predominantly in the gas phase above about 540–560°. The latter assumption makes it necessary to ascribe the suppression of the reaction in a silver vessel to gas-phase deactivation due to silver. This is discussed in some detail.

PITTSBURGH, PENNA. RECEIVED JANUARY 21, 1937

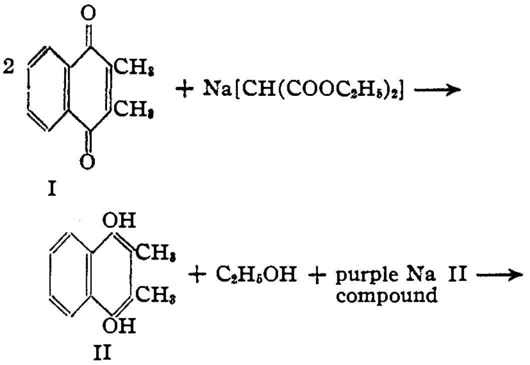
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

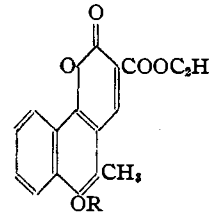
The Reaction between Quinones and Sodium Enolates. V. 2,3-Dimethylnaphthoquinone and Sodium Malonic Ester[1]

BY LEE IRVIN SMITH AND ISABELLA M. WEBSTER[2]

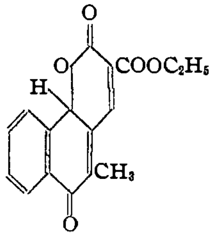
Previous papers in this series have dealt with the reaction between sodium enolates and two types of quinones: (1) duroquinone, a fully methylated para benzoquinone, and (2) trimethylquinone, a para benzoquinone with one unsubstituted position in the ring. In case 1, the reaction involved one of the methyl groups attached to the nucleus, and led ultimately to a coumarin derivative. In case 2 the reaction was most simply interpreted as involving an initial 1,4-addition of the reagent to the conjugated system which terminated in the unsubstituted position of the ring. In the latter case, the final products were benzofuran derivatives. In both cases only one molecule of reagent (sodium malonic ester) could be made to react.

In order to explore somewhat further the limits of the coumarin formation shown by duroquinone (case 1) the work described in this paper was undertaken and a benzolog of duroquinone, 2,3-dimethylnaphthoquinone (I), was selected for study. This quinone, like duroquinone, has two methyl groups attached to the quinone nucleus in positions 2 and 3, but positions 5 and 6, instead of holding methyl groups, are fused to a benzene ring. This quinone, if it were to react with sodium malonic ester in the same manner as duroquinone, should give rise to an intermediate sodium compound (II), which on hydrolysis would produce an α-naphthocoumarin derivative (III)[3] together with an equivalent amount of the hydroquinone.





III R = H
IV R = Ac



IIIa

This quinone, however, proved to be far more difficult to handle than duroquinone, and it was only after the original procedure used by Smith and Dobrovolny[4] had been modified considerably that a crystalline product could be obtained in good yield by decomposition of the sodium derivative II. In several experiments, the black quinhydrone derived from I was produced as a by-product. As this quinhydrone was apparently fairly stable in ether (the solvent used) it was necessary to allow time for the air to oxidize it back to the quinone in order to obtain the maximum yield of III from I, otherwise 3 moles of I were required to produce 1 mole of III.

The product III formed fine yellow needles melting at 212–213° with decomposition, and it had the composition and molecular weight corresponding to the formula $C_{17}H_{14}O_5$. No carbonyl derivatives could be formed using hydroxylamine or 2,4-dinitrophenylhydrazine, but the presence of one hydroxyl group was shown by the formation

---

[1] Paper IV, THIS JOURNAL, 58, 629 (1936).

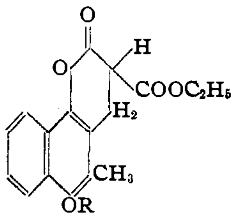
[2] Abstracted from a thesis by Isabella M. Webster, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1936.

[3] These compounds are more correctly termed 7,8-benzocoumarins. However, in the literature the term α-naphthocoumarin is used to designate them; therefore this term will be used throughout this discussion.

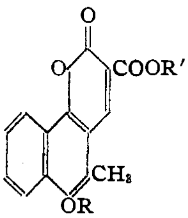
[4] Smith and Dobrovolny, THIS JOURNAL, 48, 1701 (1926).

of a pale greenish-yellow monoacetate (IV). The failure of the carbonyl reagents to react indicated that the structure was III, rather than IIIa, and the fact that the acetate IV was colored showed conclusively that it was not necessary to postulate a tautomerism between IIIa and III to explain the color of these hydroxycoumarins or the lack of it when the hydroxyl group was fixed by acetylation or methylation.[4]

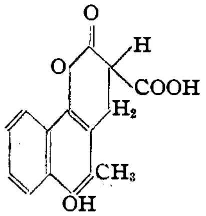
The double linkage in the pyrone ring was shown by the formation of a dihydro compound (V) when III was reduced catalytically: the dihydro compound V likewise formed a monoacetate (VI), and this same monoacetate VI was obtained when the acetate IV was reduced.



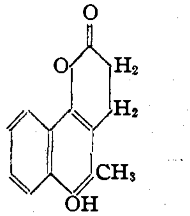
V R = H
VI R = Ac



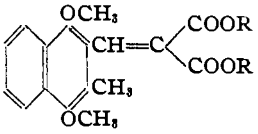
VII R = H, R′ = H
VIII R = Ac, R′ = H
XI R = CH₃, R′ = H
XII R = CH₃, R′ = CH₃



IX



X

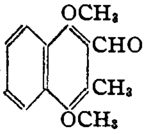


XIIa R = CH₃
XIIb R = H

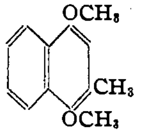
The formation of the same acetate VI regardless of whether reduction preceded or followed acetylation eliminated the possibility that the reduction had occurred at the carbonyl group of such a structure as IIIa and established the presence of a double bond in the pyrone ring of III.

The presence of the ester grouping in III was shown by the hydrolysis of III to the corresponding acid VII, which formed a monoacetyl derivative VIII. Catalytic reduction of the acid VII led to a mixture which contained at least two colorless substances. In analogy with the work of Smith and Denyes[5] this product is represented as a mixture of IX and X. These substances could not be separated by fractional crystallization, nor could IX be removed by shaking with any alkaline reagent because of the extreme ease with which the solutions were oxidized. For the same reason hydrolysis of V to IX was unsuccessful; the products in every case were yellow mixtures, and no better results were obtained when the acetate VIII was reduced. In none of these reductions, however, was there evidence of any substance which would correspond to the dimolecular products found by Smith and Denyes in the case of the coumarin from duroquinone.

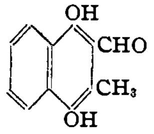
With a view to opening the coumarin ring so that the substance could be degraded further, several of the compounds in this series were methylated. It was hoped to prepare the dimethoxy compounds XIIa and XIIb, and to cleave one of these by oxidation to the aldehyde XVII which would then be synthesized. Although both methyl sulfate and methyl iodide were used, and, although the conditions were varied widely, all attempts to methylate the sodium derivative II, the ester III, the acetate IV, the acid VII or its barium salt, led only to the two methyl derivatives XI and XII, and attempts to methylate further these two products were unsuccessful. The hetero ring in this naphthocoumarin is therefore much more stable than is the case with the corresponding coumarin derived from duroquinone. The ester III reacted with diazomethane to give a *colorless* product, melting at 138–139°. From the analysis of this product, the lack of color (all of the compounds in this series except the reduced products are colored), and the reactions, it was obvious that the substance could not be either XIIa or XIIb. The substance was therefore not investigated further in connection with this work although a later research on the reaction between coumarins and aliphatic diazo compounds is planned.



XVII



XVI



XVIII

Since the coumarin ring could not be opened it was necessary to abandon further attempts at degradation, and to establish the coumarin struc-

---

(5) Smith and Denyes, THIS JOURNAL, 58, 304 (1936).

ture by direct synthesis. It was first planned to synthesize the acid XIIb as this should melt with loss of methanol to give the monomethyl derivative XI. This synthesis was unsuccessful, for the diether XVI could not be prepared from either the hydroquinone XV or its diacetate (XIV). The hydroquinone–aldehyde XVIII was prepared from the hydroquinone (XV),[6] and this aldehyde when condensed with malonic ester led directly to the ester III; when the aldehyde was condensed with malonic acid, the product was the coumarin acid VII. The reactions of III and VII, together with the syntheses of these two products from the aldehyde XVIII, leave no doubt as to the structure of the products obtained from the reaction between 2,3-dimethylnaphthoquinone and sodium malonic ester. These products are coumarin derivatives, and the course of the reaction is entirely analogous to that of the reaction between duroquinone and sodium malonic ester. The most conspicuous differences between the two series of compounds lie in the much greater stability of the hetero ring in the naphthocoumarins and in the fact that *all* of the compounds in the naphthocoumarin series (except the reduced products) are colored.

Experimental Part[6a]

2,3-Dimethylnaphthoquinone (I).—The following directions for the preparation of this quinone were found to give consistent results and excellent yields (60–80%). To a solution of 2,3-dimethylnaphthalene (10 g.) in acetic acid (350 cc.) at room temperature was added with stirring a solution of chromic acid (25.6 g.) in dilute acetic acid (130 cc. acid, 35 cc. water). The temperature was kept between 20 and 30° throughout the addition of the chromic acid, which required about fifteen minutes. The reaction mixture, after standing at room temperature for three days, was diluted with about 1.5 liters of water and allowed to stand for several hours. The quinone was filtered and washed thoroughly with water. Crystallized from alcohol, the product melted at 126–127°. Contrary to the experience of Wieser[7] it was found that the acetic acid filtrate from the quinone contained only negligible amounts of material. Steam distillation of the quinone was found to be an unsatisfactory method of purification, for considerable amounts of tars and resins were formed and the loss was great. The best method found for purification was that of Fieser,[8] which gave a product melting sharply at 127°.

1,4 - Diacetoxy - 2,3 - dimethylnaphthalene (Ib).—The quinone I (0.3 g.) was dissolved in acetic acid (10 cc.) and zinc dust was added. To the resulting red solution was added acetic anhydride (10 cc.) and a drop of sulfuric acid and the mixture was refluxed until it became colorless (thirty minutes). The cooled solution was decanted from the zinc into excess water, and the zinc was washed with hot acetic acid which was poured into the water. The white crystals melted at 184–189°; after five recrystallizations from alcohol the product melted at 189–190°.[9]

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.55; H, 5.92. Found: C, 70.55; H, 5.99.

Quinhydrone (Ic) of 2,3-Dimethylnaphthoquinone.—The quinone I (1.86 g., m. p. 121–125°) was dissolved in acetic acid (10 cc.), zinc dust was added and the mixture was refluxed until it became colorless. Water was added, and the hydroquinone was filtered. When dissolved in methanol, the hydroquinone gave a deep purple solution from which a black solid melting at 129° was isolated. Crystallized several times from 50% acetic acid, the melting point rose to 134–138°. One preparation melted at 139–144°. The quinhydrone was very unstable, even in the solid state, yellow crystals of the quinone appearing on the surface after a day in a desiccator.

Addition of Sodium Malonic Ester to the Quinone.—To a warm solution of the quinone (4.65 g.) in absolute ether (160 cc.) was added with stirring a solution of sodium malonic ester (made from sodium (0.6 g.) dry ethyl alcohol (60–80 cc.) and malonic ester (4 g.)). The addition of the reagent required about one hour; the solution turned brown, then green. Refluxing (41–43°) and stirring were continued for five and one-half hours. After about one hour the purple color of the sodium derivative II began to appear and at the end of the reaction the green color had disappeared entirely. After standing for some time, the solvent was decanted (it contained chiefly quinone and quinhydrone) from the deep purple solid. The solid was transferred to a filter with ether, washed with a small amount of water and alcohol and a large amount of ether (300 cc.) and dried. It weighed 4.3 g. From the various filtrates and washings, about 25% of the quinone used was recovered.

5 - Methyl - 6 - hydroxy - 3 - carbethoxy - α - naphthocoumarin (III) was obtained when a suspension of the sodium derivative II (4 g.) in ethyl alcohol (50 cc.) was acidified with hydrochloric acid (10 cc.). The products were 3.05 g. of III melting at 208–211° and a dark, tarry solid which yielded about half a gram of quinone when steam distilled. The coumarin crystallized from absolute ethyl alcohol in yellow needles melting at 212–213°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.43; H, 4.73; mol. wt., 298. Found: C, 68.39; H, 4.83; mol. wt. (Rast), 301, 299.

It was not necessary to isolate the sodium derivative, however, for the coumarin could be obtained by adding dilute acetic acid directly to the reaction mixture and allowing it to stand in the ice-box for some time. The product contained unchanged quinone, which was removed by boiling ether, and the residue, crystallized from absolute alcohol, melted at 211–213°. Often, especially when too much ether was used in the condensation, the quinhydrone Ic was recovered instead of the quinone.

The addition could also be carried out in dry benzene, according to the original method of Smith and Dobrovolny[4]

---

[6] Madinaveitia, (a) *C. A.*, **29**, 3830 (1935); (b) *Rev. acad. cienc. Madrid*, **31**, 617–647 (1934).

[6a] Microanalyses by J. W. Opie.

[7] *Monatsh.*, **1**, 604 (1880).

[8] Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, 1935, pp. 230, 231.

[9] Crawford, This Journal, **57**, 2000 (1935).

although the time required was long (seven days) and the yield was only about half that obtained by the procedure given above.

The coumarin III was decomposed by hydroxylamine in alkaline solution or in a solution buffered with sodium acetate, and no oxime could be obtained.

6 - Acetoxy - 5 - methyl - 3 - carbethoxy - α - naphthocoumarin (IV).—The coumarin III (1 g.) was refluxed in acetic anhydride for one hour and the solution then poured into water. The product, crystallized from acetic acid or absolute ethanol, weighed 0.9 g. and melted at 195–196°. It was pale greenish-yellow.

Anal. Calcd. for $C_{19}H_{16}O_6$: C, 67.09; H, 4.71. Found: C, 67.26; H, 5.05.

6 - Hydroxy - 5 - methyl - 3 - carbethoxy - 3,4 - dihydro-α-naphthocoumarin (V).—The coumarin (III) and about half its weight of a palladium catalyst[10] were suspended in ethanol or methanol and shaken with hydrogen under 35–40 pounds (1.16–1.34 atm.) until the mixture was colorless. The catalyst was allowed to settle, the supernatant liquid poured off through a filter, and the filtrate evaporated under reduced pressure. The product was recrystallized from ethanol, but it was necessary to exclude air as much as possible since the compound was readily oxidized. The substance was white and melted at 175–176°. Of the two solvents, ethanol was found to be much the better for the dihydro compound was much more readily oxidized in methanol than in ethanol.

Anal. Calcd. for $C_{17}H_{16}O_5$: C, 67.97; H, 5.37. Found: C, 67.70; H, 5.52.

6 - Acetoxy - 5 - methyl - 3 - carbethoxy - 3,4 - dihydro - α-naphthocoumarin (VI) was obtained when the acetyl derivative IV was reduced catalytically as above; the same product resulted when the dihydrocoumarin V was acetylated by refluxing with acetic anhydride for thirty minutes. Crystallized from alcohol, the substance was white, and the m. p. and mixed m. p. of specimens prepared by the two methods was 145–145.5°.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.27. Found: C, 66.34; H, 5.35.

6 - Hydroxy - 5 - methyl - 3 - carboxy - α - naphthocoumarin (VII).—The action of most hydrolyzing agents was accompanied by considerable decomposition and gave products which were very difficult to purify. This was especially true of 80% sulfuric acid, the reagent used by Smith and Dobrovolny[4] for hydrolysis of their ester. Sodium hydroxide caused complete decomposition and no hydrolysis product could be isolated. When applied to the *pure* ester, the following procedure was found to give good yields of a product which was readily purified. The ester III (3.6 g.) was suspended in acetone (150 cc.) and dilute hydrochloric acid (400 cc. 1:1) and the mixture was refluxed for eight hours. The mixture was then cooled and the solid filtered, washed with water and dried. It weighed 3.1 g. (95%) and formed fine orange needles melting (dec.) at 275–276° when the bath was preheated to 240° and at 263° (dec.) when the bath was at room temperature at the beginning. The acid was insoluble in benzene and petroleum ether, very slightly soluble in ether, alcohol, chloroform or ethyl acetate, and quite soluble in acetone. For recrystallization, which was difficult, acetic acid was the best solvent, although alcohol could be used.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.65; H, 3.73. Found: C, 66.60; H, 3.87.

Catalytic reduction of the acid VII in ethyl alcohol, using the method described for the reduction of the ester III, gave a colorless solution in about three hours. The solution acquired a yellow color when it was decanted from the catalyst through a filter. The solvent was evaporated to 15 cc. under reduced pressure and the solution allowed to stand, tightly stoppered, overnight. No solid separated during this time, but the solution turned deep red in color. The solvent was then evaporated completely, leaving a solid melting at 142° which was very soluble in all the common solvents except petroleum ether. Crystallization from chloroform–petroleum ether was accompanied by great losses of material and the product was tinged with red and could not be obtained pure. The highest melting point obtained was 153–161° (dec.) (IX?) and this material, after the melt had solidified, re-melted at 129–130° with no evolution of gas (X?). Although 1.4 g. of the acid VII was reduced, it was not possible to isolate from the product enough pure material for analysis. Catalytic reduction of the acid VII in sodium carbonate solution gave only red oils from which no solid could be obtained.

When the dihydro ester V was subjected to the procedure used for hydrolysis of the coumarin ester III, the colorless solution became first yellow and then orange. The solid which precipitated melted at 155–159°; addition of excess water to the cold filtrate gave a solid which melted at 120–125°. The amounts of both were very small.

6 - Acetoxy - 5 - methyl - 3 - carboxy - α - naphthocoumarin (VIII).—The acid VII was boiled for four hours with acetic anhydride, the orange color fading to yellow. The mixture was then poured into ice water and allowed to stand for some time. The product, crystallized from acetic acid, melted at 258° (dec.).

Anal. Calcd. for $C_{17}H_{12}O_6$: C, 65.37; H, 3.87. Found: C, 64.97; H, 3.87.

Catalytic reduction of this acetyl derivative in ethyl alcohol, using the palladium catalyst, gave only oils from which in only one of many experiments was any solid obtained and then in extremely small amounts.

6 - Methoxy - 5 - methyl - 3 - carboxy - α - naphthocoumarin (XI).—The coumarin acid VII (0.2 g.) in methyl sulfate (3–4 g.) and methanol (25 cc.) was refluxed while 20% aqueous potassium hydroxide was added in small portions. Each portion of the alkali caused a red color to develop, which then faded. When a color change no longer occurred, an excess of the alkali was added and the mixture was refluxed for fifteen minutes. The cold solution was acidified with sulfuric acid, sufficient water was added to dissolve the potassium salts, and the yellow insoluble precipitate was removed and crystallized several times from methyl alcohol. It melted at 222–225°, was soluble in ethyl alcohol, methyl alcohol, ether and chloroform and almost insoluble in benzene.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.58; H, 4.26; OCH_3 (one), 10.92. Found: C, 67.66, 67.55; H, 4.69, 4.61; OCH_3, 11.87.

Methylation of the ester III or the acetyl derivative IV in methyl sulfate, using the general procedure above and

---

[10] Busch and Stöve, *Ber.*, **49**, 1064 (1916).

1% aqueous sodium hydroxide as the alkali, gave the same product (XI) in yields of about 70%.

6 - Methoxy - 5 - methyl - 3 - carbomethoxy - α - naphthocoumarin (XII).—The coumarin acid VII (1 g.) was dissolved in 4% sodium methoxide–methanol (6 cc.); heated gently for thirty min. (purple color) and cooled. Methyl sulfate (1 cc.) and 4% sodium methoxide–methanol (6 cc.) were then added and the flask shaken vigorously for ten minutes. The addition of like quantities of reagents at ten-minute intervals, with vigorous shaking in between, was continued until a total of 19 cc. of methyl sulfate and 114 cc. of the alkali were added, after which the mixture was allowed to stand for fifteen hours. Concentrated ammonia (5 cc.) and water (30 cc.) were added and the mixture warmed on the steam-bath for thirty minutes. An excess of water was then added, the solution cooled and the solid removed and crystallized from methanol. It melted at 182–183° and the yield was 90%. In ether the substance showed a green fluorescence. These directions had to be followed carefully, otherwise the product was a mixture of the ethers XI and XII which was very difficult to separate, or else only the mono-ester XI resulted. The hydrolysis of the ester group in XII occurred with great ease and in most methylation reactions only the monomethyl derivative XI resulted. The dimethyl derivative was somewhat less soluble in alcohol than the monomethyl derivative.

Anal. Calcd. for $C_{17}H_{14}O_6$: C, 68.46; H, 4.69; OCH_3 (two), 20.80. Found: C, 68.46; H, 4.78; OCH_3, 21.03.

The dimethyl derivative XII when refluxed for three to four hours with 10% aqueous potassium hydroxide gave a clear yellow solution, which on acidification gave the monomethyl derivative XI, m. p. and mixed m. p. 223–225°.

The dimethyl derivative XII was also obtained (impure, m. p. 175–177°, mixed m. p. 177–182°) when the purple sodium derivative II was suspended in methanol and refluxed with excess methyl iodide. This impure specimen of XII, when hydrolyzed, gave the methoxy acid XI, m. p. and mixed m. p. 221–223°.

Many other experiments were carried out in the attempt to open the coumarin ring of the ester III or the acid VII in the hope of obtaining the ester XIIa or the acid XIIb. The procedures of various authors[11] were tried several times. All of these methods, except the ones described above, gave the monomethyl derivative XI, unchanged material or decomposition products. The barium salt of the acid XI was prepared by the method of Marschalk[12] but when refluxed with methyl sulfate and methanol it charred completely.

Aside from the substances XI and XII, the only other methyl derivative obtained was by action of diazomethane upon the ester III. This reaction led to a *white* crystalline solid (from alcohol) which melted at 138.5–139° (dec.). The analysis indicated a carbon–hydrogen ratio of approximately 1:1; qualitative tests for nitrogen were negative. No satisfactory formula for this compound has as yet been written.

2-Methylnaphthoquinone (XIII).[13,b]—2-Methylnaphthalene (12.5 g.) was dissolved in acetic acid (118 cc.) and a suspension of chromic acid (50 g.) in 80% acetic acid (90 cc.) was added in a continuous stream. After the highly exothermic reaction was over, the mixture was allowed to stand for an hour and then was diluted with water. The yellow precipitate was removed, washed well with water, dissolved while still wet in ether and the ethereal solution was filtered and dried over calcium chloride. If the crude material was orange in color, the ethereal solution was treated with charcoal before drying it. Evaporation of the ether to crystallization yielded bright yellow needles; the yield was 25–40% and the product melted at 105–107°. The quinone could be purified by steam distillation or crystallization from alcohol or 50% acetic acid. It was unstable in the light, turning from yellow to a dull tan in color.

2-Methylnaphthohydroquinone.—The quinone XIII could be reduced by any of several methods, but the isolation of the product was difficult because of the extreme ease with which the hydroquinone was oxidized to the purple quinhydrone and then to the quinone. Catalytic reduction in ether or methanol with hydrogen under 40 pounds (1.34 atm.) pressure and in the presence of the palladium catalyst gave colorless solutions, which could be used directly if a solution of the hydroquinone were desired, but from which the pure solid hydroquinone was isolated only with difficulty. Reduction with zinc and sulfuric acid gave only deep red solutions and continued boiling with the reducing agent did not cause the color to disappear. Reductive acetylation of the quinone (10 g.) in acetic acid (25 cc.), acetic anhydride (100 cc.) and sodium acetate (5 g.) by refluxing the solution with zinc dust (10 g.) gave 1,4-diacetoxy-2-methylnaphthalene in 82% yield. Crystallized from methanol, the substance was white and melted at 112.5–114°.[13]

All attempts to prepare the dimethyl ether of the hydroquinone (XVI) led to red oils which distilled with complete decomposition.

1,4 - Dihydroxy - 3 - methyl - 2 - naphthaldehyde (XVIII).[5b]—The most successful procedure for this preparation consisted in the catalytic reduction of the quinone in absolute ether, and the use of the resulting ethereal solution of hydroquinone directly for introduction of the aldehyde group. The quinone (7.5 g.) was suspended in absolute ether (160 cc.), palladium catalyst (4 g.) was added and hydrogen passed in under 40 pounds (1.34 atm.) pressure. The color disappeared in five minutes, but the reaction was allowed to continue for about thirty minutes. The catalyst was allowed to settle, the solution was decanted, the catalyst was washed with absolute ether and the solution and washings were placed immediately in the reaction flask for the next step. Zinc cyanide (9.1 g.) was added, and with stirring and cooling (0°), dry hydrogen

---

[11] (a) Meyer, *Monatsh.*, **24**, 837 (1903); (b) Perkin and Robinson, *J. Chem. Soc.*, **91**, 1079 (1907); (c) Decker and Koch, *Ber.*, **40**, 4794 (1907); (d) Freudenberg, *ibid.*, **53**, 1424 (1920); (e) Stoermer and Friemel, *ibid.*, **44**, 1843 (1911); (f) Stoermer and Friderici, *ibid.*, **44**, 644 (1911); (g) Tiemann, *ibid.*, **8**, 1135 (1875); (h) Chakravarti, *J. Ind. Chem. Soc.*, **7**, 247 (1930); (i) Houben–Weyl, "Die Methoden der org. Chem.," George Thieme Verlag, 1923, Vol. III, p. 11, 103; (j) Freudenberg, *Ann.*, **433**, 234 (1923); *Ber.*, **56**, 1191 (1923); (k) Haworth, *J. Chem. Soc.*, 2681 (1928); (l) Kohn and Grun, *Monatsh.*, **46**, 75 (1925); (m) Späth and Klager, *Ber.*, **67**, 859 (1934).

[12] Marschalk, *Ber.*, **45**, 585 (1912).

[13] (a) Fries and Lohmann, *Ber.*, **54**, 2912 (1921); (b) Madinaveitia and S. de Buruaga, *C. A.*, **24**, 359 (1930); (c) Anderson and Newman, *J. Biol. Chem.*, **103**, 406 (1933).

chloride was passed in rapidly until the solution became saturated (one and one-half hours) and then more slowly for two hours longer.[14] The milky solution gradually cleared and then an orange solid slowly separated. The ether was decanted, and after washing the solid with fresh ether it was warmed with water (50–100 cc.) until all the imide hydrochloride decomposed. The mixture was cooled and the aldehyde was removed and crystallized from 50% acetic acid, dilute alcohol or chloroform–petroleum ether. The yield was 5.6 g. (64%) and the melting point was 158–160°. The chief impurity in the crude aldehyde was a black substance (quinhydrone?). Steam distillation of the aldehyde gave only quinone in the distillate and a residue of red oil which solidified on cooling; vacuum distillation was also unsatisfactory as a method of purification. The aldehyde could not be converted into an oxime, but with aniline it gave a precipitate of beautiful red needles.

Condensation with Malonic Ester.—To the aldehyde (1.44 g.) in alcohol (2 cc.) there was added piperidine (0.76 g.) and ethyl malonate (2 cc.). The mixture was warmed on the steam-bath until a clear solution resulted, then set aside for a day. The product which had crystallized from the solution was allowed to stand with hydrochloric acid for fifteen to twenty minutes, filtered and washed with cold alcohol and ether. Crystallized from alcohol, the product weighed 0.43 g. and melted at 209–211°; the mixed melting point with a specimen of III (m. p. 208–209°) was 208–209°. Acetylation of this product gave the same acetyl derivative (IV) as was obtained from the ester III; m. p. and mixed m. p. 193–195°.

Condensation of the aldehyde (1 g.) with malonic ester (2 cc.) in acetic acid (2 cc.) led to a solid (0.05 g.) which was chiefly the acetyl derivative VIII. It melted at 248–253°; the mixed m. p. with VIII (m. p. 258°) was 246–250°.

Condensation with Malonic Acid.—To the aldehyde (1.4 g., crude) and malonic acid (0.7 g.) in dry methanol (7 cc.) was added one drop of piperidine and the solution was refluxed on the steam-bath for eighteen hours. A small amount of chloroform was added and the solution was filtered. The chloroform was evaporated from the filtrate, a little methanol was added and the yellow solid was filtered and washed with water and dilute hydrochloric acid. The solid melted at 273–275°; the mixed melting point with a specimen of the acid VII (m. p. 273–275°) was also 273–275° (copper block).

Summary

1. Sodium malonic ester reacts with 2,3-dimethylnaphthoquinone to give a purple sodium derivative which when treated with acid gives 5-methyl-6-hydroxy-3-carbethoxy-α-naphthocoumarin.

2. The physical and chemical properties of this coumarin and a number of its derivatives have been described, and the structure of the coumarin was proved by an independent synthesis from 1,4-dihydroxy-3-methyl-2-naphthaldehyde.

3. The course of the reaction between the methylated naphthoquinone and sodium malonic ester is entirely analogous to that between duroquinone and sodium malonic ester, but the hetero ring in the naphthocoumarin is much more resistant to opening by alkaline reagents.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 8, 1937

---

[14] Adams and Levine, THIS JOURNAL, **45**, 2373 (1923).

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

The Reaction between Quinones and Sodium Enolates. VI. Duroquinone and Sodium Acetoacetic Ester[1]

BY LEE IRVIN SMITH AND DAVID TENENBAUM[2]

In the first paper of this series[3] it was shown that the fully methylated quinone, duroquinone, reacted with sodium malonic ester to give a coumarin derivative (I). In a later paper, Smith and MacMullen[4] showed that trimethylquinone, with one unsubstituted position in the ring, reacted with malonic ester and with acetoacetic ester to give benzofuran derivatives, malonic ester giving only one product (Ia), while acetoacetic ester gave two products (Ia and Ib). These products were the result of an initial 1,4-addition of the reagent to the quinone conjugated system which terminated in the free position, but this reaction was not accompanied by the oxidative step which occurred when the coumarin was formed from duroquinone. The fact that acetoacetic ester gave two products suggested a study of the reaction between this reagent and duroquinone. If the reaction followed the same course as that of malonic ester, the product would be the acetylcoumarin II; but there was also the possibility that the intermediate addition product (IIa) would be oxidized to a form which could undergo self-condensation leading to the *amphi*-naphthoquinone derivative IIb. These products would themselves be of interest,

---

[1] Paper V, THIS JOURNAL, **59**, 662 (1937).

[2] Abstracted from a thesis by David Tenenbaum, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1936.

[3] Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926).

[4] Smith and MacMullen, *ibid.*, **58**, 629 (1936).