[CONTRIBUTION FROM THE ORGANIC CHEMICALS DEPARTMENT, JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND COMPANY]

Structure and Properties of Dinaphthofurandiones

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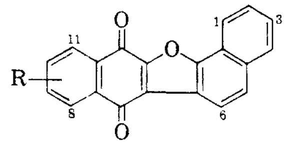
Mixtures of about equal amounts of 9-nitro- and 12-nitrodinaphtho[2,1-2',3']furan-8,13-dione (III and IV) are formed in the condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 2-naphthol in pyridine. Under the same conditions 1-naphthol gives 8-nitro- and 11-nitrodinaphtho[1,2-2',3']furan-7,12-dione (X and IX), with the latter in slightly larger amount.

Methods for the separation of these nitro isomers and for the determination of their structures are given. The physical properties of several derivatives of these nitrodinaphthofurandiones are discussed. The amino and benzamido dinaphthofurandiones are interesting dyes for natural and synthetic fibers.

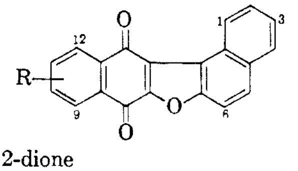
As established by Buu-Hoï[1] and by Suryanarayana [2] the condensation of 2,3-dichloro-1,4-naphthoquinone with 1- and 2-naphthol gives the dinaphthofurandiones of structures I and II, respectively. No work has been reported, however, concerning the structures of the dinaphthofurandiones obtained in these condensations when substituents are present in the benzenoid ring of 2,3-dichloro-1,4-naphthoquinone.

This paper demonstrates that the condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 2-naphthol in pyridine gives a mixture of 9-nitro (III) and 12-nitrodinaphtho [2,1-2', 3']furan-8,13-dione (IV), in approximately equal amounts.



Dinaphtho[1,2-2',3']furan-7,12-dione

I. R = H
IX. R = 11-NO_2
X. R = 8-NO_2
XI. R = 11-NH_2
XII. R = 8-NH_2

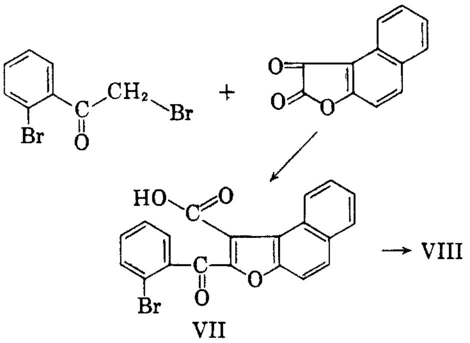


Dinaphtho[2,1-2',3']furan-8,13-dione

II. R = H
III. R = 9-NO_2
IV. R = 12-NO_2
V. R = 9-NH_2
VI. R = 12-NH_2
VIII. R = 9-Br

The two nitro isomers were separated by means of their different solubilities in concentrated sulfuric acid. Orientation of the 9-nitroisomer (III) was established by reducing the nitro group to the amino and replacing the latter by a bromine atom. Comparison of this bromo derivative with an authentic specimen of 9-bromodinaphtho [2,1-2',3']-furan-8,13-dione (VIII) confirmed its identity. This structure proof of III is obviously also an indirect proof for the structure of IV, since the latter can have only the alternative structure.

Authentic 9-bromodinaphtho [2,1-2',3']furan-8,13-dione (VIII) was synthesized from *o*-bromophenacyl bromide and naphtho[2,1-b]furan-1,2-dione, according to the following route:



VII

This route is similar to that developed by Chatterjea[3] for the preparation of 7-methylbenzo [*b*]naphtho[2,3-*d*]furan-6,11-dione. The last step of this route, the ring closure, was carried out by treating the carbonyl chloride derived from VII with aluminum chloride in nitrobenzene at room temperature. Under these conditions a 35% yield of the cyclized product (VIII) was obtained and 63% of the acid (VII) was recovered unchanged.

The physical properties of the two nitro isomers and their derivatives are summarized in Table I. The 9-nitro isomer (III) has a higher melting point than the 12-nitro (IV) and the 9-amino isomer (V) has a lower melting point than the 12-amino (VI). These results are in line with those observed in the 5- and 8-substituted thiophanthraquinones[4] and in the 2- and 3-substituted dibenzofurans.[5,6] The visible spectra of the 9- and 12-nitro isomers are identical. In comparison with these nitro isomers, the visible absorption maximum of the 9-amino isomer shows a bathochromic shift (Δ λ of 32 mμ), whereas the absorption maximum of the 12-amino isomer shows a hypsochromic shift (Δ λ of 22 mμ). The infrared spectra of the

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[1] Ng, Ph. Buu-Hoï and P. Demerseman, *J. Chem. Soc.*, 4699 (1952).

[2] B. Suryanarayana and B. D. Tilak, *Proc. Indian Acad. Sci.*, **37-A**, 81 (1953).

[3] J. N. Chatterjea, *J. Indian Chem. Soc.*, **32**, 265 (1955).

[4] H. E. Schroeder and V. Weinmayr, *J. Am. Chem. Soc.*, **74**, 4357 (1952).

[5] W. Borsche and W. Bothe, *Ber.*, **41**, 1940 (1908).

[6] H. Gilman, G. E. Brown, W. G. Bywater, and W. H. Kirkpatrick, *J. Am. Chem. Soc*, **56**, 2473 (1934).

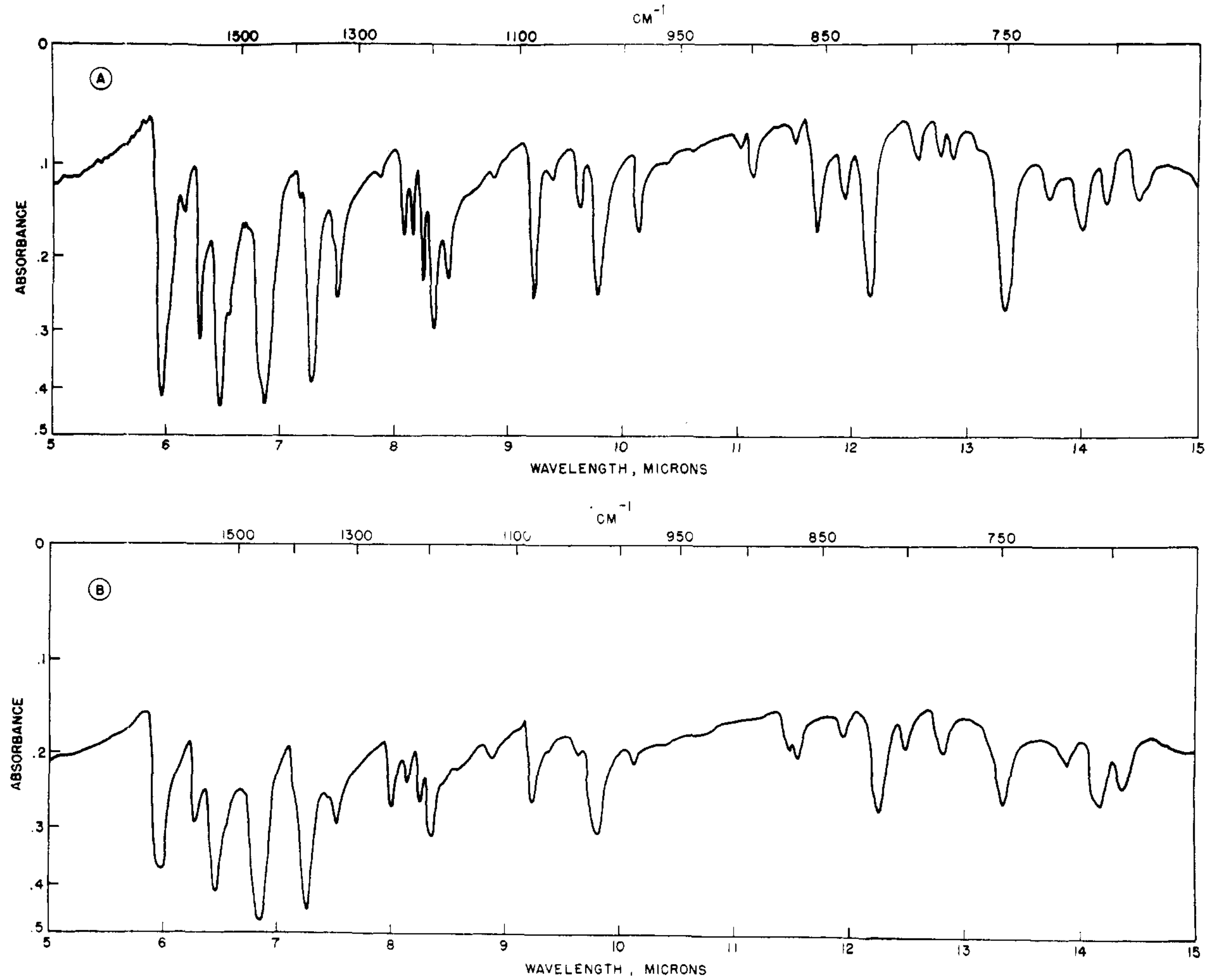

Fig. 1. Infrared spectra of the nitrodinaphtho[2,1-1′,2′]furan-8,13-diones
A: 9-Nitro isomer (III)
B: 12-Nitro isomer (IV)

nitro isomers are similar up to about 8 μ, both isomers exhibiting the characteristic bands of carbon-carbon double bonds, of the carbonyl and of the nitro groups (Fig. 1). A good region for differentiation is 8–15 μ, where the individual isomers present the following bands: isomer III at 11.15, 11.65, 12.15, 13.70 and 14.50 μ and isomer IV at 8.0, 12.25 and 14.35 μ.

The condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 1-naphthol gives a mixture of 11-nitro- (IX) and 8-nitrodinaphtho[1,2-2′,3′]furan-7,12-dione (X), with the former in slightly larger amount. In this case also the two isomers were separated by means of their different solubilities in concentrated sulfuric acid.

Attempts to prepare these isomers by an unambiguous route failed. However, the comparison of the properties of the 9-nitro (III) and 12-nitrodinaphtho[2,1-2′,3′]furan-8,13-dione (IV) and their derivatives with the properties of IX and X and their derivatives, respectively, indicate that IX should be the 11-nitro- and X the 8-nitrodinaphtho-[1,2-2′,3′]furan-7,12-dione (see Table I).

The dinaphthofurandiones described here are highly colored compounds. The amino and the benzamido derivatives were found useful as dyes for natural and synthetic fibers. These derivatives show, in comparison with the anthraquinone analogs, higher molar extinction coefficients and, in the case of the 9- and 11-amino isomers, a strong bathochromic shift of the absorption maxima (see Table I).

EXPERIMENTAL[7]

Condensation of 2-naphthol with 2,3-dichloro-5-nitro-1,4-naphthoquinone. 9- and 12-Nitrodinaphtho[2,1-2′,3′]furan-8,13-dione (III *and* IV). 2,3-Dichloro-5-nitro-1,4-naphthoquinone of m.p. 174° (13.5 g.), prepared by the method of Fries,[8] was added to a solution of 2-naphthol (8.0 g.) in

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[7] All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. The visible spectra were obtained in o-dichlorobenzene and recorded on a Cary Model 14 Spectrophotometer. The infrared spectra were taken in Nujol mulls on a Perkin-Elmer Model 21 Recording Spectrophotometer equipped with sodium chloride optics.

[8] K. Fries, W. Pense, and O. Peeters, *Ber.*, 61, 1395 (1928).

TABLE I

PHYSICAL PROPERTIES OF ANTHRAQUINONE AND DINAPHTHOFURANDIONE DERIVATIVES

Derivatives	M.P., °C.	Absorption Maxima[a] λ, mμ	$\epsilon^b \times 10^{-3}$
Anthraquinone			
1-Amino	245	462	6.0
1-Benzamido	246	418	6.2
Dinaphthofuran-8,13-dione			
9-Nitro (III)	342	468	5.8
12-Nitro (IV)	314	468	5.8
9-Amino (V)	298	500	9.8
12-Amino (VI)	338	446	9.2
9-Benzamido	342	480	15.0
12-Benzamido	300	450	10.0
Dinaphthofuran-7,12-dione			
11-Nitro (IX)	344	452	5.3
8-Nitro (X)	322	452	5.3
11-Amino (XI)	302	496	8.2
8-Amino (XII)	362	440	7.5
11-Benzamido	292	470	13.0
8-Benzamido	310	450	9.6

[a] Solvent: *o*-dichlorobenzene. [b] Molar Extinction Coefficient, ε, defined as $\frac{\text{Optical Density}}{\text{C l}}$, where C is concentration g. mol./liter and l is cell length in cm.

pyridine (150 ml.). A dark brown suspension was formed and the temperature rose to 50°C. The mixture was then heated to 100–110°C. in about 1 hr. and kept at this temperature for an additional three hr. After stirring for twelve hr. at room temperature, the orange precipitate was collected, washed with ethanol, and dried. The crude product (13.5 g.) was repeatedly extracted with boiling water to remove the nitropyridinium compound.[2,9] The residue (11.0 g.), m.p. 284–286°, was a mixture of III and IV. Microscopic examination showed the presence of yellow and orange crystals.

Anal. Calcd. for $C_{20}H_9NO_5$: C, 70.0; H, 2.6; N, 4.1. Found: C, 70.1; H, 2.7; N, 4.0.

The aqueous extract by concentration gave the nitropyridinium compound as yellow crystals (2.5 g.) of m.p. 302–304°.

Anal. Calcd. for $C_{15}H_7N_2O_5$: C, 61.0; H, 2.7; N, 9.5. Found: C, 60.6; H, 2.7; N, 9.4.

The above mixture of nitro isomers III and IV (5 g.) was stirred at 15–18° for 1 hr. with concentrated sulfuric acid (200 ml.). A deep blue slurry was obtained. The insoluble material was collected, washed first with concentrated sulfuric acid and then with ice water, dried and crystallized from *o*-dichlorobenzene to yield 2.3 g. of III as long. yellow needles; m.p. 342–344°.

Anal. Calcd. for $C_{20}H_9NO_5$: C, 70.0; H, 2.6; N, 4.1. Found: C, 70.0; H, 2.7; N, 4.0.

The sulfuric acid filtrate was drowned slowly on ice to give 2.5 g. of IV as orange precipitate of m.p. 310°, which after crystallization from *o*-dichlorobenzene yielded short orange-red needles; m.p. 314–316°.

Anal. Calcd. for $C_{20}H_9NO_5$: C, 70.0; H, 2.6; N, 4.1. Found: C, 70.0; H, 2.6; N, 4.0.

9-Aminodinaphtho[2,1-2′,3′]furan-8,13-dione (V). 9-Nitrodinaphtho[2,1-2′,3′]furan-8,13-dione (III) (2.0 g.) was added to a stirred solution of sodium hydrosulfite (10 g.) and sodium hydroxide (10 g.) in water (400 ml.). After 15 minutes at 35° the slurry changed to a clear orange solution. The agitation was continued at 35–40° for 1 hr., then the solution was filtered and the filtrate oxidized with air for 2 hr. The dark violet precipitate (1.7 g.), m.p. 296–298°, crystallized from nitrobenzene, yielded V as violet feathery needles; m.p. 298–300°.

Anal. Calcd. for $C_{20}H_{11}NO_3$: C, 76.6; H, 3.5; N, 4.4. Found: C, 76.6; H, 3.5; N, 4.4.

The benzamide of V was obtained by heating V (0.07 g.) at 100° for 1 hr. with an excess of benzoyl chloride (0.07 ml.) in dry pyridine (2 ml.). Bright orange needles (0.07 g.) of m.p. 342° (*o*-dichlorobenzene) were obtained.

Anal. Calcd. for $C_{27}H_{15}NO_4$: C, 77.7; H, 3.6; N, 3.35. Found: C, 77.8; H, 3.7; N, 3.4.

The *p*-toluenesulfonamide of V was obtained by boiling V (0.1 g.) for 1 hr. with an excess of *p*-toluenesulfonyl chloride (0.2 g.) in dry pyridine (5 ml.). Orange crystals (0.12 g.) of m.p. 284–286° (acetic acid) were obtained.

Anal. Calcd. for $C_{27}H_{17}NO_5S$: C, 69.0; H, 3.6; S, 6.8. Found: C, 69.3; H, 3.8; S, 6.5.

9-Bromodinaphtho[2,1-2′,3′]furan-8,13-dione from V. A fine slurry of V (0.12 g.) in 85% phosphoric acid (25 ml.) was diazotized at 10°C. with sodium nitrite (0.03 g.). The resulting violet diazonium solution was poured slowly into a solution of cuprous bromide (0.7 g.) in 48% hydrobromic acid (12 ml.) and stirred for 1 hr. at room temperature, while diluting with water (50 ml.). After stirring an additional 0.5 hr. at 80–100°, the orange precipitate was filtered off, washed with water and dried (0.13 g.; m.p. 320–324°). Crystallization from acetic acid gave 0.1 g. of 9-bromo dinaphtho[2,1-2′,3′]-furan-8,13-dione as orange crystals; m.p. 330–332°.

Anal. Calcd. for $C_{20}H_9BrO_3$: C, 63.6; H, 2.4; Br, 21.2. Found: C, 63.3; H, 2.5; Br, 20.8.

12-Aminodinaphtho[2,1-2′,3′]furan-8,13-dione (VI). The amine VI was prepared from the nitro isomer IV (2.0 g.) by the procedure described for the isomeric amine V. A 95% yield of VI was obtained as dark brown crystals; m.p. 338–340° (nitrobenzene).

Anal. Calcd. for $C_{20}H_{11}NO_3$: C, 76.6; H, 3.5; N, 4.4. Found: C, 76.5; H, 3.5; N, 4.4.

The benzamide of VI crystallized from chlorobenzene as red-orange crystals, m.p. 300°.

Anal. Calcd. for $C_{27}H_{15}NO_4$: C, 77.7; H, 3.6; N, 3.35. Found: C, 77.3; H, 3.7; N, 3.4.

The *p*-toluenesulfonamide of VI crystallized from acetic acid as orange crystals of m.p. 282–284°. The mixed m.p. with the *p*-toluenesulfonamide of V was 253–260°.

Anal. Calcd. for $C_{27}H_{17}NO_5S$: C, 69.0; H, 3.6; S, 6.8. Found: C, 69.0; H, 3.7; S, 6.7.

Chromatographic separation of the 9- and 12-amino isomers (V and VI). The mixture of the nitro isomers III and IV was reduced with alkaline sodium hydrosulfite as described for V and the resulting mixture of aminodinaphthofurandiones (m.p. 272–284°) dissolved in benzene was chromatographed on alumina. Elution with benzene yielded two bands: a brownish-orange band, which after evaporation of the solvent and crystallization from toluene, gave VI (40–50%) as dark brown crystals (m.p. 338°) and a violet band which gave V (50–60%) as violet crystals (m.p. 298–300°).

Proof of structure of 9-bromodinaphtho[2,1-2′,3′]furan-8,13-dione from V. *2-(o-Bromobenzoyl)naphtho[2,1-b]furan-1-carboxylic acid* (VII). This acid was prepared from naphtho[2,1-*b*] furan-1,2-dione[10] and *o*-bromophenacyl bromide[11] by a method similar to that described by Chatterjea[3] for the synthesis of 7-methylbenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione. A 70% yield of pale yellow crystals of m.p. 174–176° was obtained.

Anal. Calcd. for $C_{20}H_{11}BrO_4$: C, 60.7; H, 3.0; Br, 20.2. Found: C, 60.5; H, 2.8; Br, 20.1.

9-Bromodinaphtho[2,1-2′,3′]furan-8,13-dione (VIII). Acid VII (3 g.) was converted into the acid chloride by stirring it with thionyl chloride (30 ml.) at room temperature for 16

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[9] B. Eistert, *Ber.*, **80**, 47 (1947).

[10] M. Giua, *Gazz. Chim. Ital.*, **54**, 509 (1924).

[11] R. L. Lutz and 15 Co-workers, *J. Org. Chem.*, **12**, 664 (1947).

hr. After removal of the thionyl chloride, the residue was dissolved in nitrobenzene (30 ml.) and aluminum chloride (12 g.) was added gradually at 20–25°. The mass turned dark then violet. After overnight stirring at room temperature, the reaction product was drowned in ice and hydrochloric acid and the nitrobenzene was steam distilled. The residue was removed by filtration and slurried with an excess of dilute sodium hydroxide solution to separate unreacted starting material. The alkali insoluble product was purified by vatting to yield 1.1 g. of crude material, m.p. 325–328°, which on crystallization from toluene (Darco) gave 1.0 g. of VIII as orange crystals; m.p. 330–332°.

Anal. Calcd. for $C_{20}H_9BrO_3$: C, 63.6; H, 2.4. Found: C, 63.4; H, 2.4.

The alkaline filtrate upon acidification with concentrated hydrochloric acid gave 1.9 g. of unreacted 2-(*o*-bromobenzoyl)naphtho[2,1-*b*]furan-1-carboxylic acid (VII); m.p. 174–176°.

A mixture of VIII with the bromo compound obtained from V (m.p. 330–332°) melted at 330–332°. The identity of the two bromo derivatives was further substantiated by comparison of the infrared spectra.

9-(p-Tolylsulfonamido)dinaphtho[2,1-2′,3′]furan-8,13-dione. A mixture of VIII (0.2 g.), *p*-toluenesulfonamide (0.14 g.), sodium carbonate (0.08 g.), cuprous chloride (0.01 g.) and nitrobenzene (15 ml.) was heated at 200° for 6 hr. The crude product was removed by filtration, washed and crystallized from acetic acid to yield bright yellow crystals (90% yield) of m.p. 286–288°.

Anal. Calcd. for $C_{27}H_{17}NO_5S$: C, 69.0; H, 3.6. Found: C, 69.3; H, 3.8.

The identity of this derivative of VIII with the *p*-toluenesulfonamide obtained from V was established by mixed m.p. determinations and infrared spectra. On the other hand, the mixed m.p. of the *p*-toluenesulfonamides of VIII and VI (m.p. 282–284°) showed a significant depression (mixed m.p. 253–260°).

Condensation of 1-naphthol with 2,3-dichloro-5-nitro-1,4-naphthoquinone. 8- and 11-Nitrodinaphtho[1,2-2′,3′]furan-7,12-diones (X and IX). 2,3-Dichloro-5-nitro-1,4-naphthoquinone of m.p. 175° (13.5 g.), prepared by the method of Fries,[8] was reacted with 1-naphthol (8.0 g.) in the manner described for the nitro isomers III and IV. The precipitate, after filtration and repeated extraction with boiling water, gave 11.5 g. of an orange product of m.p. 306–308°, which was a mixture of X and IX. Microscopic examination showed the presence of orange-yellow and pale yellow crystals.

Anal. Calcd. for $C_{20}H_9NO_5$: C, 70.0; H, 2.6; N, 4.1. Found: C, 70.1; H, 2.7; N, 4.0.

The above mixture of nitro isomers X and IX (5 g.) was stirred with concentrated sulfuric acid in the manner described for the mixture of nitro isomers III and IV. The insoluble material crystallized from *o*-dichlorobenzene yielded 2.6 g. of IX as bright orange crystals; m.p. 344–346°.

Anal. Calcd. for $C_{20}H_9NO_5$: C, 70.0; H, 2.6; N, 4.1. Found: C, 70.0; H, 2.7; N, 4.0.

The sulfuric acid filtrate, drowned slowly on ice, gave 2.1 g. of X as a red-brown precipitate; m.p. 314–322°. Crystallization from *o*-dichlorobenzene yielded yellow crystals (m.p. 320–324°) with little loss.

Anal. Calcd. for $C_{20}H_9NO_5$: C, 70.0; H, 2.6; N, 4.1. Found: C, 70.2; H, 2.7; N, 4.0.

8-Aminodinaphtho[1,2-2′,3′]furan-7,12-dione (XII). The amine XII, obtained from the nitro isomer X as described for the amine V, crystallized from nitrobenzene as red-brown crystals of m.p. 362–364°.

Anal. Calcd. for $C_{20}H_{11}NO_3$: C, 76.6; H, 3.5; N, 4.4. Found: C, 76.8; H, 3.3; N, 4.6.

The benzamide of XII crystallized from chlorobenzene as orange needles, m.p. 310–312°.

Anal. Calcd. for $C_{27}H_{15}NO_4$: C, 77.7; H, 3.6; N, 3.35. Found: C, 77.5; H, 3.3; N, 3.4.

11-Aminodinaphtho[1,2-2′,3′]furan-7,12-dione (XI). The amine XI, obtained from the nitro isomer IX, crystallized from nitrobenzene as violet-red crystals, m.p. 302–304°.

Anal. Calcd. for $C_{20}H_{11}NO_3$: C, 76.6; H, 3.5; N, 4.4. Found: C, 76.6; H, 3.3; N, 4.5.

The benzamide of XI crystallized from chlorobenzene as orange needles, m.p. 292–294°.

Anal. Calcd. for $C_{27}H_{15}NO_4$: N, 3.35. Found: N, 3.4.

Chromatographic separation of the 8- and 11-amino isomers (XII and XI). The mixture of the isomeric amines XII and XI (m.p. 294–298°), obtained from the mixture of the nitro isomers X and IX by reduction with alkaline sodium hydrosulfite, was chromatographed as described for the isomeric amines V and VI. The brownish-orange band gave XII (40% of the mixture) as dark red crystals, m.p. 362–364°, and the bright violet band gave XI (60%) as red crystals, m.p. 302–304°.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

A New Synthetic Route to Methoxytetralones

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5-Methoxy-1-tetralone has been prepared from 8-chloro-5-methoxy-1-tetralone by preferential hydrogenolysis of the halogen atom. The chlorotetralone has also been converted to 5-chloro-8-methoxy-1-tetralone in low yield. The infrared and ultraviolet spectra of these compounds are discussed.

Although 5-methoxy-1-tetralone has been previously prepared, it, 8-methoxy-1-tetralone and their derivatives are relatively inaccessible, compared with the well known 6- and 7-methoxytetralones. 5-Methoxytetralone has been prepared from coumarin[1] in low yield by a six-step synthesis, and also by hydrogenation of substituted naphthalene derivatives,[2] followed by appropriate conversions. The preparation of 7-methoxytetralone from anisole *via* β-(4-methoxybenzoyl)propionic

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[1] J. Lockett and W. F. Short, *J. Chem. Soc.*, 787 (1939).

[2] (a) E. Hardegger, D. Redlich, and A. Gal, *Helv. Chim. Acta*, **27**, 628 (1944). (b) D. Papa and E. Schwenk, *J. Org. Chem.*, **14**, 366 (1949).