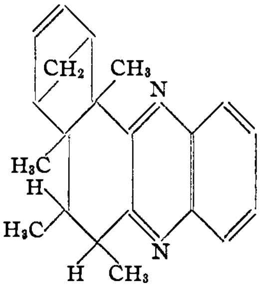
[16] Schroeter, Lichtenstadt and Irineu, *Ber.*, **51**, 1601 (1918).

[17] O. Fischer, *Ber.*, **24**, 720 (1891).

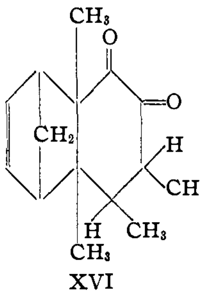
and β-naphthoquinone both form β- rather than α-oximes.[3,18]



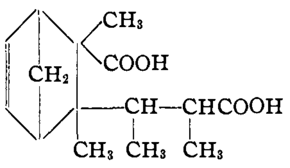
VIII, R = H XIII, R = Ac



XV



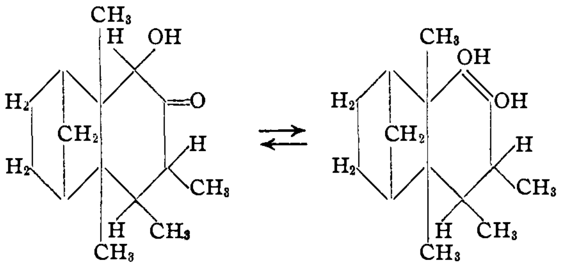
XVI



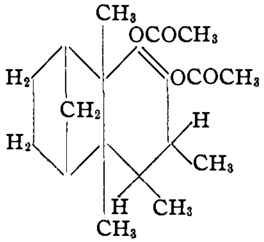
V

Reduction of I or of VII using low pressures of hydrogen and a platinum oxide catalyst,[19] or a catalyst of palladinized calcium carbonate[20] gave a colorless tetrahydro derivative of I (VIII). The fact that VIII could be obtained from VII indicated that VII was an intermediate product in the reduction of I to VIII. The reduction product VIII formed a monoacetate (XIII), a mono oxime (XIV) and a phenazine (XV). These derivatives were different from the corresponding derivatives of VII. The tetrahydro derivative VIII, in the Grignard machine, consumed two moles of reagent and liberated one mole of gas. Oxidation of VIII with chromic acid gave a yellow diketone (XVI) different from I. The diketone XVI gave the same phenazine (XV) as was obtained from VIII. Cleavage of the diketone XVI by alkaline hydrogen peroxide gave a dibasic acid (V), and this same acid (V) was obtained by catalytic reduction of the dibasic acid IV. Hence the second mole of hydrogen reduced the same double bond in I, VII and IV. These relationships would hold equally well no matter which double bond, the one in the bridged ring, or the one conjugated with the carbonyl group, was reduced, but the possibility that the double bond in the bridge ring would be preferentially reduced was considered to be rather remote.

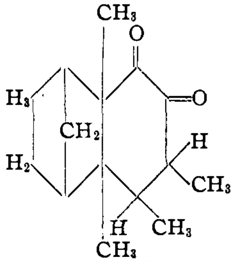
Reduction of I, VII or VIII using high pressures of hydrogen and a Raney nickel catalyst[21] gave a colorless hexahydro derivative of I (IX). Compounds VII and VIII were therefore probably intermediates in the reduction of I to IX.



IX



XVII



XVIII

The reduction product IX in the Grignard machine consumed two moles of reagent and liberated two moles of gas. The substance failed to form an oxime, but reacted with acetic anhydride to form a diacetate (XVII). No compound reactive toward phenylhydrazine could be obtained by the action of Criegee's reagent[22] on IX. That reduction had occurred at the double bond of the bridged ring was indicated by the relatively high melting point of IX (147°) in comparison with the melting points of VII and VIII (96 and 83°, respectively). A similar (though smaller) increase in melting point was observed by Diels and Alder[23] when the double bond in the bridged ring of cyclopentadiene-*p*-quinone was reduced. On one occasion, oxidation of IX by chromic acid gave a yellow crystalline diketone (XVIII) containing four atoms of hydrogen more than the addition product I. Unfortunately, this oxidation could never be repeated in spite of many attempts. However, the one successful experiment gave enough material for analysis. Because of this result, the reduction product IX was given

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[18] See also Ref. 6, compounds II and III, which do not form semicarbazones.

[19] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[20] Büsch and Stöve, *Ber.*, **49**, 1064 (1916).

[21] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[22] Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

[23] Diels and Alder, *ibid.*, **460**, 98 (1928).

the double formula, although it was practically always obtained as the diol. The hexahydro derivative IX could not be further reduced. This fact was surprising, for the Raney catalyst practically always reduces all carbonyl groups and all double bonds.

The step-wise reduction of cyclopentadiene-prehnitenequinone is interesting when compared with similar reduction products of the para series, because the first step in the reduction of the ortho series can be established. In the para series, this is impossible, because the first step in the reduction can be explained either by direct addition of hydrogen to the double bond, or by addition to the carbonyl groups with a subsequent shift of hydrogen. The analogy between the two series is not entirely complete, however, for in the present work the quinone was fully substituted. It is planned to investigate further the addition of cyclopentadiene to the unsubstituted *o*-benzoquinone, to do more exploratory work upon the reduction products and to investigate in some detail the oxidation and dehydrogenation of these and similar substances.

The authors are greatly indebted to Dr. A. F. Thompson, Jr., who carried out all the Grignard analyses discussed in this paper.

Experimental Part

Cyclopentadiene-prehnitenequinone (I).—Freshly prepared prehnitenequinone (5 g.)[7] was immediately dissolved in 95% alcohol (50–75 cc.). Freshly distilled cyclopentadiene (6 cc.) was added, and the mixture was refluxed on the steam-bath until the bright red color changed to clear yellow (three to four hours). The solution was cooled in a freezing mixture (ice and salt), the solid was removed and the filtrate evaporated to one-third its volume for a second crop. When recrystallized from alcohol, the substance formed bright yellow needles of m. p. 181–182°. The yield was 4.5 g. (63%) and it could not be increased by the use of more cyclopentadiene. If less cyclopentadiene were used, some of the quinone decomposed before addition occurred. The alcoholic filtrates, when evaporated, deposited only a brown viscous oil, from which no solid could be obtained.

An alternative method, which avoided the isolation of the quinone, was as follows: dihydroxyprehnitene (5 g.)[7] was dissolved in ether and shaken with silver oxide (10 g.)[24] for forty-five minutes. The solution was filtered, evaporated on the steam-bath until crystals began to form, then 95% alcohol (60–75 cc.) was added, and evaporation was continued until all the ether was removed. The mixture was cooled slightly and was then refluxed with cyclopentadiene (6 cc.) as described above. The yield was 3.7 g. (53% based on the dihydroxy compound, 70% based on the amount of quinone which could have been isolated).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 78.2; H, 8.1.

The semicarbazone (II), prepared in the usual manner, formed pale yellow needles which darkened at 207° and melted with decomposition at 213–214°.

Anal. Calcd. for $C_{16}H_{21}O_2N_3$: C, 66.9; H, 7.35. Found: C, 67.1; H, 7.4.

The phenazine (III) was formed quantitatively when the calculated amounts of I and *o*-phenylenediamine were warmed in acetic acid or alcohol. Recrystallized from alcohol, it formed white needles which melted at 182–183°.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.4; H, 7.35. Found: C, 83.0; H, 7.3.

Reduction of I with zinc and acetic acid gave VII; low pressure catalytic reduction gave VIII; high pressure reduction gave IX (see below).

Clemmensen Reduction. Attempt to Prepare X.—The addition product I (11 g.) was dissolved in acetic acid (40–50 cc.), and the solution was refluxed for eight hours with amalgamated zinc and hydrochloric acid. At the end of this time the solution was still slightly colored, and after standing overnight it became a deep reddish-purple. More zinc and hydrochloric acid were added, and the solution again refluxed for eight hours. The solution was distilled with steam. The *residue* was extracted with ether, the ether evaporated and an attempt was made to distil the residual oil under reduced pressure. It decomposed completely below 110° under 15 mm. The *steam distillate*, which contained about half of the material, was extracted with ether, the ether washed with carbonate and dried over sodium sulfate. The ether was removed and the bright yellow oil fractionated under 14 mm. The products were: A, 0.9 g., b. p. 75–85°; B, 1.4 g., b. p. 85–100°; C, 0.9 g., b. p. 101–103°. Fraction C was analyzed.

Anal. Calcd. for $C_{15}H_{22}$ (X): C, 89.02; H, 10.98. Calcd. for $C_{15}H_{22}O$: C, 82.4; H, 10.1. Found: C, 84.2; H, 10.6.

The substance probably contained oxygen and was impure, but not enough material was available for further purification.

Selenium Dehydrogenations.—Three grams of the above oil was heated to 280–300° for forty hours with 3 g. of selenium. The thick, brown, malodorous oil was extracted with ether, the ether washed with water and dried over sodium sulfate. Removal of the ether left an oil which distilled between 160–280°, but the amount (0.5 cc.) was so small that an accurate boiling point could not be obtained. The distillate was analyzed. Found: C, 86.0; H, 10.8. A similar dehydrogenation of I by selenium likewise led to a malodorous brown oil, which could not be purified.

Cleavage. The Dibasic Acid (IV).—The addition product (I) (0.5 g.) was dissolved in methyl alcohol and cleaved by addition of excess 15% hydrogen peroxide followed by enough 10% sodium hydroxide to give an alkaline reaction. The yellow color disappeared at once. Most of the methyl alcohol was removed by warming on the steam-bath, then an equal volume of water was added and the

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[24] (a) Willstätter and Pfannenstiel, *Ber.*, **37**, 4744 (1904); (b) Willstätter and Muller, *ibid.*, **41**, 2580 (1908); (c) **44**, 2171 (1911).

solution was cooled and acidified with hydrochloric acid. The white precipitate (0.52 g.) was recrystallized twice from dilute alohol and once from 95% alcohol, and then it melted at 239–240° (dec.). The acid was somewhat soluble in hot water, and quite soluble in most organic solvents.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.1; H, 7.6. Found: C, 67.9; H, 7.5.

The Dibasic Acid (V).—The acid IV (0.5 g.) was dissolved in sodium carbonate solution and shaken overnight under 3 atm. pressure of hydrogen in the presence of palladinized calcium carbonate.[19,20] The catalyst was filtered off and the filtrate acidified with hydrochloric acid. The white solid (0.5 g.) when recrystallized twice from 95% alcohol, melted at 228°. The mixed m. p. with IV (239–240°) was 132°. The acid decolorized permanganate, but no solid product could be obtained.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.6; H, 8.34. Found: C, 67.26; H, 8.26.

The Bromo Acid (VI).—The acid IV (0.5 g.) was dissolved in chloroform, the solution cooled in ice and the calculated amount of bromine in chloroform was added slowly (one hour). The bromine was decolorized rapidly. The chloroform was evaporated under reduced pressure to about half its volume and the white solid was filtered off. The substance, when recrystallized from alcohol, formed an amorphous white powder of m. p. 249–250° (dec.). It was very insoluble in most organic solvents.

Anal. Calcd. for $C_{15}H_{20}O_4Br_2$: C, 42.45; H, 4.75. Found: C, 41.6, 41.6; H, 4.75, 4.62.

Ozonolysis of the Bromo Acid (VI).—In sodium carbonate solution[25] at 0° the substance was unaffected even after six hours by a stream of ozonized oxygen containing 6.2% O_3 by weight. In ethyl bromide (250–300 cc.)[14] the acid VI (2 g.) was subjected for three hours to a stream of ozonized oxygen (7.8% O_3 by wt., 10.4 liters per hour) and then allowed to stand overnight. The solvent was removed under reduced pressure and the resulting oil was warmed on the steam-bath with water (50 cc.), acetic acid (2 cc.), zinc dust (1 g.), silver nitrate and hydroquinone (one small crystal of each). A brown, viscous mass formed at once, from which no solid product could be isolated.

The Dihydro Compound (VII).—The addition compound (I) (1 g.) was warmed on the steam-bath with acetic acid (15–20 cc.). Zinc dust (1.5 g.) and then an equal volume of water were added and the heating continued until the solution became colorless (one hour). The solution was decanted through a filter, and the zinc was extracted twice with boiling water (50 cc. each time). The filtrate and extractions were combined and when cooled, the solution deposited 0.9 g. of a white solid, m. p. 90–93°. Two recrystallizations from dilute alcohol at 50° gave a product with a camphor-like odor, m. p. 95.5–96°.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.5; H, 8.68. Found: C, 77.6; H, 8.6.

The acetyl derivative XI was obtained from VII by the action of acetic anhydride. Recrystallized from dilute alcohol at 50°, it was white and melted at 77–78°. It was essential that no sulfuric acid be used in the acetylation, otherwise a tarry product resulted from which no acetate could be isolated.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.4; H, 8.1. Found: C, 74.2; H, 8.0.

The oxime XII was obtained from VII in the usual manner. Recrystallized from aqueous alcohol, the substance formed white needles and melted at 184–185°.

Anal. Calcd. for $C_{15}H_{21}O_2N$: C, 72.8; H, 8.58. Found: C, 72.5; H, 8.55.

The phenazine III, white, m. p. and mixed m. p. 183°, was obtained when VII was treated with *o*-phenylenediamine as described under I.

Oxidation. The addition product I was obtained when VII (0.5 g.) in acetic acid (5–10 cc.) was oxidized at 0° by chromic acid (1.5 g.) in water (5 cc.) and acetic acid (10 cc.); m. p. and mixed m. p. 181–182°.

Reduction.—Low pressure catalytic reduction of VII gave VIII; high pressure reduction gave IX (see below).

The Tetrahydro Compound VIII.—The addition product I (5 g.) was dissolved in warm absolute alcohol (125 cc.), palladinized calcium carbonate (0.2–0.3 g.)[20] was added to the cooled solution, and the mixture was subjected to the action of hydrogen under 3 atm. pressure. The reaction was complete in three minutes, and no further absorption of hydrogen took place even after two hours. The solution was filtered and the filtrate evaporated at once, as it acquired a yellow color on standing in the air. Most of the solvent was removed on the steam-bath, and the last traces under reduced pressure. The residue was a light yellowish-brown syrup, which crystallized on standing overnight in a vacuum desiccator. The product was recrystallized twice by dissolving it in 95% alcohol and inoculating. It formed white needles, yield 4.5 g., m. p. 82–83°; mixed m. p. with VII (95°), 64–67°.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.86; H, 9.47. Found: C, 76.64, 76.79; H, 9.3, 9.35.

Reduction of I or of VII in a similar manner, using the platinic oxide catalyst of Adams[19] likewise gave VIII as the only product.

The acetyl derivative XIII was obtained from VIII by the action of acetic anhydride alone. It formed white needles when crystallized from dilute alcohol, and melted at 91°.

Anal. Calcd. for $C_{17}H_{24}O_3$: C, 73.86; H, 8.76. Found: C, 73.43, 73.66; H, 8.78, 8.39.

The oxime XIV, prepared in the usual manner and recrystallized from dilute alcohol, was white and melted at 169–170°.

Anal. Calcd. for $C_{15}H_{23}O_2N$: C, 72.2; H, 9.3. Found: C, 72.2; H, 9.2.

The phenazine XV was formed from VIII by the same procedure used for the preparation of III. It was white and melted at 181–182°. The mixed m. p. with III (182–183°) was 162–165°.

Anal. Calcd. for $C_{21}H_{24}N_2$: C, 82.84; H, 7.95. Found: C, 83.0; H, 8.25.

Oxidation. The Diketone XVI.—The tetrahydro compound VIII (1 g.) was dissolved in acetic acid (10 cc.) and oxidized at 0° by addition of a solution of chromic acid

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[25] Haworth, *J. Chem. Soc.*, **93**, 588 (1908).

(2.5 g.) in water (5 cc.) and acetic acid (10 cc.). After thirty minutes, bright yellow needles separated; the solution was then poured onto ice and the solid (0.7 g.) filtered off. Recrystallization from alcohol gave glistening yellow needles, m. p. 141–141.5°. It gave the same phenazine (XV) as was obtained from VIII.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.54; H, 8.68. Found: C, 77.5; H, 8.69.

Cleavage.—The diketone XVI (0.5 g.) was dissolved in methyl alcohol and the solution treated with hydrogen peroxide and alkali as described in the preparation of IV above. The product was the dicarboxylic acid V, m. p. and mixed m. p., 229–230°.

Reduction.—High pressure catalytic reduction of VIII (Raney catalyst) gave IX (see below).

The Hexahydro Compound IX.—The addition compound I (5 g.) was suspended in 95% alcohol (50 cc.), a small amount of Raney nickel catalyst[26] was added, and the material was placed in the bomb of a high pressure reduction apparatus.[27] The initial pressure of the gas was 1800 lb.; the temperature was raised to 185° and the bomb was shaken for five hours. After standing overnight, the catalyst was filtered off and the filtrate evaporated to dryness, first on the steam-bath, and then under reduced pressure at room temperature. The colorless, viscous oil which remained was moistened with a few drops of low-boiling petroleum ether, and placed in a vacuum desiccator overnight. The next day the oil was cooled in a freezing mixture and petroleum ether was added, a drop at a time, with stirring. Gradually an amorphous, somewhat sticky, white solid separated (2 g.). A small second crop could be obtained by evaporating the filtrate in a vacuum desiccator and repeating the stirring with petroleum ether, but the oil could never be converted completely to a solid. The white solid, after three recrystallizations from ether–petroleum ether, melted at 146–147°.

Anal. Calcd. for $C_{15}H_{26}O_2$ (addition of 8H): C, 75.57; H, 11.00. Calcd. for $C_{15}H_{24}O_2$ (addition of 6H): C, 76.20; H, 10.23. Found: C, 76.20, 76.23, 76.52; H, 10.60, 10.31, 10.21.

The dihydro compound (VII) and the tetrahydro compound (VIII) both gave the same product, IX, when reduced in the same way.

The hexahydro compound IX gave no oxime, nor could any phenazine be formed. Only an oil resulted when IX in acetic acid was treated with lead tetraacetate;[22,28] this oil did not react with phenylhydrazine.

The diacetyl compound XVII resulted when IX was refluxed for two hours with acetic anhydride alone. It was crystallized by dissolving it in aqueous alcohol and allowing the solution to stand for two weeks in the ice box. The substance formed white needles and melted at 81–82°.

Anal. Calcd. for $C_{19}H_{28}O_4$: C, 71.21; H, 8.80. Found: C, 71.48, 70.91; H, 9.05, 8.64.

The diketone XVIII was obtained once when IX (0.5 g.) was dissolved in acetic acid (5–10 cc.) and oxidized at 0° by a solution of chromic acid (1 g.) in water (5 cc.) and acetic acid (5 cc.). After standing in the ice-bath for two hours, the mixture was poured into ice water. The precipitated solid was recrystallized from dilute alcohol. It was yellow, melted at 96–97°, and was different from I and XVI.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.86; H, 9.47. Found: C, 76.58; H, 9.25.

All attempts to repeat this oxidation, using various specimens of IX, led to grayish or tan amorphous solids.

Summary

1. The diene reaction between a fully substituted, mononuclear *o*-benzoquinone and cyclopentadiene has been carried out. The reaction leads to a single product, one mole of the diene reacting with one of the quinone.

2. The product can be reduced in steps, but complete reduction and removal of the oxygen could not be accomplished.

3. Evidence is given for the structures of the addition product, the products of reduction, and their derivatives.

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 28, 1935

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[26] Covert, Connor and Adkins, THIS JOURNAL, **52**, 4349 (1930); *ibid.*, **54**, 1651 (1932).

[27] Connor and Adkins, *ibid.*, **54**, 4678 (1932).

[28] Dimroth and Schweizer, *Ber.*, **56**, 1377 (1923).