

(VIII) was dissolved in 10 cc. of carbon tetrachloride. A 20% solution of bromine in carbon tetrachloride was added very slowly at room temperature until there was no further absorption of bromine. The carbon tetrachloride was evaporated at room temperature and the light yellow residual oil was crystallized from methyl alcohol by scratching and cooling in a dry-ice-acetone bath. There was obtained after three crystallizations from methyl alcohol 0.5 g. of a compound; m. p. 108.5–109.5°.

*Anal.* Calcd. for  $C_{25}H_{28}O_2Br_2$ : C, 57.69; H, 5.38. Found: C, 57.87; H, 5.42.

**The Reaction of Sodium Iodide with the Dibromo Derivative.**—Three-tenths gram of the dibromo compound was dissolved in 4 cc. of acetone. To this solution was added 1 cc. of 0.6 molal sodium iodide solution. The reaction mixture turned yellow then red. After one and one-half hours a crystal of sodium thiosulfate was added. The solution was allowed to stand twelve hours at room temperature, then poured into water, extracted with ether, the ether extracts dried over anhydrous sodium sulfate and the ether evaporated. There remained a semi-crystalline material which was crystallized twice from methyl alcohol; m. p. 106–107°. A mixed melting point with the unsaturated compound (VIII) showed no depression.

**Reaction of Acetyl Chloride on the Pentadiene (VIII) in the Presence of Zinc Chloride.**—A mixture of 0.8 g. of the unsaturated compound (VIII), 3 cc. of acetyl chloride and 0.1 g. of powdered anhydrous zinc chloride was refluxed for one hour. The dark red solution was poured on ice. A light yellow precipitate formed immediately. The mixture was filtered and the solid crystallized from absolute ethyl alcohol. After three recrystallizations there was obtained 0.6 g. of a compound, m. p. 177–178°. This compound gave a positive iodoform test.

*Anal.* Calcd. for  $C_{29}H_{34}O_4Cl_2$ : C, 67.31; H, 6.58; Cl, 13.72; mol. wt., 517. Found: C, 67.70; H, 6.71; Cl, 13.59; mol. wt. (in boiling chloroform), 501.

**Nitration of the Pentadiene (VIII).**—One-half gram of the unsaturated compound was dissolved in 20 cc. of concentrated sulfuric acid at 5°. The orange solution was

cooled to 0° and 2 cc. of concentrated nitric acid added dropwise with stirring. The mixture was allowed to stand for ten minutes, then poured on ice. A white precipitate formed immediately. The solid was isolated and recrystallized twice from glacial acetic acid. There was obtained 0.2 g. of a solid melting at 258–259°.

*Anal.* Calcd. for  $C_{25}H_{24}O_{10}N_4$ : C, 55.55; H, 4.44; N, 10.37. Found: C, 55.56; H, 4.38; N, 10.31.

**Action of Paraformaldehyde on 1,4-Di-(2,4,6-trimethylbenzoyl)-butane.**—A mixture of 2.5 g. of the diketone, 0.5 g. of paraformaldehyde, 0.1 g. of potassium carbonate and 60 cc. of ethyl alcohol was refluxed for ten hours on a hot-plate. The mixture was poured into ice water and the solution acidified with dilute hydrochloric acid. It was allowed to stand for thirty minutes; the solid which precipitated was isolated and crystallized from methyl alcohol. There was obtained 0.7 g. of a compound melting at 122–123°.

*Anal.* Calcd. for  $C_{26}H_{30}O_2$ : C, 83.37; H, 8.07. Found: C, 83.65; H, 8.09.

### Summary

Acetomesitylene reacts with paraformaldehyde to form a monomethylol derivative,  $C_9H_{11}COCH_2CH_2OH$ , and a dimolecular product,  $C_9H_{11}COCCH=CH(CH_3)COC_9H_{11}$ . The mode of

formation and structure of this unsaturated compound have been discussed.

Propiomesitylene gives a methylene derivative,  $C_9H_{11}COC(CH_3)=CH_2$ . Isobutyromesitylene gives a monomethylol derivative,  $C_9H_{11}COC(CH_3)_2CH_2OH$ .

The diketones, 1,3-di-(2,4,6-trimethylbenzoyl)-propane and 1,3-di-(2,4,6-trimethylbenzoyl)-butane, react in the normal fashion to yield unsaturated ketones.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## 4-Alkyl Derivatives of 1,2-Naphthoquinone

BY LOUIS F. FIESER AND CHARLES K. BRADSHAW

In an investigation with Seligman<sup>1</sup> it was found that an alkyl substituent in the quinonoid ring of  $\alpha$ -naphthoquinone inhibits the usual 1,4-additions to the conjugated system, whereas such additions occur readily with 3-alkyl-1,2-naphthoquinones. The unsaturated system (a) of the para quinones, however, like that (b) of the ortho quinones con-

- (a)  $—COCH=C(R)CO—$   
 (b)  $—CH=C(R)COCO—$   
 (c)  $—C(R)=CHCOCO—$

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

tains an ethylenic linkage sufficiently active for the addition of dienes.<sup>1–3</sup> It seemed of interest to investigate for comparison the character of the system (c) of a 4-alkyl-1,2-naphthoquinone with respect to both 1,4-additions and the addition of dienes. For this purpose we first synthesized 4-methyl-1,2-naphthoquinone and, as the compound exhibited certain unusual properties but proved too sensitive for extensive study,

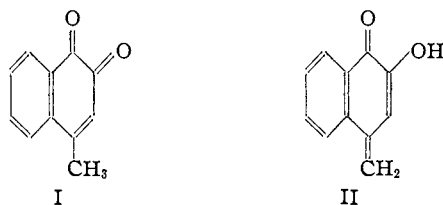
(2) Fieser and Seligman, *Ber.*, **68**, 1747 (1935).

(3) Fieser and Dunn, *THIS JOURNAL*, **59**, 1016 (1937).

we later prepared the more stable 4-benzyl derivative.

The quinones can be obtained under suitable conditions from the corresponding 4-alkyl-1-naphthols through the 2-*p*-sulfo benzeneazo and 2-amino derivatives. 4-Methyl-1-naphthol was prepared from  $\alpha$ -methyl naphthalene through the sulfonate,<sup>4</sup> and a convenient method of preparing 4-benzyl-1-naphthol was found in the condensation of benzoyl chloride with 1-methoxynaphthalene,<sup>5</sup> high-pressure hydrogenation of the resulting ketone, and demethylation. This method is much more satisfactory than the direct benzylation of  $\alpha$ -naphthol.<sup>6</sup>

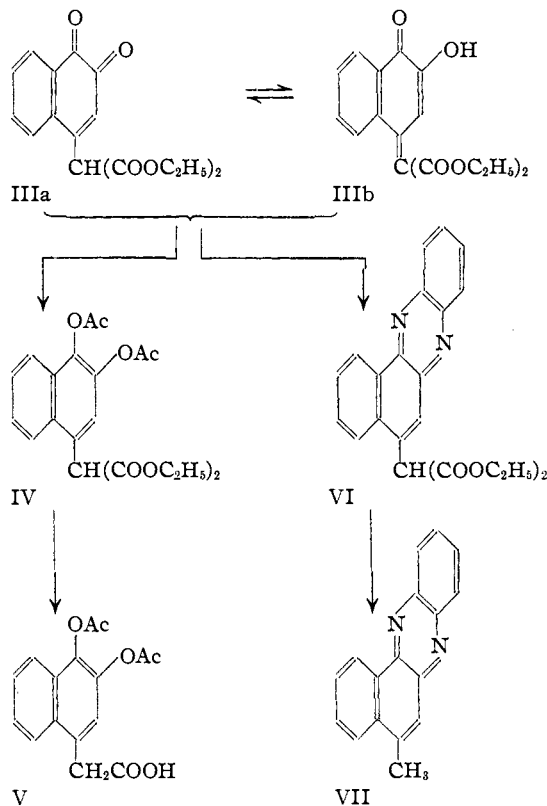
Although 4-methyl-1,2-naphthoquinone (I) has not been described heretofore in the literature, Dean and Nierenstein<sup>7</sup> reported the preparation



of a substance of the same composition which they regarded as having the structure of the acidic tautomer II. The two substances are entirely different in properties, however, and there is little likelihood that they are tautomers. Our compound when freshly prepared forms needles of an orange color characteristic of many ortho quinones, it melts with decomposition at 109°, is sensitive to heat even in neutral solvents, and tends to decompose on storage within a brief period. The substance is attacked rapidly by alkali, but seems to have no acidic properties indicative of the structure II. Normal quinone properties are shown in reductive acetylation to a hydroquinone diacetate and, particularly clearly, in the ability of the compound to function as the oxidant in an oxido-reduction system, as already reported.<sup>8</sup> The value found for the normal potential (0.531 v. in alcohol) is consistent with the structure I, and all of the properties indicate that the compound is indeed 4-methyl-1,2-naphthoquinone. While the existence of a tautomer of the formula II is conceivable, Dean and Nierenstein's substance does not have the properties to

be expected for such a compound. While 2-hydroxy-1,4-naphthofuchson-1,<sup>9</sup> the diphenyl derivative of II, is orange, their substance is red. In contrast to our quinone, their compound melts at a very high temperature (248–250°) and is stable in boiling pyridine. In the absence of information concerning the molecular weight, there is little reason to believe that the substance has the structure II and it is more probably a polymolecular condensation product arising from either I or II.

The substance of Dean and Nierenstein was obtained by the action of boiling pyridine on a crystalline yellow compound first prepared by Sachs and Craveri<sup>10</sup> by the condensation of 1,2-naphthoquinone-4-sulfonate with malonic ester. Without presenting any evidence of structure, these authors provisionally formulated the substance as 2-hydroxy-1,4-naphthoquinone-4-dicarboxymethide, IIIb, rather than as 4-dicarboxymethyl-1,2-naphthoquinone, IIIa. On



investigating the compound further, we have found that it can react in both tautomeric forms. As expected for the acidic form IIIb, it forms an

(4) Elbs and Christ, *J. prakt. Chem.*, **106**, 17 (1923).

(5) Fierz-David and Jaccard, *Helv. Chim. Acta*, **11**, 1042 (1928).

(6) Bakunin and Barberio, *Gazz. chim. ital.*, **33** (2), 487 (1903).

(7) Dean and Nierenstein, *J. Chem. Soc.*, **109**, 593 (1916).

(8) Fieser and Fieser, *This Journal*, **57**, 491 (1935).

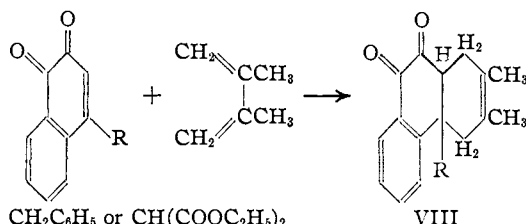
(9) Fieser and Hartwell, *ibid.*, **57**, 1484 (1935).

(10) Sachs and Craveri, *Ber.*, **38**, 3685 (1905).

acetate, and the yellow color of the crystalline solid is suggestive of this structure rather than that of an ortho quinone. Quinone properties, on the other hand, are indicated by the smooth reduction with sodium hydrosulfite to a colorless hydroquinone, and by conversion in the usual way to a hydroquinone diacetate (IV). The most conclusive indication of the existence of the quinone form IIIa in solution is that the yellow compound forms with its colorless dihydro derivative an electromotively active oxido-reduction system,<sup>8</sup> and the normal potential (0.598 v., in alcohol) is about that expected for a quinone of the formula IIIa. This tautomer probably predominates in acidic or neutral solutions, but the substance is definitely able to react in the acidic form IIIb. As far as can be judged the situation is similar to that encountered in diphenylmethyl- $\beta$ -naphthoquinone and its tautomer hydroxy- $\alpha$ -naphthofuchson.<sup>9</sup>

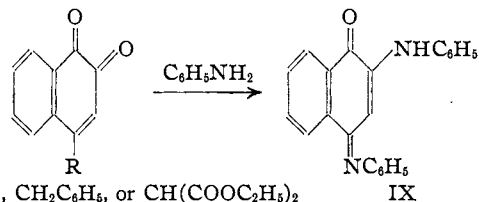
In seeking to relate the tautomeric malonic ester III to our synthetic 4-methyl-1,2-naphthoquinone, it seemed desirable to avoid possible secondary changes in the quinonoid nucleus during the degradation. An attempt to utilize the hydroquinone diacetate IV for this purpose was unsuccessful; the monobasic acid V was obtained satisfactorily but could not be decarboxylated. The results were better with the phenazine derivative VI, for this was converted by alkaline hydrolysis and decarboxylation by the copper-quinoline method into the methylnaphthophenazine VII. This substance proved to be identical with the azine prepared by the action of *o*-phenylenediamine on 4-methyl-1,2-naphthoquinone.

4-Methyl-1,2-naphthoquinone seemed far too sensitive a substance to withstand the heat treatment ordinarily required to effect the addition of dienes and the reaction was not tried. The reaction of 2,3-dimethylbutadiene was investigated with the 4-benzyl derivative and with the 4-malonic ester compound (III) (in the latter case by J. T. Dunn), and in each case a slow addition was observed and there was isolated a small amount of crystalline material having the composition of the expected hydrophenanthrene derivative VIII. An alkyl group at the 4-position, like a chlorine atom,<sup>3</sup> does not entirely inhibit the addition and perhaps stabilizes the  $\beta$ -naphthoquinonoid system sufficiently to make possible the isolation of the addition product. The reactions are slow, however, and the quinones



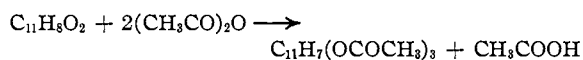
so sensitive that the preparation of the hydrophenanthrenes in quantity would present difficulties.

It was found previously<sup>1</sup> that the 1,4-addition of aniline, characteristic of unsubstituted quinones, proceeds readily with 3-alkyl-1,2-naphthoquinones but fails completely with 2-alkyl-1,4-naphthoquinones. On investigating the action of excess aniline in boiling alcohol on the 4-methyl, 4-benzyl, and 4-dicarbethoxymethyl derivatives of 1,2-naphthoquinone it has been found that reaction occurs in each case with displacement of the 4-substituent and formation of 2-anilino-1,4-naphthoquinone-4-anil (IX), identical with the



substance resulting from the interaction of  $\beta$ -naphthoquinone with aniline.<sup>11</sup>

In contrast to the behavior of 2-alkyl-1,4-naphthoquinones,<sup>1</sup> 4-methyl- and 4-benzyl-1,2-naphthoquinones react readily with acetic anhydride containing a trace of sulfuric acid (Thiele reagent), giving crystalline, colorless products in good yield. The analytical data indicate that the substances are formed, as in the usual Thiele reaction, by the addition of one molecule of acetic anhydride to the quinone and the replacement of a hydrogen atom by the acetyl group, the reaction with the methyl compound being formulated as follows



4-Chloro-1,2-naphthoquinone<sup>3</sup> was investigated for comparison and found not to react with the Thiele reagent, whereas the 3-chloro isomer, like corresponding bromoquinones of the phenanthrene series,<sup>12</sup> reacts smoothly if slowly without disturbance of the halogen atom. It seems remark-

(11) Zincke, *Ber.*, **15**, 481 (1882).

(12) Fieser and Dunn, *This Journal*, **59**, 1024 (1937).

able that addition should occur in the cases noted without displacement of the 4-alkyl substituent. Beyond finding that the product from the methylated quinone yields phthalic acid on oxidation, the "abnormal triacetates" were not characterized further in the present work. The nature of the reaction will be discussed in a subsequent paper with Mary Fieser reporting an investigation of an interesting transformation product of 4-benzyl-1,2-naphthoquinone encountered at the close of the present study. It was found that on treatment with either concentrated sulfuric acid or alkali the orange quinone is converted into a yellow, acidic substance of the same composition, and that the yellow compound can be obtained also by the action of alcoholic hydrochloric acid on the abnormal triacetate. These experiments can be described most appropriately in the report of the further study of the problem.

### Experimental Part<sup>13</sup>

#### 4-Methyl-1,2-naphthoquinone

Potassium 4-methylnaphthalene-1-sulfonate<sup>4</sup> may be obtained directly from the sulfonation mixture without isolation of the barium salt.<sup>4</sup> Concentrated sulfuric acid (125 cc.) was stirred with cooling into 70 g. of  $\alpha$ -methyl-naphthalene and the mixture was allowed to stand at room temperature for five days, when it had become nearly solid, and then poured into an equal volume of water. The crystalline sulfonic acid was collected after cooling to 0° and dissolved with 75 g. of potassium chloride in 300 cc. of water. On cooling, the potassium salt crystallized in a condition satisfactory for fusion; yield, 79 g. (58%). The *p*-toluidine salt forms long needles from water, m. p. 232–233°. 4-Methyl-1-naphthol was prepared according to Elbs and Christ<sup>4</sup> and distilled twice in vacuum and obtained as a light yellow solid, m. p. 79–81° (which turns brown on standing), in 52–56% yield.

**4-Methyl-2-amino-1-naphthol Hydrochloride.**—The coupling of 4-methyl-1-naphthol with diazotized sulfanilic acid and the reduction of the dye were conducted according to the procedure employed with  $\beta$ -naphthol<sup>14</sup> and the amine hydrochloride was obtained as nearly colorless needles in 52% yield.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>ONCl: C, 63.01; H, 5.73. Found: C, 63.26; H, 6.13.

**4-Methyl-1,2-naphthoquinone.**—A filtered solution prepared from 24 g. of ferric chloride crystals, 5 cc. of concentrated hydrochloric acid, and 150 cc. of water was added all at once to a filtered solution of 8.8 g. of the amine hydrochloride and a few crystals of stannous chloride in 2.5 l. of water containing 10 cc. of concentrated hydrochloric acid. In a few seconds the quinone separated as an orange-yellow microcrystalline precipitate which was washed very thoroughly with water before being dried;

yield, 6.5 g. (89%). When crystallized from methanol with avoidance of undue heating, the compound was obtained as well-formed orange needles which melted completely with extensive decomposition at 109°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>: C, 76.74; H, 4.65. Found: C, 76.97; H, 5.00.

On storage, even in the dark, the orange needles darken within a few weeks and eventually acquire a dark purplish black color. The product of decomposition has little solubility in the usual solvents and is comparatively high melting. Decomposition occurs also when a solution of the quinone in methanol is boiled for some time. The quinone does not dissolve in dilute alkali in the cold and decomposes badly when heated.

**4-Methyl-1,2-diacetoxynaphthalene**, obtained by reductive acetylation of the quinone with acetic anhydride, zinc dust, and sodium acetate, formed colorless needles, m. p. 124.5–125.5°, from dilute acetic acid.

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>: C, 69.77; H, 5.43. Found: C, 69.91; H, 5.64.

**3-Chloro-4-methyl-1,2-naphthoquinone** was prepared by passing a rapid stream of dry chlorine into a suspension of 0.5 g. of 4-methyl-1,2-naphthoquinone in 5 cc. of glacial acetic acid. The quinone soon dissolved, and the reddish solution was poured into boiling water. The solution was cooled rapidly to 0° and the crystalline product which separated was recrystallized from chloroform. The quinone forms orange-red microcrystals which decompose at 150–160°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>Cl: C, 63.92; H, 3.42. Found: C, 63.92; H, 3.65.

On oxidation with permanganate as below, the chloro compound gave phthalic acid, identified as the anhydride. It was thought that the chloroquinone might be convertible into the 4-methyl-1,2,3-triacetoxynaphthalene, but the halogen atom proved to be unreactive toward both silver acetate and sodiomalonic ester. This bears out the observations of Hirsch.<sup>15</sup>

**4-Methyl-1,2-naphthophenazine (VII)**, prepared by heating the quinone with *o*-phenylenediamine hydrochloride, sodium acetate, and acetic acid for one hour on the steam-bath and adding water, crystallized from alcohol as flat, shiny, yellow needles melting at 174°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>: C, 83.57; H, 4.96. Found:<sup>16</sup> C, 83.85; H, 4.70.

#### 4-Benzyl-1,2-naphthoquinone

**4-Benzyl-1-naphthol.**—The preparation of 4-benzoyl-1-methoxynaphthalene<sup>5</sup> was improved by adding aluminum chloride (23.1 g.) in portions to  $\alpha$ -methoxynaphthalene (24.7 g.) and benzoyl chloride (24.7 g.) in nitrobenzene (200 cc.) at 0°, allowing the mixture to warm slowly to 25°, and continuing the stirring for a total of eighteen hours. The collected product was distilled in vacuum and crystallized from alcohol; yield, 34.7 g. (84%), m. p. 81–82°. Reduction by the Clemmensen method was unsatisfactory, but hydrogenation of the ketone in alcohol at 175° and 2500 lb. (167 atm.) pressure using copper-barium chromite catalyst proceeded well. The 4-benzyl-

(13) The melting points are uncorrected except as noted.

(14) Fieser, *Org. Syntheses*, **17**, 9 (1937).

(15) Hirsch, *Ber.*, **33**, 2412 (1900).

(16) Analysis by Mrs. G. M. Wellwood.

**1-methoxynaphthalene**,<sup>17</sup> after distillation and crystallization from alcohol, was obtained as colorless plates, m. p. 83–84°, in 84–86% yield. Demethylation of the ether (58 g.) was accomplished by boiling for twelve hours in glacial acetic acid (580 cc.) with 40% hydrobromic acid (75 cc.). The product was collected after dilution with water, dried, and crystallized from petroleum ether, giving small, colorless crystals, m. p. 122.5–123.5°; yield, 37.2 g. (68%).

**4-Benzyl-1,2-naphthoquinone**.—4-Benzyl-1-naphthol (4.88 g.) was dissolved in a solution of 2.5 g. of sodium hydroxide in 190 cc. of water and coupled with sulfanilic acid by the standard procedure.<sup>14</sup> The solution of the dye was stirred mechanically at room temperature and 10 g. of sodium hydrosulfite was added, keeping the solution alkaline by the addition of sodium hydroxide as required. When reduction was complete (twenty minutes), the amine was precipitated by acidification of the straw colored solution with acetic acid, and after stirring for one-half hour the precipitate was collected and the moist amine transferred immediately to 400 cc. of boiling water containing 2.5 cc. of concentrated hydrochloric acid and a few crystals of stannous chloride. The mixture was stirred mechanically for just ten minutes and the solution of amine hydrochloride filtered through a thin layer of Norite, diluted to a volume of two liters, and treated with 30 cc. of 6 *N* sulfuric acid. The resulting suspension of the amine sulfate was cooled to 10° and an aqueous solution of 5 g. of potassium dichromate added. Oxidation proceeded slowly and stirring was continued for three hours (odor of benzaldehyde) before collecting the quinone. The washed and dried product weighing 2.4–3 g. (46–58%) was suitable for most purposes, but could be freed from a small amount of dark material most satisfactorily by crystallization from cyclohexane, in which the impurity is practically insoluble. The quinone crystallizes as orange plates which begin to soften at about 130° and melt with decomposition at 143°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>O<sub>2</sub>: C, 82.22; H, 4.88. Found: C, 82.02; H, 5.00.

The quinone does not decompose on storage. It crystallizes from alcohol on the microscope slide as clusters of rectangular plates and only a faint coloration is produced when alkali is added. When moistened with a little alcohol, treated with bisulfite solution and warmed gently, the quinone dissolves very easily to give a colorless solution. The addition of soda produces a yellow coloration but no precipitate; on adding hydrochloric acid and warming, an oily product separates. The phenazine derivative of the quinone forms yellow needles from alcohol, m. p. 195.5–196°, corr.

The potential of the oxidation–reduction system was determined by Mary Fieser. Titration of the quinone with titanous chloride in 0.1 *M* 50% alcoholic hydrochloric acid, 0.2 *M* in lithium chloride, gave the results  $E_0 = 0.5636, 0.5606, 0.5616$  v. (av. 0.562 v.).

**4-Benzyl-1,2-diacetoxynaphthalene**, prepared by reductive acetylation, separates from alcohol as small, colorless prisms, m. p. 96–96.5°, corr.

*Anal.* Calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>: C, 75.43, H, 5.43. Found: C, 75.48; H, 5.59.

**4-Dicarbethoxymethyl-1,2-naphthoquinone (IIIa)—2-Hydroxy-1,4-naphthoquinone-4-dicarbethoxymethide (IIIb)**

**Preparation**.—Although Sachs and Craveri<sup>10</sup> reported few details of the preparation, the experience in this Laboratory has been that for even moderate success it is necessary to control the conditions with great care and to work very rapidly. The following procedure was worked out by E. L. Martin. The specified quantities of all reagents should be made ready in advance. D. M. Bowen has found that the quantities can be increased fourfold without influencing the yield.

Five and one-half grams of pure potassium 1,2-naphthoquinone-4-sulfonate<sup>18</sup> was added to 120 cc. of water at 75° in an Erlenmeyer flask, this was shaken vigorously to dissolve the quinone and the solution was quickly cooled to 50–55° in ice and then removed from the bath. Ten cubic centimeters of 10% potassium hydroxide solution was added quickly to a prepared solution of 4.5 g. of diethyl malonate in 60 cc. of alcohol; the mixture was shaken twice and poured immediately into the solution of the potassium salt. The cherry-red solution was shaken for one minute, cooled rapidly in an ice-bath to 30°, and (without further cooling) acidified with 6 *N* hydrochloric acid, added by drops with stirring. The solution became cloudy and, on stirring, deposited a crystalline yellow product. After cooling to 0°, this was washed with water and dried; yield, 1.5 g. (24%). One crystallization from dilute acetic acid gave yellow prisms, m. p. 105–106°. An alcoholic solution of the compound gives a characteristic blue color when 1% sodium carbonate solution is added.

The acetate (of IIIb) was obtained by heating the substance with acetic anhydride and sodium acetate for two hours on the steam-bath, or by heating the compound (0.5 g.) with acetic anhydride (10 cc.)–sulfuric acid (1 drop) for one hour on the steam-bath (yield 0.6 g.). Recrystallized from dilute alcohol or acetic acid, the acetate formed light yellow plates, m. p. 93–94°. It gives no color reaction with 1% sodium carbonate solution in alcohol.

*Anal.* Calcd. for C<sub>19</sub>H<sub>18</sub>O<sub>7</sub>: C, 63.69; H, 5.03. Found: C, 63.94; H, 5.16.

**4-Dicarbethoxymethyl-1,2-dihydroxynaphthalene** was prepared by adding aqueous sodium hydrosulfite solution to a hot alcoholic solution of the quinone until the yellow color was discharged; on cooling to 0° the hydroquinone was deposited in a colorless condition. Recrystallized from aqueous alcohol containing a trace of hydrosulfite, the compound formed colorless, granular crystals, m. p. 132°, dec.

*Anal.* Calcd. for C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>: C, 64.15; H, 5.66. Found: C, 64.39; H, 5.95.

**4-Dicarbethoxymethyl-1,2-diacetoxynaphthalene**.—A solution of the quinone (4.6 g.) in equal parts of acetic acid and acetic anhydride was heated with 5 g. of fused sodium acetate and 4 g. of zinc dust until colorless, and water was added cautiously to the filtered solution to

(17) Dziewoński and Dziecielewski, *Bull. intern. acad. Polonaise*, **A**, 273 (1927).

(18) L. F. Fieser, M. Fieser and Martin, *THIS JOURNAL*, **57**, 491 (1935).

decompose the excess anhydride. The diacetate, which separated in a colorless condition (5.6 g., 96%), was recrystallized from dilute acetic acid and formed cottony clusters of fine needles, m. p. 95–96°.

*Anal.* Calcd. for  $C_{21}H_{22}O_8$ : C, 62.66; H, 5.51. Found: C, 62.94; H, 5.77.

**1,2-Diacetoxynaphthalene-4-acetic Acid.**—A solution of 1.9 g. of the above diacetate in 20 cc. of glacial acetic acid was refluxed with 6 cc. of concentrated hydrochloric acid for two hours, and the solution was then evaporated to complete dryness at reduced pressure. The residue was heated with acetic anhydride (15 cc.)–sulfuric acid (2 drops) for forty-five minutes on the steam-bath and the solution was poured into 20 cc. of water containing 0.2 g. of barium chloride crystals. The filtered solution was evaporated to dryness at reduced pressure, and on extracting the residue with benzene and adding petroleum ether the product was obtained in a crystalline condition; yield, 1 g. (68%). Recrystallization from benzene–ligroin gave colorless microcrystals, m. p. 158–159°. After several weeks the substance began to turn violet. Attempted decarboxylation with copper powder resulted in extensive decomposition.

*Anal.* Calcd. for  $C_{16}H_{14}O_8$ : C, 63.56; H, 4.67. Found: C, 63.76; H, 4.73.

**4-Dicarbethoxymethyl-1,2-naphthophenazine (VI)**, prepared in the usual way, formed very pale yellow, fibrous needles from alcohol and melted at 164–165°.

*Anal.* Calcd. for  $C_{28}H_{26}O_4N_2$ : C, 71.10; H, 5.19. Found:<sup>16</sup> C, 71.07; H, 5.15.

The substituted malonic ester was hydrolyzed and decarboxylated by refluxing the material (1 g.) in 20 cc. of 10% potassium hydroxide solution for one and one-half hours. The crude acetic acid derivative separated on acidification as a yellow, gelatinous mass (0.35 g.). One crystallization from glacial acetic acid gave small, pale yellow plates, m. p. 168–172°, and without further purification 0.1 g. of this material was heated in 4 cc. of quinoline with 0.1 g. of copper bronze at 140–190° until carbon dioxide was no longer evolved. The solution was cooled, filtered, and partially neutralized with dilute acid. A yellow product separated, and on crystallization from alcohol it formed yellow needles melting at 174° and giving no depression when mixed with the sample of **4-methyl-1,2-naphthophenazine (VII)** prepared from 4-methyl-1,2-naphthoquinone.

*Anal.* Calcd. for  $C_{17}H_{12}N_2$ : C, 83.57; H, 4.96. Found:<sup>16</sup> C, 83.20; H, 4.70.

#### Diels–Alder Reaction

**4-Benzyl-1,2-naphthoquinone—2,3-Dimethylbutadiene (VIII, R = CH<sub>3</sub>).**—On heating the quinone (0.5 g.) with 2,3-dimethylbutadiene (1 cc.) in absolute alcohol (10 cc.) at 100°, the color appeared to fade slowly in the course of seventy-two hours, although slight decomposition made it difficult to judge the course of the reaction. The alcoholic solution was concentrated to a volume of 5 cc. and diluted with water, when the reaction product was obtained as a yellow solid (0.5 g.). On crystallization from alcohol the substance formed small, yellow needles, m. p. 179–179.5°, corr.

*Anal.* Calcd. for  $C_{23}H_{22}O_2$ : C, 83.60; H, 6.72. Found:<sup>16</sup> C, 83.32, 83.31; H, 6.76, 6.74.

**4-Dicarbethoxymethyl-1,2-naphthoquinone—2,3-Dimethylbutadiene (Experiment by J. T. Dunn).**—A mixture of the carefully purified quinone (2 g.), diene (5 cc.), and absolute alcohol (20 cc.) was heated at 100° for five days, although no starting material could be induced to crystallize after eight hours. The slightly darkened solution was diluted with water and extracted with ether, giving a viscous reddish oil. After obtaining seed from ether–petroleum ether, the main portion of oil slowly crystallized from this solvent when seeded in the cold. Four recrystallizations gave nearly colorless needles melting at 127–128°, corr.

*Anal.* Calcd. for  $C_{28}H_{24}O_8$ : C, 69.67; H, 6.10. Found:<sup>16</sup> C, 69.70, 69.57. H, 6.88, 9.47.

#### Reactions of the Quinones with Aniline

In a typical experiment 2 g. of 4-methyl-1,2-naphthoquinone was dissolved in 30 cc. of alcohol, 4 cc. of aniline was added and the solution was warmed on the steam-bath for one hour and allowed to stand overnight. Red needles of 2-anilino-1,4-naphthoquinone-4-anil slowly separated; yield, 1 g. The recrystallized material formed silky red needles, m. p. 181–182°, and did not depress the melting point of a sample prepared according to Zincke.<sup>11</sup>

*Anal.* Calcd. for  $C_{22}H_{16}ON_2$ : C, 81.46; H, 4.97. Found:<sup>16</sup> C, 81.50; H, 4.82.

Treated in the same way, the 4-benzyl and 4-dicarbethoxymethyl compounds gave a substance of the same m. p. and mixed m. p., and in the first case the product was analyzed with similar results (Found:<sup>16</sup> C, 81.50; H, 5.12).

#### Thiele Reaction

**With 4-Methyl-1,2-naphthoquinone.**—One gram of 4-methyl-1,2-naphthoquinone was stirred into 5 cc. of acetic anhydride containing one drop of concentrated sulfuric acid; the material soon dissolved, and after warming the solution for a few minutes on the steam-bath it was filtered from a small amount of dark material and poured into water. The reaction product separated in a clean condition and one crystallization from dilute alcohol gave pure material; yield, 1.45 g. (79%). The **abnormal triacetate** forms cottony needles melting at 101–102°.

*Anal.* Calcd. for  $C_{17}H_{16}O_6$ : C, 64.55; H, 5.06. Found: C, 64.84; H, 5.00.

The compound is easily hydrolyzed by dilute aqueous alkali in the cold, and the solution rapidly acquires an intense, deep green color. Discoloration also occurred on attempting to isolate the product by conducting the hydrolysis in an atmosphere of nitrogen.

Oxidation of the triacetate was effected by adding a saturated aqueous solution of 5.4 g. of potassium permanganate in small portions to a refluxing mixture of 1 g. of the triacetate and 150 cc. of water containing 8 g. of potassium hydroxide. When a permanent pink color was obtained the addition was discontinued and the mixture was refluxed for two hours longer. After acidification, the manganese dioxide was dissolved with the addition of sulfur dioxide and the solution was evaporated to dryness. The powdered residue was extracted with ether in the Soxhlet apparatus. The material left on evaporating the

ether gave on sublimation colorless needles of a product (m. p. 130–131°) which was identified as phthalic anhydride by mixed melting point determination.

**With 4-Benzyl-1,2-naphthoquinone.**—A solution of 1 g. of the quinone in 20 cc. of acetic anhydride containing one drop of concentrated sulfuric acid was heated for one hour on the steam-bath, and then clarified with Norite and poured into water. The precipitated material, crystallized from methanol, formed colorless prisms, m. p. 139.5–140°, corr.; yield, 0.8 g. The compound depresses the melting point of 1,2,4-triacetoxynaphthalene (m. p. 135°).

*Anal.* Calcd. for  $C_{23}H_{20}O_6$ : C, 70.37; H, 5.14. Found: C, 70.41; H, 5.09.

The same compound was obtained by heating the quinone with acetic anhydride and sodium acetate for one hour on the steam-bath.

**3-Chloro-1,2,4-triacetoxynaphthalene** was obtained by heating 3-chloro-1,2-naphthoquinone (1 g.) with acetic anhydride (10 cc.)–sulfuric acid (2 drops) on the steam-bath for three hours and crystallizing the product from alcohol (yield, 0.85 g.). It forms colorless microcrystals, m. p. 172–173°.

*Anal.* Calcd. for  $C_{16}H_{13}O_6Cl$ : C, 57.04; H, 3.89. Found: C, 57.03; H, 4.14.

Treated in the same way, 4-chloro-1,2-naphthoquinone was recovered unchanged.

## Summary

4-Methyl- and 4-benzyl-1,2-naphthoquinone have been synthesized and the former substance has been converted into a derivative obtainable by the degradation of the known 4-dicarbethoxymethyl-1,2-naphthoquinone.

The 4-methyl, 4-benzyl, and 4-dicarbethoxymethyl compounds all react with aniline with displacement of the 4-alkyl group. The first two compounds unexpectedly react with acetic anhydride–sulfuric acid to give colorless triacetates. The benzyl and malonic ester derivatives slowly add 2,3-dimethylbutadiene.

The three alkyl derivatives all have properties characteristic of true quinones, and the dicarbethoxymethyl compound is capable also of reacting in the tautomeric form to give an acetate. A substance described in the literature as the acidic tautomer of 4-methyl-1,2-naphthoquinone is believed to have some other structure.

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## The Dissociation of Hydantoin

BY LUCY W. PICKETT AND MARGARET MCLEAN

In a recent paper, Zief and Edsall<sup>1</sup> have shown that hydantoin and 5,5'-dimethylhydantoin have nearly equal dissociation constants, and have pointed out that the ionizing hydrogens are thus shown to be from the imino rather than the methylene group in hydantoin. The results of a series of electrometric titrations which are presented here not only confirm this conclusion, but also show from which nitrogen the dissociation occurs and to what extent dissociation is affected by the presence of various other substituents in the hydantoin molecule. The results of this study support the observations of the chemical behavior of these same compounds as reported by Hahn and co-workers.<sup>2</sup>

### Experimental

**Compounds.**—The substances used were purified analyzed samples of compounds whose preparation has been described<sup>2</sup> and were kindly supplied by Dr. Hahn. Their structural formulas and melting points are given in Table I

(1) Zief and Edsall, *THIS JOURNAL*, **59**, 2245 (1937).

(2) Hahn and Evans, *ibid.*, **50**, 806 (1928); Hahn and Litzinger, *ibid.*, **54**, 4663 (1932); Litzinger, *ibid.*, **56**, 673 (1934); Hahn and Seikel, *ibid.*, **58**, 647 (1936); unpublished work.

together with numbers by which they will be designated in the paper.

**Methods.**—The cell used in most of the measurements consisted of a hydrogen and a saturated calomel electrode which were frequently checked by measuring the *pH* of 0.1 *N* hydrochloric acid. The potential of the calomel electrode was taken as 0.2473 v. at 25°. Measurements were made with a Leeds and Northrup simplified potentiometer and galvanometer no. 2420.

In one typical series of experiments, samples weighing 0.4142 m. e. were dissolved in 25 ml. of water which had been freed from carbon dioxide. In most cases it was necessary to heat to 50° in order to effect complete solution, after which the solutions were cooled in an atmosphere of hydrogen and titrated at constant temperature with carbonate-free potassium hydroxide (0.04467 *N*) using a microburet.

A glass electrode was used for some determinations in order to check the results obtained with the hydrogen electrode and thus be certain that the substances used were not reduced at the hydrogen electrode. The results by the two methods agreed.

In addition to the titrations, the *pH*'s of solutions containing an equal number of equivalents of acid and of salt were measured in each case. These solutions were made by dissolving a weighed quantity of the sample in a measured volume of standard base. Concentrations varying from 0.05 to 0.005 *N* were used in some cases in