weighed 2.20 g. (74%) after one recrystallization from acetone, had m.p. 163–164°, and was optically inactive.

Racemization of Ethyl D(–)-**Mandelate**.—Sodium (0.13 g.) was finely divided in toluene (25 ml.) as before. The toluene was decanted and dry ether (15 ml.) added. A solution of ethyl D(–)-mandelate (1.00 g.) in dry ether (15 ml.) was added with stirring, which was continued at room temperature for five hours. Water was cautiously added, the ether layer separated, dried, and the solvent removed to give 0.44 g. of 96% racemized ethyl mandelate, $[\alpha]^{25}\mathrm{D}$ –5.98° (*c* 7.53, chloroform).

Ethyl L(–)- **and** D(+)-**2-Phenyldiglycolates**.—Ethyl D-(–)-mandelate (5.0 g.), ethyl bromoacetate (50 ml.), silver carbonate (15 g.), Drierite (15 g.) and glass beads were stirred with a Hershberg stirrer at 55–60° for 24 hours under protection from moisture and light. The filtered mixture was freed of ethyl bromoacetate by steam distillation, the residue extracted with ether, and the crude product isolated as in the case of D,L-ester above. The crude material (10.4 g.) was fractionated into three fractions as follows: (1) 3.54 g., b.p. 96–103° (1 mm.), $[\alpha]^{25}\mathrm{D}$ –6° (*c* 7.25, chloroform); (2) 0.73 g., b.p. 103–136° (1 mm.), and (3) 4.43 g., b.p. 136–140° (1 mm.); $[\alpha]^{25}\mathrm{D}$ –96° (*c* 7.30, chloroform). Fraction (3) was redistilled to give a product of b.p. 145–148° (0.5 mm.) and $[\alpha]^{25}\mathrm{D}$ –95° (*c* 4.96, chloroform). In a similar experiment the final ester had $n^{25}\mathrm{D}$ 1.4818 and $[\alpha]^{25}\mathrm{D}$ –90° (*c* 4.30, chloroform). The product analyzed poorly, presumably due to the unavoidable contamination of the desired product with the low-boiling forerun in the quantities at hand.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.2; H, 6.81. Found: C, 61.9; H, 6.71.

Ethyl D(+)-2-phenyldiglycolate was prepared in exactly the same way, and with corresponding results, from ethyl L(+)-mandelate. The desired fraction, on redistillation, had b.p. 137–140° (1 mm.), $n^{25}\mathrm{D}$ 1.4827, and $[\alpha]^{25}\mathrm{D}$ 92° (*c* 5.25, chloroform). Its analysis was also low.

Anal. Found: C, 59.6; H, 6.82.

The Low-Boiling Forerun.—The low-rotating, low-boiling foreruns obtained in the previous syntheses of ethyl D- and L-2-phenyldiglycolates were combined and redistilled. The middle cut, comprising 60% of the total, had b.p. 93–95° (1 mm.), $n^{23}\mathrm{D}$ 1.4383, and d^{23}_{25} 1.146. Its analyses proved slightly high, presumably due to residual contamination by higher boiling material.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.5; H, 7.38; sapn. equiv., 95.1. Found: C, 51.6, 51.7; H, 6.97, 6.90; sapn. equiv., 99.6.

The material proved to be ethyl diglycolate on ammonolysis. A sample of the redistilled product (0.50 g.) was dissolved in ethanol (3 ml.) and saturated with ammonia. After 15 hours 0.18 g. of solid was filtered, m.p. 182.5–183°. Resaturation of the mother liquors with ammonia produced an additional 0.15 g. (total 95%) of solid after several days. On recrystallization from ethanol the product had m.p. 183.5–184.5°, unchanged on admixture with an authentic sample of diglycolamide (m.p. 184–184.5°).

Anal. Calcd. for $C_4H_8O_3N_2$: C, 36.64; H, 6.10. Found: C, 36.48, 36.59; H, 6.13, 6.19.

The authentic sample was prepared by esterification of diglycolic acid followed by similar ammonolysis.

L(–)- **and** D(+)-**2-Phenyldiglycolamides**.—The above redistilled ethyl L(–)-2-phenyldiglycolate (2.0 g.) was dissolved in absolute ethanol (20 ml.) and treated with liquid ammonia (*ca.* 8 ml.) as before. The crude product, isolated as usual, weighed 0.96 g. (61%) and had m.p. 162.5–164.5°. This was recrystallized thrice from acetone to give a product having m.p. 170° and $[\alpha]^{25}\mathrm{D}$ –111.3° (*c* 3.50, ethanol).

Anal. Calcd. for $C_{10}H_{12}O_3N_2$: C, 57.75; H, 5.81. Found: C, 57.99; H, 5.77.

D(+)-2-Phenyldiglycolamide was prepared in an identical fashion with similar results from ethyl D(+)-2-phenyldiglycolate of $[\alpha]^{25}\mathrm{D}$ 92.2°. The crude amide had m.p. 168–170.5° and was obtained in 74% yield. Two recrystallizations from acetone gave a product of m.p. 174–174.5° and $[\alpha]^{23}\mathrm{D}$ 106.2° (*c* 0.570, ethanol).

Anal. Calcd. for $C_{10}H_{12}O_3N_2$: C, 57.75; H, 5.81. Found: C, 57.62; H, 5.79.

A mixed m.p. of this material with D,L-2-phenyldiglycolamide, m.p. 160–161°, was 158.5–160.5°. The ratio of active to racemic amide in the mixture was about $^1/_{10}$.

Infrared Spectra.—The infrared spectra (Fig. 1) of the two D-2-phenyldiglycolamides from L-mandelic acid and from β-D-glucosylbenzene were determined in mineral oil suspension using a Perkin–Elmer Infrared Spectrometer for the region 8–15 μ. The authors are indebted to Professor John H. Wise of Stanford University for his kindness in determining these spectra. The vertical displacements of the two curves in Fig. 1 arise as a result of the differing sample thicknesses in the two measurements.

STANFORD, CALIFORNIA
EVANSTON, ILLINOIS

RECEIVED MARCH 21, 1951

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

Action of Pyridine and Iodine upon Two *o*-Phenolic-1,4-diketones: 4,6,7-Trimethylcoumarandione and its 5-Hydroxy Derivative

BY LEE IRVIN SMITH AND RICHARD REMSEN HOLMES[1]

The two phenolic 1,4-diketones, Ia and Ib, have been subjected to the action of pyridine and iodine, followed by action of alkali. In this manner, Ia is converted into the coumarandione II, the structure of which has been proved by two independent syntheses. The chemistry of II has been explored, and in particular it has been converted into its 5-hydroxy derivative III, and the structure of the latter has also been confirmed by an independent synthesis. It was not possible to convert 5-hydroxy-4,6,7-trimethylcoumarandione III into the related quinone IX, nor could the lactone ring of III be opened by action of ethanol. Conversion of II into III—a derivative of a hydroquinone—*via* a sequence of reactions ordinarily leading to a quinone illustrates the peculiar properties of these highly methylated compounds. In contrast to the behavior of Ia, the diketone Ib was not converted into a pyridinium iodide by action of pyridine and iodine . Instead the product of this reaction was the oxindigo XII.

In a previous paper[2] the preparation, and certain aspects of the chemistry of the two phenolic 1,4-diketones, Ia and Ib have been discussed. Another paper[3] has dealt with the reduction of Ia and the behavior of the isomeric diols so obtained. The present paper constitutes a report of the behavior of the diketones Ia and Ib, when subjected to the action of iodine and pyridine, followed by action of alkali, a sequence found by King, McWhirter and Barton[4] to be effective for degradation of *o*-hydroxyketones to salicylic acids.

The product produced from Ia by this sequence of reactions, 4,6,7-trimethylcoumarandione (II), as

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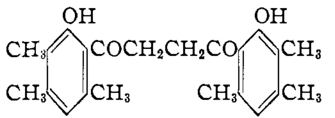
(1) Abstracted from a thesis by Richard Remsen Holmes, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, July, 1950. American Chemical Society Predoctoral Fellow, 1946–1950.

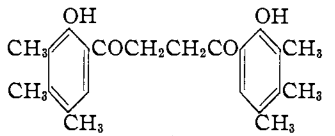
(2) L. I. Smith and R. R. Holmes, THIS JOURNAL, **73**, 3847 (1951).

(3) L. I. Smith and R. R. Holmes, *ibid.*, **73**, 3851 (1951).

(4) L. C. King, M. McWhirter and D. M. Barton, *ibid.*, **67**, 2089 (1945).

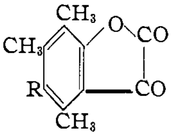


Ia

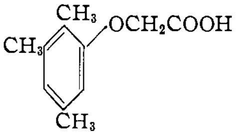


Ib

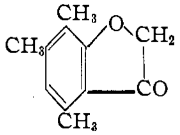
well as the 5-hydroxy derivative III of II, have been synthesized and their chemistry has been explored.



II, R = H
III, R = OH
VIII, R = NO$_2$



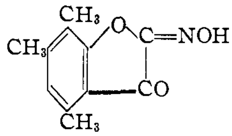
IV



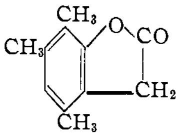
V

When the diketone Ia was boiled with pyridine and iodine, a yellow, high melting (280° dec.) compound, containing iodine and soluble in pyridine, was produced. This substance was not obtained analytically pure, but in analogy with the work of King, *et al.*,[4] it was regarded as a pyridinium iodide of Ia. But when this compound was subjected to the action of alkali, no methylated salicylic acid resulted; instead, the product, formed in about 20% yield, was a yellow solid melting at 149–151°, but with a neutral equivalent of 194. The substance was not a carboxylic acid, for it was insoluble in cold aqueous bicarbonate; it was, however, soluble in hot aqueous bicarbonate with evolution of gas, and was instantly soluble in cold aqueous sodium hydroxide. Acidification of the alkaline solutions reprecipitated the substance unchanged. The substance was unaffected by action of aqueous sulfurous acid, hence was not a quinone. In considering the possible paths which could lead to formation of an acid from a methyl ketone by actions of pyridine and iodine, it seemed likely that an α-keto acid would be an intermediate; if so, and the original ketone were an *o*-hydroxy ketone, the α-keto acid might be expected to undergo ring closure to a coumarandione. In the case of the diketone Ia, a double transformation of this type would lead to the coumarandione II. This coumarandione II was not known, but it was synthesized and found to be identical with the degradation product of Ia. The exact mechanism by means of which II is formed from Ia is not clear, but transformation of Ia into II by this "modified haloform" reaction establishes the presence of the grouping –COCH$_2$– in the diketone Ia.

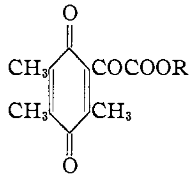
2,3,5-Trimethylphenoxyacetic acid (IV) was prepared by condensation of chloroacetic acid with the phenoxide at 180°; this acid was then cyclized, by action of sulfuric acid to 4,6,7-trimethylcoumaranone (V).[5] The coumaranone V could also be prepared directly, by action of chloroacetyl chloride upon 2,3,5-trimethylphenol in the presence of aluminum chloride.[6] Nitrosation of V gave the isonitroso compound VI, which upon hydrolysis gave the coumarandione II, identical with the product obtained from Ia. The dione II was formed directly from 2,3,5-trimethylphenol by action of oxalyl chloride in benzene or tetrachloroethane, and in excellent yield, in contrast to the results reported in the literature for this method of making coumarandiones.[7]



VI



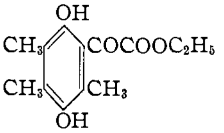
VII



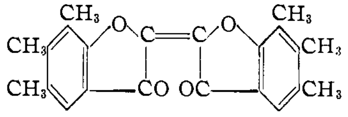
IX, R = H
X, R = C$_2$H$_5$

When the coumarandione II was subjected to the conditions of the Clemmensen reduction, two products were formed. One of these was 4,6,7-trimethylisocoumaranone (VII), and the other was a high-melting material, probably bimolecular, which was not investigated further. Nitration of II lead to a mononitro derivative VIII in good yield.

Having in hand the coumarandione, conversion of it into a related quinone (IX or X) was of some interest, for such a quinone might be expected to show new types of addition reactions. The coumarandione II was coupled with diazotized sulfanilic acid and the resulting azo dye (not isolated) was reduced by action of stannous chloride. Oxidation of the amino compound (also not isolated) by action of ferric chloride produced a red compound $C_{11}H_{10}O_4$ (III) melting at 188–190°, in low yield. The red substance was stable at its melting point, but evolved gas at 220–230°; it was a lactone, for it was insoluble in cold aqueous bicarbonate, although soluble in hot aqueous bicarbonate and in cold aqueous alkali; it was precipitated unchanged when these alkaline solutions were acidified. The substance was unaffected by action of aqueous sulfurous acid, and hence was not a quinone. It appeared to be 4,6,7-trimethyl-5-hydroxycoumarandione (III), and this formulation was verified by an independent synthesis of III from trimethylhydroquinone and oxalyl chloride. The yield of III, prepared by either method, was low, but addition of aluminum chloride to the



XI



XII

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(5) L. I. Smith, J. A. King, C. O. Guss and J. Nichols, THIS JOURNAL, **65**, 1594 (1943).

(6) K. Fries and G. Finck, *Ber.*, **41**, 4271 (1908).

(7) (a) R. Stollé and E. Knebel, *Ber.*, **54**, 1213 (1921); (b) H. Staudinger, *ibid.*, **41**, 3558 (1908); (c) R. Stollé, R. Bergdoll, M. Luther, A. Auerhahn and W. Wacker, *J. prakt. Chem.*, **128**, 1 (1930).

mixture of trimethylhydroquinone and oxalyl chloride led to no improvement, and an attempt to convert II into III by way of the *p*-nitroso compound[8] failed because II was completely unaffected by action of ethyl nitrite and hydrochloric acid. It was surprising that the usual synthesis of quinones *via* the diazo coupling led in this case to a derivative of the hydroquinone (III); it is possible that the quinone was initially formed and was reduced at the expense of the intermediate amino compound. In conformity with this explanation, III was found to be unaffected by action of ferric chloride.

Oxidation of III to the quinone IX was unsuccessful. Nor was it possible to open the lactone ring of III, and so convert it into XI, by action of boiling ethanol for prolonged periods of time—a result in striking contrast with the behavior of the unsubstituted coumarandione analogous to II, which is converted completely into the ethyl ester of the ortho hydroxyketo acid by action of boiling ethanol for 30 minutes.[9]

The isomeric 1,4-diketone Ib differed greatly from Ia in its behavior toward pyridine and iodine. The product of this reaction was an orange solid, $C_{22}H_{20}O_4$, melting at 305–306° with decomposition. The substance was insoluble in all the common organic solvents, but could be recrystallized from hot nitrobenzene. It was insoluble in aqueous alkali and in Claisen alkali, hence was not a phenol. The substance is formulated as a hexamethyloxindigo XII, a formulation which is in agreement with the physical and chemical properties.[10]

Experimental Part[11]

Oxalyl Chloride.—Anhydrous oxalic acid[12] (380 g.) was added in portions to a stirred and cooled (0°) mixture of phosphorus pentachloride (1870 g.) and phosphorus oxychloride (1 kg.). The ice was allowed to melt, the mixture was stirred for 18 hours, and the clear liquid was distilled at high (20:1) reflux ratio through a column (2.5 × 90 cm.) packed with glass helices. The product (240 g., 45%) was a water-white liquid (lachrymator) boiling at 60–62° (750 mm.). This procedure is considerably more rapid and convenient than the original one of Staudinger.[13]

4,6,7-Trimethylcoumarandione (II).—A solution of the diketone Ia[2] (24 g., 0.068 mole) and iodine (35 g., 0.136 mole) in pyridine (600 cc.) was warmed on the steam-bath for one hour. The yellow solid was removed from the cooled mixture, washed with cold water, then with ether, and added to aqueous ethanol (150 cc., 1:1) containing potassium hydroxide (15 g., 0.27 mole). The mixture was boiled for 12 hours; undissolved material was then removed and the filtrate was acidified. The black, tarry material was taken up in ether (300 cc.) and the ether solution was extracted first with aqueous sodium bicarbonate (5%) and then with aqueous sodium hydroxide (5%). Acidification of the bicarbonate extract produced little or no material; acidification of the hydroxide extract produced a solid, which was removed, crystallized from ethanol, then from a mixture of benzene and petroleum ether (b.p. 60–68°). It was then chromatographed from benzene-petroleum ether onto magnesium sulfate, when it was obtained as tiny yellow needles (3 g., 24%) melting at 145–149°. The analytical sample, crystallized twice from the same solvent pair, and then sublimed at 140° (2–3 mm.), melted at 149–151°. A mixture of this material with a specimen prepared by an independent method (see below) melted at 148–150°.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.30; H, 5.30; neut. equiv., 190. Found: C, 69.63; H, 5.67; neut. equiv., 194, 194.

The compound was stable at its melting point, but evolved gas at 220°. It was unaffected by action of cold, saturated aqueous sulfur dioxide for eight hours. Nor could II (10 g.) be nitrosated when its solution in ethanol (200 cc.) containing hydrochloric acid (100 cc.) was subjected for 24 hours to the action of sodium nitrite (25 g.); unchanged II (9 g.) was recovered.

2,3,5-Trimethylphenyloxyacetic Acid (IV).—A mixture of water (50 cc.), sodium hydroxide (20 g.), 2,3,5-trimethylphenol (13.5 g.) and chloroacetic acid (18.8 g.) was heated at 180° in a bomb for 18 hours, with shaking. The mixture was dissolved in hot water and the solution was acidified. The solid was removed, dissolved in ether (500 cc.) and the ethereal solution was shaken with aqueous sodium carbonate (300 cc.). A white solid separated; this was removed. The ether layer, removed from the filtrate and evaporated, left a residue (5 g.) of 2,3,5-trimethylphenol. The white solid was added to the aqueous layer from the filtrate, the mixture was heated until solution was complete, then acidified and cooled. The white solid (10 g., 78% corrected for recovered phenol) melted at 130–131°, in agreement with the value in the literature.[5]

4,6,7-Trimethylcoumaranone (V). A.—The acid IV (12 g.) was warmed (90°) with sulfuric acid (150 cc.) for 20 minutes, and the clear solution was poured into ice (1 kg.) and water (1 l.). The solid (8 g., 73%) was removed, washed with water, dried and crystallized from a mixture of benzene and petroleum ether (b.p. 60–68°) when it was white and melted at 88–90°.[5]

B.—Aluminum chloride (132 g.) and 2,3,5-trimethylphenol (135 g.) were stirred and heated (140°) in tetrachloroethane (500 cc.) until vigorous evolution of hydrogen chloride ceased (two hours). Chloroacetyl chloride (112 g.) was then added (1.5 hours) to the hot, stirred solution, after which the solution was boiled for four hours and poured into iced hydrochloric acid (2 l., 1:1). The organic layer was removed and distilled with steam (four hours) to remove the solvent, and the residual dark oil (180 g.) was removed and cooled. The solid (V, 70 g.) was removed; the oily filtrate was dissolved in ethanol (500 cc.) and the solution was boiled with sodium acetate (75 g.) for two hours. The mixture was poured into water, the solid was removed and distilled. After a small fore-run of trimethylphenol, the material gave a distillate (56 g.) of a pale yellow oil which solidified on cooling. This material was combined with the solid obtained from the dark oil, and the whole, recrystallized from benzene–petroleum ether, weighed 126 g. (70%) and melted at 86–89° alone or when mixed with V from A above.

2-Oximino-4,6,7-trimethylcoumaran-3-one (VI).—The coumaranone V (7.9 g.) was dissolved in acetic acid (75 cc.), powdered sodium nitrite (10 g.) was added and the mixture was allowed to stand at room temperature for 12 hours with occasional shaking. More nitrite (5 g.) was added, the mixture was shaken thoroughly, and allowed to stand for 12 hours more. The semi-solid mixture was poured into water (500 cc.), the mixture was warmed (80°), and the pale yellow solid was removed and crystallized from acetic acid; it crystallized as a hemi-hydrate. The long yellow needles (7 g., 70%) melted at 253–254° (dec.) and the substance sublimed readily just below the melting point.

Anal. Calcd. for $C_{11}H_{11}O_3N \cdot {}^1/_2H_2O$: C, 61.62; H, 5.59. Found: C, 61.37; H, 5.99.

4,6,7-Trimethylcoumarandione (II). A.—The oximino compound VI (3 g.) was dissolved in boiling acetic acid (50 cc.); hydrochloric acid (35 cc.) was added to faint turbidity, the mixture was cleared by addition of acetic acid (5 cc.) and boiled for five minutes. The cooled solution deposited a solid which was removed and crystallized from a mixture of benzene and petroleum ether (b.p. 60–68°) when it weighed 2 g. (69%) and melted at 146–148°. A mixture of this material with II derived from the diketone Ia melted at 148–150°.

B.—A solution of oxalyl chloride (50 g.) and 2,3,5-trimethylphenol (27 g.) in tetrachloroethane (300 cc.) was refluxed overnight in a dry atmosphere. The cooled solution was washed with water, then with aqueous bicarbonate

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[8] P. Karrer and O. Hoffmann, *Helv. Chim. Acta*, **23**, 1126 (1940).

[9] K. Fries and W. Pfaffendorf, *Ber.*, **45**, 154 (1912).

[10] K. Fries and E. Pusch, *Ann.*, **442**, 272 (1925); K. Fries and K. Saftien, *ibid.*, **442**, 284 (1925).

[11] Microanalyses by R. Amidon, J. Buckley, W. Cummings, W. Hunter, R. Kelly, F. Robinson and H. Turner. All melting points are uncorrected.

[12] E. Bowden, *Org. Syntheses*, **10**, 78 (1930).

[13] H. Staudinger, *Ber.*, **41**, 3558 (1908).

(5%), and the solvent was removed by distillation. The product gave a distillate (30 g., 78%) boiling at 150–160° (3 mm.) which solidified on cooling and then melted at 148–150° alone or when mixed with II prepared as in A above.

5-Nitro-4,6,7-trimethylcoumarandione (VIII).—A cold (0°) solution of sodium nitrate (4.4 g.) in sulfuric acid (60 cc.) was added dropwise and with vigorous stirring to a cold (0°) solution of the coumarandione II (10 g.) in sulfuric acid (60 cc.). The solution was kept at 0° for 30 minutes and then poured over ice. The yellow solid (11 g., 92%, m.p. 165–170°) was removed and crystallized twice from a mixture of ethyl acetate and petroleum ether (b.p., 60–68°) when it melted at 178–178.5°.

Anal. Calcd. for $C_{11}H_9O_5N$: C, 56.17; H, 3.86; N, 5.96. Found: C, 56.31; H, 3.63; N, 6.17.

The nitro compound was stable at the melting point, but evolved gas at 210–220°. It was soluble in hot bicarbonate (5%) and in cold alkali (5%), but insoluble in cold bicarbonate. When the alkaline solutions were acidified, VIII was recovered unchanged.

4,6,7-Trimethylcoumaran-2-one (VII).—The coumarandione II (9.5 g.) was refluxed for 14 hours with amalgamated zinc (25 g.) and aqueous hydrochloric acid (200 cc., 1:1). The solid (2 g.) which sublimed into the condenser was removed and crystallized from petroleum ether (b.p., 60–68°) when it melted at 121–123°. This substance VII was not soluble in aqueous alkali (5%) even on warming, but it dissolved in boiling alkali. Acidification of the cooled solution regenerated unchanged VII.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.87. Found: C, 75.21; H, 7.22.

The non-volatile solid remaining in the flask was removed and dissolved in acetone. The solution was filtered to remove the zinc and the filtrate was evaporated. The residue (6 g.) was insoluble in ether, alcohol, benzene or dioxane. After several crystallizations from hot ethyl acetate, a product melting at 255° was isolated. This was insoluble in warm alkali, but dissolved when the suspension was boiled. The compound was not investigated further.

5-Hydroxy-4,6,7-trimethylcoumarandione (III). A.—A cold solution of diazotized sulfanilic acid (10.5 g.) was poured, with stirring, into a solution of the coumarandione II (9.5 g.) in water (100 cc.) containing potassium hydroxide (17 g.). The deep red solution was allowed to stand overnight at room temperature and was acidified with hydrochloric acid. The orange solid was not removed; stannous chloride (22.5 g.) and hydrochloric acid (20 cc.) were added, and the mixture was boiled gently until the solid dissolved (30 minutes). The solution was divided into two equal parts: to one part, ferric chloride (45 g.) was added and the mixture was distilled with steam. The distillate contained trimethylquinone (2 g.); the residue was a red tar from which no crystalline material could be isolated. To the other half of the solution ferric chloride (45 g.) was added and the mixture was allowed to stand at room temperature for two hours. It was then extracted with three 250-cc. portions of a mixture of benzene and ether (1:1), the persistent emulsion was broken by repeated filtration through Hi-Flo, the organic layer was removed, dried (sodium sulfate) and the solvent was removed by distillation under reduced pressure (100 mm.). The residue, when cooled, deposited a solid (2 g.) which, crystallized from a mixture of cyclohexane and ethyl acetate, formed scarlet needles melting at 188–190°.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.24; H, 5.02.

B.—Trimethylhydroquinone (15 g.) and oxalyl chloride (38 g.) were dissolved in tetrachloroethane (150 cc.) and the solution was refluxed for 12 hours in a dry atmosphere. The solvent was removed by steam distillation; the red solid (12 g.) was removed from the cooled residue and boiled with aqueous sodium bicarbonate (5%, 300 cc.) and the insoluble trimethylhydroquinone (4 g.) was removed. The filtrate was acidified and the orange solid (2.5 g.) was removed. Concentration of the mother liquor yielded an additional 1 g. of product. The combined solids were recrystallized from hot water, yielding III melting at 188–190° alone or when mixed with the product from A above.

Substance III was unaffected by action of boiling ethanol, with or without inclusion of sulfuric acid. Likewise, cold aqueous or ethanolic ferric chloride had no effect upon III, nor was there any oxidation or any other change when a chloroform solution of III was shaken with aqueous ferric chloride. When III in ethanol was boiled for 30 minutes with ferric chloride, nothing could be recovered from the solution. Action of sodium dichromate in dilute sulfuric acid upon III at 50° for 30 minutes produced no change, but when the solution was boiled, III was completely destroyed.

Hexamethyloxindigo (XII).—The diketone Ib (2.05 g.) was boiled for 2.5 hours with pyridine (75 cc.) containing iodine (2.5 g.) and the mixture was cooled to 40°. The solid (1.1 g.) was removed and boiled with pyridine (50 cc.) and the insoluble solid was removed by filtration of the hot mixture. The filtrate, on cooling, deposited unchanged Ib (0.4 g., m.p. and mixed m.p. 243–247°). The orange solid insoluble in hot pyridine was recrystallized from boiling nitrobenzene (100 cc.) when it formed tiny orange plates melting at 305–306° (dec.). The substance was insoluble in aqueous alkali (5%) and in Claisen alkali. It (0.5 g.) was insoluble in boiling pyridine (250 cc.) or in boiling acetic acid (800 cc.), or in any other organic solvent except nitrobenzene.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.57; H, 6.17.

MINNEAPOLIS 14, MINNESOTA RECEIVED MARCH 15, 1951

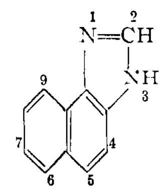
[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Synthesis of Some Substituted Naphth[1,2]imidazole Derivatives

BY JOHN A. STEPHENS[1] AND CLIFF S. HAMILTON

The chemistry of certain naphth[1,2]imidazole derivatives which bear a substituent on the naphthalene nucleus has been investigated. Several new compounds of this class and various intermediates have been prepared and are reported along with some of their properties.

The present investigation was undertaken to study the chemistry of some naphth[1,2]imidazoles which bear a substituent on the naphthalene nucleus. The syntheses of a number of compounds based upon the naphth[1,2]imidazole nucleus (I) and some of their properties are reported.



I

Several new intermediates were prepared during the course of this work. Two of these, 1,5-diamino-2-acetamidonaphthalene and 1,6-diamino-2-acetamidonaphthalene, were found to possess an unexpected degree of stability since neither exhibited any evidence of deterioration upon exposure to the air.

Several methods for the preparation of naphth[1,2]imidazoles are extant and require suitable

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[1] Parke, Davis and Company Fellow.