the residual yellow, mobile oil was dissolved in 10 ml. of anhydrous ether and added slowly, with shaking, to an ice-cold solution of 2.4 g. (100% excess) of isobutylamine in 40 ml. of anhydrous ether. After the mixture had stood at room temperature for one hour, the precipitated amine hydrochloride was dissolved by the addition of cold dilute hydrochloric acid, and the ether layer was washed with water, 10% potassium hydroxide solution, and water, then dried and evaporated to dryness. The white solid remaining was recrystallized twice from petroleum ether (b.p. 60–70°) to give 1.0 g. (50%) of colorless needles, m.p. 91.5–92.5°, λ_{max} 228.5 mμ in 95% ethanol (ϵ 37,150).

Anal. Calcd. for $C_{14}H_{23}NO$: C, 76.08; H, 10.49; N, 6.32. Found: C, 76.20; H, 10.41; N, 6.25.

The mixed melting point with a sample of all-*trans*-affinin prepared by elaidinization of natural affinin[1] was 91.5–92.0°.

The maleic anhydride adduct crystallized from benzene as colorless needles, m.p. and mixed m.p. with the previously reported adduct[1] 175°.

BELTSVILLE, MARYLAND

[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY]

The Alkaline Oxidation of 2-Naphthol

BY GOSTA BRUNNSTROM

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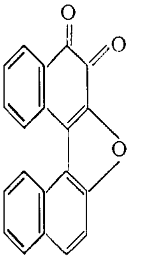
In studies of the action of air on 2-naphthol in the presence of sodium hydroxide, a new compound was isolated and identified as dinaphtho[2,1,1′,2′]furan-5,6-dione. Other products identified were 1,1′-bi-2-naphthol, 4-(2-carboxyphenyl)-5,6-benzocoumarin and dinaphtho[2,1,2′,3′]furan-8,13-dione.

The oxidation of 2-naphthol has been the subject of a number of investigations. Generally, mild oxidizing agents lead to the formation of such compounds as binaphthols and binaphthylene oxides, etc.[1–3] Stronger oxidizing agents usually disrupt the naphthalene ring, with the formation of acids, such as carboxyphenylglycolic acid, phthalonic acid, carboxycinnamic acid, etc.[4–8] Recently, Raacke-Fels, *et al.*,[8] using hydrogen peroxide and a small amount of ammonium molybdate under acid conditions, obtained from 2-naphthol a red substance, which was later identified by Bader[9] as 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone. This seems to be the only case of the actual isolation of a quinone from the oxidation of 2-naphthol, although unidentifiable materials sometimes have been obtained.

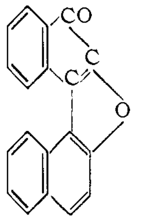
This investigation was undertaken to study the oxidation of 2-naphthol in the presence of sodium hydroxide. On exposure to air, solutions of 2-naphthol in aqueous sodium hydroxide darken on standing. Also, small amounts of sodium hydroxide will cause 2-naphthol to turn almost black in air, particularly at elevated temperatures. To obtain relatively large amounts of the substances causing the discoloration, more extreme conditions were used. Mixtures of powdered 2-naphthol and powdered sodium hydroxide were heated at about 70° for about a week. Under these conditions, 40–60% of the 2-naphthol was converted into various reaction products. The presence of quinones was indicated by color test when the reaction product of 2-naphthol, sodium hydroxide and air was extracted with benzene. The yellow color of the extract changed to violet-red upon the addition of more 2-naphthol and shaking with ammonium hydroxide. Under similar conditions, 1,4-naphthoquinone gives a yellow color and 1,2-naphthoquinone gives a reddish color. The compound responsible for the violet color was isolated and purified.

Physical and chemical properties and the empirical formula $C_{20}H_{10}O_3$ indicated the compound to have structure I, dinaphtho[2,1,1′,2′]furan-5,6-dione.

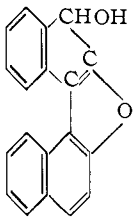
Evidence for I being a 1,1′-binaphthyl derivative was obtained by: (a) zinc dust distillation to naphthalene and dinaphtho-[2,1,1′,2′]-furan, (b) oxidation to *o,o′*-oxalyldibenzoic acid (II) and (c) potassium hydroxide fusion to 2-naphthol, phthalic acid, oxalic acid and an acid III identified as α-[2-hydroxy-1-naphthyl]-*o*-toluic acid.[10] Compound III, obtained by degradation, as well as a sample prepared by the procedure of Fieser,[10] both had a melting point and a mixed melting point of 175°. Fieser reports 187°. The infrared spectrum, degradative oxidation product and ring closure to 1-hydroxy-7-pleiadone (IV), left little doubt as to its structure.



I



V



VI

The presence of a 1,2-quinoid group was indicated when a quantitative yield of the corresponding azine was obtained on reaction of I with *o*-phenylenediamine. No methylation resulted on treatment with dimethyl sulfate. The absence of hydroxyl groups was also confirmed by examination of the infrared absorption spectrum of I. Reduc-

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(1) V. Merz and W. Weith, *Ber.*, **14**, 187, 195 (1881).

(2) G. R. Clemo and R. Spence, *J. Chem. Soc.*, 2811 (1928).

(3) R. Pummerer and G. Cherbuliez, *Ber.*, **52**, 1414 (1919).

(4) E. Ehrlich and R. Benedikt, *Monatsh.*, **9**, 927 (1888).

(5) E. Ehrlich, *ibid.*, **10**, 115 (1889).

(6) O. Dischendorfer and W. Danziger, *ibid.*, **48**, 315 (1927).

(7) J. Böeseken and L. von Königsfeldt, *Rec. trav. chim.*, **54**, 313 (1935).

(8) I. D. Raacke-Fels, C. H. Wang, R. K. Robins and B. E. Christensen, *J. Org. Chem.*, **15**, 627 (1950).

(9) A. Bader, THIS JOURNAL, **73**, 3731 (1951).

(10) L. Fieser, *ibid.*, **53**, 3557 (1931).

tive acetylation of I gave the corresponding diacetyl derivative. The location of the 1,2-quinoid group in position shown is indicated also by the degradation studies described above. The low order of reactivity of the remaining oxygen function indicated it was probably involved in an ether linkage.

Compounds previously described in the literature and also isolated in this study were 4-(carboxyphenyl)-5,6-benzocoumarin,[5,6,8,9] dinaphtho-[2,1,2',3']furan-8,13-dione[2] and 1,1'-bi-2-naphthol.

Other products, whose structures were neither proven or known, were isolated. In two cases, there were sufficient analytical data and information from reaction behavior to warrant suggesting the structures V, 8-indeno-[2,1]-naphtho-[1,2]-furan-8-one, and VI, 8-indeno[2,1]-naphtho-[1,2]-furan-8-ol.

Although the yield of oxidation products varied somewhat with the reaction conditions, the approximate yields (not counting unreacted 2-naphthol) from 2-naphthol of pure products isolated are given in the Experimental part.

Experimental

Isolation of the Reaction Products.—2-Naphthol (99.9% pure), 720 g. (5.0 moles), was finely ground and mixed well with 100 g. (2.5 moles) of sodium hydroxide. The mixture was spread out on an enamel tray, put in an oven and held at 60–70°. At first, the mass slowly melted. It was cooled and reground. The process was repeated once every day for about a week, until the mass no longer melted and had become almost black. After a final grinding, the mixture was stirred with a solution of 100 g. of sodium hydroxide in 3 liters of water for two hours. The greenish-black insoluble salt of I was filtered and washed with 1 liter of 95% alcohol and then with 1 liter of benzene. The filtrate and washes were combined. I was liberated by slurrying the salt in alcohol and acidifying with hydrochloric acid. I was washed with alcohol and hot water and purified by boiling with about 400 ml. of alcohol. The yield of crude I was 75 g. (10% yield). It formed brown needles from toluene, m.p. 253–254°. I dissolves in concd. sulfuric acid with a deep blue color.

Anal. Calcd. for $C_{20}H_{10}O_3$: C, 80.5; H, 3.4. Found: C, 80.5; H, 3.4.

The combined filtrate and washes from the salt of I were diluted with 3 liters of water and stirred for about an hour. The benzene phase (A) was separated and washed with 500 ml. of water. The aqueous phase and wash water were combined (B). (A) was stirred with 25 ml. of 70% sulfuric acid. A dark precipitate formed in the sulfuric acid layer. The acid plus solid were separated and washed with 250 ml. of benzene. The process was repeated until (A) gave no precipitate with 70% sulfuric acid. Acid-washed (A) was combined with the benzene washings and saved. To the combined acid–solid layers was added a rather large amount of water and 100 ml. of benzene. The acid layer was separated and discarded. After adding excess 5% sodium hydroxide solution and stirring, the solid phase disappeared. The benzene solution was separated, washed with sodium chloride solution, dried with sodium sulfate and evaporated. The residue was dissolved in toluene and the solution allowed to evaporate in a loosely covered beaker. After some time, crystals deposited. These were purified by washing with 1:1 hexane–benzene and crystallized from toluene. There was about 1 g. of product V which formed white leaflets; m.p. 291–292°; ultraviolet spectrum, $\lambda_{max.}$ 237.5, 317 and 331 mμ.

Anal. Calcd. for $C_{19}H_{10}O_2$: C, 84.4; H, 3.7. Found: C, 84.4; H, 3.7.

From the partially evaporated mother liquor of V a product VI was obtained by further evaporation. Crystallization from alcohol yielded less than 1 g. of white needles; m.p. 237–239°; ultraviolet spectrum, $\lambda_{max.}$ 321, 324 and 372.5 mμ.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.5. Found: C, 83.6; H, 4.5.

Fusion of V with potassium hydroxide gave benzoic acid, 2-naphthol and a small amount of III (m.p.'s and mixed m.p.'s). V dissolved in alcoholic sodium hydroxide on warming to give a deep green solution. Solution in concentrated sulfuric acid, V yellow red, green fluorescence, VI erosin red. V and VI seemed to be structurally similar; on reduction with sodium amalgam in alcoholic acetic acid, V is converted into VI, and conversely VI is converted into V by oxidation with chromic acid in acetic acid.

Acid-washed (A) was washed with 50 ml. of 20% sodium hydroxide and sodium chloride solution, dried with sodium sulfate and evaporated. The residue was dissolved in toluene and the solution allowed to evaporate in a loosely covered beaker. The crystals which deposited were purified by washing with 1:1 hexane–benzene solution and recrystallized from toluene. There was about 3 g. of a product VII, forming white needles, m.p. 319–321°. *Anal.* C, 84.4; H, 5.0. The infrared absorption spectrum indicated the presence of a hydroxyl group and a possible ether linkage. No structure is suggested for VII. The solution in concentrated sulfuric acid is yellow. By further evaporation of the mother liquor of VII about 3 g. of a product VIII was obtained; bronze leaflets from toluene, m.p. 272–273°. The infrared absorption spectrum indicated the presence of carbonyl and ether linkages. The solution in benzene is yellow with a greenish fluorescence and in concd. sulfuric acid blue. The molecular weight (determined by the lowering of the freezing point of dimethylaniline) was 300. VIII seems to be identical with a quinone, dinaphtho-[2,1,2',3']furan-8,13-dione described by Clemo and Spence[2] (m.p. 268°).

Anal. Calcd. for $C_{20}H_{10}O_3$: mol. wt. 298.1; C, 80.5; H, 3.4. Found: C, 80.3; H, 2.9.

VIII was converted to the *o*-quinone, dinaphtho[1,2,-1',2']furan-12,13-dione, by their method. Its m.p. 256–257° agreed with that (256°) found by them. It is isomeric with I. A mixed m.p. with I gave a depression of about 40°.

(B) was neutralized with sodium bicarbonate. The precipitated organics were extracted at 30–40° with 1.5 liters of benzene. The benzene solution was washed with 500 ml. of 5% sodium chloride. The wash and carbonate solution were combined (C). The benzene solution was allowed to evaporate in a loosely covered beaker. After several weeks the crystals which had formed were filtered and washed with a little benzene. There was 150 g. (20% yield) of a product IX, m.p. 218°. IX was identified as 1,1'-bi-2-naphthol by mixed m.p. with an authentic sample.

(C) was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was dried and evaporated. A solution of the residue in toluene was allowed to evaporate in a loosely covered beaker. In about two weeks, the crystals were filtered off, washed with toluene and crystallized from acetic acid. There was 30 g. (4% yield) of a product X, m.p. 277–278°. Solubility of X in sodium bicarbonate indicated a carboxylic acid. Oxidation with permanganate gave II (m.p. and mixed m.p. on authentic sample).[11] Potassium hydroxide fusion gave benzoic acid, phthalic acid, 2-naphthol, III (m.p.'s and mixed m.p.'s) and a product having a m.p. of 160–161°. *Anal.* C, 82.9; H, 4.4, indicates the formula $C_{18}H_{12}O_2$. It was not further identified. The infrared absorption spectrum of X indicated the presence of a carboxyl group, one other different carbonyl group and no hydroxyl group. The properties and analysis of X identify it as 4-(2-carboxyphenyl)-5,6-benzocoumarin (lit. m.p. 279°).[9] A mixed m.p. with an authentic sample[6] gave no depression.

Anal. Calcd. for $C_{20}H_{12}O_4$: neut. equiv., 316; C, 75.9; H, 3.8. Found: neut. equiv., 320; C, 75.2; H, 3.7.

The toluene mother liquor from X (combined with the toluene wash) was extracted with 100-ml. portions of saturated sodium bicarbonate solution. The combined bicarbonate extracts were neutralized with sodium hydroxide, diluted to about 800 ml. and the solution saturated with sodium chloride. After some time a precipitate formed which was filtered off and washed with saturated brine. The precipitate, a salt of a carboxylic acid, was treated with hydrochloric acid to liberate the compound XI. This was

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(11) C. Graebe and P. Juillard, *Ann.*, **242**, 221 (1887).

recovered by ether extraction and crystallized from toluene. There was 25 g. (3% yield). It formed compact crystals, m.p. 240–241°. The infrared absorption spectrum indicated the presence of hydroxyl, carboxyl and carbonyl groups; ultraviolet spectrum, $\lambda_{max.}$ 293, 305, 322 and 336 mμ. Oxidation of XI with permanganate gave phthalic acid and II and potassium hydroxide fusion gave III (m.p.'s and mixed m.p.'s). A solution of XI in concentrated sulfuric acid utrned green on heating. XI esterified easily to the methyl ester, m.p. 163°, apparently with the simultaneous formation of a lactone ring. No hydroxyl appears in the 3 μ region of the infrared spectrum, while two bands occur at 5.79 and 5.85 μ, indicative of two carbonyl functions.

Anal. Calcd. for $C_{22}H_{18}O_6$: neut. equiv., 378.4; C, 69.8; H, 4.8. Found: neut. equiv., 380; C, 70.2; H, 4.9.

Methyl ester: *Anal.* Calcd. for $C_{23}H_{18}O_5$: C, 73.8; H, 4.9. Found: C, 73.3; H, 4.7.

The sodium carbonate–sodium chloride filtrate from XI was acidified with hydrochloric acid and extracted with ether. The ether was separated, dried and evaporated. The residue, containing mono- and dibasic acids, was esterified by reaction at room temperature with twice its volume of 5% methanolic hydrochloric acid for 24 hours. Dilution with water precipitated the esters which were extracted with benzene along with unesterified acids. Recovery of the latter from the benzene was made by washing with 5% sodium carbonate solution. The corresponding acids were recovered by evaporation of the benzene solution of the esters, saponification, acidification and ether extraction. After evaporation of the ether, the residue was dissolved in toluene and the solution allowed to evaporate as in the isolation of X. Acidification, ether extraction, etc., of the carbonate wash was similarly performed. In this manner, further quantities of X and XI were obtained as first fractions from the toluene evaporations. From the toluene mother liquor of the esterifiable acids a small amount of an acid XII was isolated. XII crystallized from toluene in white needles, m.p. 240–250°. *Anal.* C, 70.0; H, 4.1, indicates the formula $C_{22}H_{16}O_6$. Similarly, from the toluene mother liquor of the unesterified acids, small amounts of two additional acids XIII and XIV were obtained. XIII crystallized from toluene in white needles, m.p. 213–214°. *Anal.* C, 62.5; H, 4.0, indicates the formula $C_{20}H_{16}O_8$. XIV crystallized from toluene in white needles, m.p. 259–262°. *Anal.* C, 72.0; H, 3.9, indicates the formula $C_{20}H_{14}O_5$. Further identification of XII, XIII and XIV was not attempted.

Experiments with the Quinone (I). (a) Ammonia Test.—2-Naphthol (2 g.) and a trace of quinone was transferred to a 1″ test-tube. Fifteen ml. of benzene and 3 ml. of 10% ammonium hydroxide were then added. The mixture was shaken until all the 2-naphthol was dissolved. In about five minutes a violet-red color developed in the benzene layer, which had its greatest intensity after one hour.

(b) **Reaction with *o*-Phenylenediamine.**—Hot, nearly saturated solutions of I and *o*-phenylenediamine in equivalent amounts in acetic acid were mixed. The condensation product started to crystallize out in a very short time and the reaction was completed after a few minutes heating. Crystallization from acetic acid afforded the azine derivative, m.p. 261–262°. The yield was almost quantitative.

Anal. Calcd. for $C_{26}H_{14}N_2O$: C, 84.3; H, 3.8; N, 7.6. Found: C, 83.9; H, 3.7; N, 7.9.

(c) **Reductive Acetylation.**—I (2.0 g.) was boiled under reflux with 25 ml. of acetic anhydride, 5 g. of sodium acetate and 5 g. of zinc dust. After three hours 10 ml. of water was added slowly through the condenser. When cool, the acetyl compound was collected and recrystallized from acetic acid; yield about 1 g., m.p. 181–182°.

Anal. Calcd. for $C_{24}H_{16}O_5$: C, 75.0; H, 4.2. Found: C, 75.1; H, 4.0.

(d) **Zinc Dust Distillation.**—Two grams of I was mixed with about 30 g. of zinc dust and heated in the usual manner. About 0.2 g. of distillate was recovered by ether extraction. The naphthalene (0.1 g.) was sublimed off. The residue was extracted with hexane which took up most of the dinaphthofuran. Crystallization from toluene–hexane gave a material which melted broadly between 135–140°. Mixed m.p. with an authentic sample of dinaphtho[2,1,1′,2′]-furan gave no depression.

Anal. Calcd. for $C_{20}H_{12}O$: C, 89.5; H, 4.5. Found: C, 89.4; H, 4.5.

(e) **Fusion with Potassium Hydroxide.**—Forty grams of potassium hydroxide and 2 ml. of water were melted in a 200-ml. iron crucible. Ten grams of I was then added in small portions while stirring continuously with a copper wire. The powdery quinone turned almost at once into a semi-solid lump. When the mass became homogeneous, the heating was continued for about three to four minutes. The melt was dissolved in about 400 ml. of water, the solution was filtered with nuchar, acidified with hydrochloric acid, cooled and extracted with ether. To the acid liquor was added about 3 g. of calcium chloride. On alkalizing with ammonia a precipitate was obtained which was identified as calcium oxalate. The ether layer was washed with water then shaken with 200 ml. of saturated sodium bicarbonate solution for one-half hour. The salt of III gradually came out. It was filtered off and the ether and bicarbonate solution separated. On slurrying the salt in water, acidifying and extracting with ether, III was obtained in nearly pure form. It was obtained from dilute alcohol in white needles; m.p. 174–175°. Yield was about 3 g.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1. Found: C, 77.6, H, 4.9.

The bicarbonate solution from above was acidified and extracted with ether. The ether was washed with water, dried with sodium sulfate, treated with some nuchar, filtered and evaporated. The residue was dissolved in an equal volume of toluene, covered and left standing. The crystals formed were filtered off, washed with a little benzene (about 2.5 g. yield) and crystallized from dilute alcohol. The material was identified as phthalic acid through its anhydride (m.p. and mixed m.p.)

The ether layer, separated from the bicarbonate solution, sometimes had a reddish violet color, which appeared due to a quinone, formed apparently by oxidation in the air of some hydroxyl compound from the fusion. It was obtained in one experiment by filtering the solution of a fusion melt after neutralization with carbon dioxide, acidifying the filtered-off material and dissolving in ether. The ether solution was then washed with an exact amount of normal sodium hydroxide, in which the material dissolved with a greenish-blue color, and then neutralizing with sodium bicarbonate solution. After again extracting with ether, washing with sodium chloride solution, drying and evaporating the ether, a residue was obtained, which when crystallized from toluene formed violet-brown needles, m.p. 206–208°, dissolved in concentrated sulfuric acid with blue color and in sodium hydroxide with similar blue color. *Anal.* C, 77.5; H, 5.0. The exact conditions of formation and its characteristics were not further investigated.

The ether solution from the bicarbonate wash was washed with 50 ml. of 4% sodium hydroxide and the extract acidified and extracted with ether. The residue obtained on evaporation of the ether was heated in an oven at about 110–120° to sublime off 2-naphthol. The residue was dissolved in toluene and the solution left standing loosely covered. Crystals (about 1–2 g.) were obtained which formed needles from toluene, m.p. 244°. *Anal.* C, 78.9; H, 3.2. Its solution in concentrated sulfuric acid turned green on heating. The material was not further investigated.

Potassium Hydroxide Fusion of XI.—Performed similar to above. There was obtained a 60–70% yield of acid III.

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