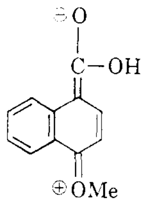
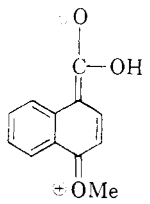
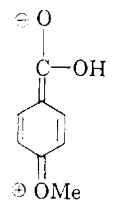
dissociation of benzoic and of 1-naphthoic acid are the same. The fact that the 4-fluoro and, particularly, the 4-methoxy-1-naphthoic acids are relatively weaker than the linear relation would predict, as shown by the low Δ values, is indicative of a greater resonance interaction in these 1-naphthoic acids, containing substituents with large +M effects, than in the corresponding benzoic acids—*i.e.*, as in the case of the 4(−M)-substituted 1-naphthoxide ions, the "naphthoquinone type" structures (IV) and (V) contribute more to the resonance hybrid of the acid than the "benzoquinone type" does in the benzoic acid case (VI).



IV



V



VI

However, because of the rather large experimental uncertainty of the dissociation constants of substituted 1-naphthoic acids, these conclusions are drawn with some diffidence. As in the case of the naphthols and phenols, nonpolar effects must be responsible for the greater acidity of the substituted 1-naphthoic acids compared with the correspondingly substituted benzoic acids. In this case, however, the dominant effect must be steric inhibition of mesomerism because in the absence of this factor the 1-naphthyl group, with a presumed greater +M effect than phenyl, should stabilize the acid relative to the anion and consequently inhibit dissociation.

Acknowledgment. The authors are indebted to the Research Fund Committee, of the University of New Zealand, for financial assistance.

CHRISTCHURCH, NEW ZEALAND

[CONTRIBUTION FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Structure and Properties of Benzonaphthofurandione Derivatives

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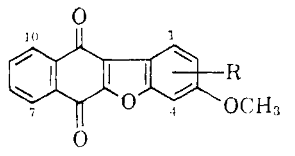
Received January 27, 1961

Nitration of 3-methoxybenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione (I) gives derivatives with nitro groups in the benzene ring. Derivatives with a nitro group in the naphthalene system could not be obtained by direct nitration and were prepared by condensing 2,3-dichloro-5-nitro-1,4-naphthoquinone with 3-methoxyphenol. Several nitro- and aminomethoxybenzonaphthofurandiones are described and their spectral characteristics discussed. The 7- and 10-substituted benzonaphthofurandiones are useful as dyes.

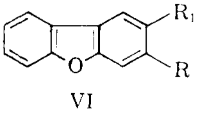
The object of this study has been to investigate the structure and the properties of nitro and amino derivatives of 3-methoxybenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione (I).[1,2]



I. R = H
II. R = 2-NO$_2$
III. R = 2-NH$_2$
IV. R = 2,4-(NO$_2$)$_2$
V. R = 2,4-(NH$_2$)$_2$

The interest in these compounds lies in their attractive properties as dye-intermediates and as dyes for synthetic fibers. The present paper reports that the nitration of I yields the 2-nitro (II) and the 2,4-dinitro derivatives (IV). The 7-nitro (VII) and the 10-nitro isomer (XI) could not be prepared by direct nitration and are obtained by condensing 2,3-dichloro-5-nitro-1,4-naphthoquinone with 3-methoxyphenol.

Nitration of I in sulfuric acid with one equivalent of nitric acid gave a 70% yield of a mononitro derivative, which by oxidative degradation with potassium permanganate gave nitro-free phthalic acid, thus demonstrating that the nitro group is not in the naphthalene system. (Under the same conditions the 7-nitro derivative (VII) gave 3-nitrophthalic acid). Analogy with the structurally related dibenzofurans (VI), obtained by electrophilic substitution reactions,[3,4] suggested structure II.



VI

R = —OCH$_3$, —NH$_2$, —NHCOCH$_3$, etc.
R$_1$ = —NO$_2$, —Br, etc.

Evidence to support this structure is provided by the spectral characteristics. The nitro group in

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[1] St. v. Kostanecki and V. Lampe, *Ber.*, **41**, 2375 (1908).

[2] J. N. Chatterjea, *J. Indian Chem. Soc.*, **31**, 101 (1954).

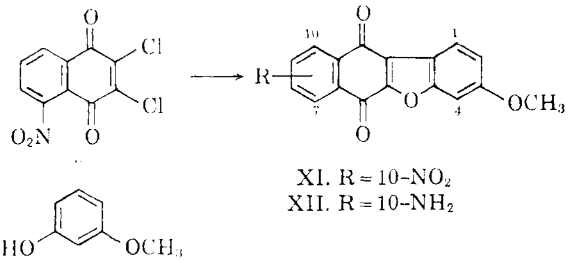
[3] H. Gilman, G. E. Brown, W. G. Bywater, and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56**, 2473 (1934).

[4] P. R. Van Ess, *Iowa State Coll. J. Sci.*, **12**, 164 (1937).

II produces a noticeable hypsochromic shift in the absorption maximum of the parent compound I (Table I), indicating conjugation with the furan oxygen. This is in line with the spectral characteristics of dibenzofuran and its nitro derivatives.[5] Additional evidence is given by the failure to obtain an azo compound by coupling a solution of diazotized *p*-nitroaniline with the amine III, obtained by reduction of II.[6]

Nitration of I in sulfuric acid with two equivalents of nitric acid yielded a dinitro compound which, like the mononitro II, gave a nitrogen-free phthalic acid by oxidative degradation. Structure IV postulated by Kostanecki[7] was substantiated by the following facts. The diamine V, obtained by reduction of IV, (a) coupled smoothly[8] with a solution of diazotized *p*-nitroaniline to give 1-(*p*-nitrophenylazo) - 2,4 - diamino - 3 - methoxybenzonaphthofurandione and (b) did not form the corresponding phenazine derivative by condensation with phenanthrenequinone.

In an earlier paper[9] it was shown that the condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 1-naphthol gives a mixture of two isomeric nitrodinaphthofurandiones. It is found now that when in this condensation 1-naphthol is replaced by 3-methoxyphenol a mixture of two nitro-3-methoxybenzonaphthofurandiones (VII and XI) is obtained.

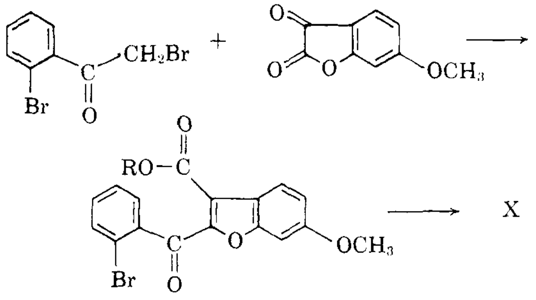


XI. R = 10-NO$_2$
XII. R = 10-NH$_2$

VII. R = 7-NO$_2$
VIII. R = 7-NH$_2$
X. R = 7-Br

Unlike the isomeric nitrodinaphthofurandiones, these nitro isomers could not be separated by means of their solubilities in concentrated sulfuric acid. Only repeated fractional crystallizations from benzene yielded pure isomers. Orientation of the 7-nitro isomer (VII) 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 sample of 7-bromo-3-methoxybenzo[*b*]naphtho[2,3 - *d*]furan - 6,11-dione (X) confirmed its identity. This structure proof of VII is obviously also an indirect proof for the structure of XI, since the latter can have only the alternative structure.

Authentic 7-bromo-3-methoxybenzonaphthofurandione (X) was synthesized from *o*-bromophenacyl bromide and 6-methoxybenzofuran-2,3-dione, according to the following route:



IX

This route is similar to that used for the preparation of 9-bromodinaphtho[2,1-2′,3′]furan-8,13-dione.[9] The last step of this route, the ring closure, was carried out at room temperature and gave a conversion considerably superior to that obtained in the case of the analogous dinaphthofurandione derivative.

The spectral characteristics of the 7- and 10-nitro isomers (VII and XI) are identical, whereas the absorption maximum of the 2-nitro (II) shows a considerable hypsochromic shift (Table I). It is interesting to note that, in comparison with these nitro isomers, the absorption maxima of the 2- and 7-amino isomers (III and VIII) show a bathochromic shift (88 and 50 mμ, respectively), whereas the absorption maximum of the 10-amino isomer (XII) shows a hypsochromic shift (16 mμ). The

TABLE I

Absorption Maxima of Methoxy Benzonaphthofurandiones[a]

Compound	λ, mμ	$\epsilon^b \times 10^{-3}$
Methoxybenzonaphthofurandione (I)	430	3.3
2-Nitro (II)	402	5.1
7-Nitro (VII)	450	5.2
10-Nitro (XI)	450	5.2
2-Amino (III)	490	5.7
7-Amino (VIII)	500	7.2
10 Amino (XII)	434	7.0

[a] Solvent: *o*-dichlorobenzene. [b] Molar extinction coefficient, ϵ, defined as $\frac{\text{optical density}}{Cl}$, where C is concentration g. mole/liter and l is cell length in cm. The ϵ of 1-aminoanthraquinone (m.p. 245–246°) is 6.0 at the absorption maximum of 462 mμ.

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(5) A. Cerniani, R. Passerini, and G. Righi, *Boll. Sci. Facolta' Chim. Ind. Bologna*, **12**, 75 (1954).

(6) In substituted anilines "when a free hydrogen atom is not available in the *para* position to the amino group, the *ortho* position is rarely attacked, unless strongly activated." K. H. Saunders, *The Aromatic Diazo Compounds*, 2nd ed., Ed. Arnold, London 1949, p. 201.

(7) St. v. Kostanecki and V. Lampe, *Ber.*, **41**, 2800 (1908).

(8) It is known that "diazonium salts are rapidly decomposed by *o*-phenylenediamine." K. Venkatamaran, *The Chemistry of Synthetic Dyes*, ed., Academic, Inc., New York, 1952, Vol. I, p. 417.

(9) M. F. Sartori, *J. Org. Chem.*, **24**, 1756 (1959).

data for the 7- and 10-amino isomers (VIII and XII) are in line with those observed in the 9- and 12-aminodinaphtho[2,1-2′,3′]furan-8,13-diones.[9] In comparison with 1-aminoanthraquinone, the derivatives with the amino group in the naphthalene system (VIII and XII) possess higher molar extinction coefficients and the 7-amino isomer shows a strong bathochromic shift of the absorption maximum.

EXPERIMENTAL[10]

3-Methoxy-2-nitrobenzo[b]naphtho[2,3,-d]furan-6,11-dione (II). 3-Methoxybenzo[*b*]naphtho[2,3,-*d*]furan-6,11-dione (I, m.p. 292–294°) was prepared from 2,3-dichloro-1,4-naphthoquinone and 3-methoxyphenol by the method used by Eistert[11] for the synthesis of the 3-hydroxy compound. To a solution of I (2.78 g., 0.01 mole) in concd. sulfuric acid (20 ml.), cooled to 5°, nitric acid (*d.* 1.4; 1.0 g.; 0.011 mole) was added dropwise in about 15 min., while stirring. The greenish-blue solution was stirred for 1 hr. at 5°, then poured slowly on ice water. A bright yellow slurry was obtained. The insoluble material was collected, washed with water and dried. After crystallization from acetic acid a 70% yield of II was obtained as bright yellow crystals of m.p. 318–320°.

Anal. Calcd. for $C_{17}H_9NO_6$: C, 63.2, H, 2.8, N, 4.3. Found: C, 63.1, H, 2.9, N, 4.3.

Oxidative degradation of II. A solution of II (2 g.) in concd. sulfuric acid (80 ml.) was added slowly to hot water (160 ml.) with vigorous agitation. To the pale yellow suspension obtained, 8 g. of finely powdered potassium permanganate was added in portions over about 1 hr., keeping the temperature at 90–95°. After the addition of the permanganate was completed, the agitation was continued for an additional 10 min. at 90–100°. The dark slurry was decolorized with sodium bisulfite and the clear solution was extracted with ether. Evaporation of the dried ether layer gave 1.1 g. of almost colorless material which, when heated to gentle boiling with acetic anhydride (1.5 ml.) for 5 min. and cooled to room temperature, yielded long white needles of m.p. 130–132°. A mixture of this product with an authentic sample of phthalic anhydride (m.p. 130–132°) melted at 130–132°.

2-Amino-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione (III). 3-Methoxy-2-nitrobenzo[*b*]naphtho[2,3,-*d*]furan-6,11-dione (II, 2 g.) was added to a stirred solution of sodium hydrosulfite (10 g.) and sodium hydroxide (10 g.) in water (400 ml.), blanketed with nitrogen. After 15 min. at 35° the slurry changed to a clear yellow 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 precipitate (1.8 g.), m.p. 280–290° was crystallized from *o*-dichlorobenzene to give a 90% yield of III as dark red crystals, m.p. 290°.

Anal. Calcd. for $C_{17}H_{11}NO_4$: C, 69.5; H, 3.7; N, 4.7. Found: C, 69.3; H, 3.7; N, 4.7.

2,4-Dinitro-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione (IV). 3-Methoxybenzo[*b*]naphtho[2,3-*d*]furan-6,11-dione (I) was nitrated with 2 equivalents of nitric acid, following the method described for II. After crystallization from acetic acid an 80% yield of IV was obtained as pale yellow crystals of m.p. 244–246° dec.

Anal. Calcd. for $C_{17}H_8N_2O_8$: C, 55.2; H, 2.2; N, 7.6. Found: C, 54.9; H, 2.1; N, 7.6.

Oxidative degradation of IV. A fine slurry of IV (2.0 g.) in dilute sulfuric acid, treated with potassium permanganate as described for II, gave phthalic anhydride (m.p. 130–132°).

2,4-Diamino-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione (V). This diamine was prepared from IV, by following the procedure described for III. A 92% yield of V was obtained as dark red crystals of m.p. 220–222° (acetic acid).

Anal. Calcd. for $C_{17}H_{12}N_2O_4$: C, 66.2; H, 3.9; N, 9.1. Found: C, 65.4; H, 3.9; N, 8.9.

1-(p-Nitrophenylazo)2,4-diamino-3-methoxybenzonaphthofurandione. A solution of diazotized *p*-nitroaniline (0.5 g.) in dilute hydrochloric acid was added slowly at 5–10° to a solution of V (1.0 g.) in 85% phosphoric acid (80 ml.) and concd. hydrochloric acid (5 ml.). After stirring 1 hr. at 5–10°, the *p*H of the dark red solution was raised to 5 by addition of a saturated solution of sodium acetate and the agitation was continued for an additional 2 hr. The dark brown precipitate was filtered off, washed with water and dried. The crude product (1.2 g.) crystallized from *o*-dichlorobenzene gave 1.2 g. of 1-(*p*-nitrophenylazo)-2-4-diamino-3-methoxybenzonaphthofurandione as red brown crystals; m.p. 298–300°.

Anal. Calcd. for $C_{23}H_{15}N_5O_6$: C, 60.6; H, 3.1; N, 15.4. Found: C, 60.3; H, 3.2; N, 15.6.

3-Methoxy-7(and 10)-nitro-benzo[b]naphtho[2,3-d]-furan-6,11-dione (VII *and* XI). 2,3-Dichloro-5-nitro-1,4-naphthoquinone (m.p. 174°, 22 g.), prepared by the method of Fries[12] was added to a solution of 3-methoxyphenol (12 g.) in pyridine (140 ml.). An orange suspension was formed and the temperature rose to 50° in about 5 min. The mixture was then heated to 100° in about 1 hr. and kept at this temperature for an additional 6 hr. After stirring 12 hr. at room temperature the orange precipitate was collected, washed with ethanol and dried. The crude product (20.5 g.) was repeatedly extracted with boiling water to remove the nitropyridinium compound.[11,13] The residue (11.5 g.) of m.p. 276–278° was a mixture of VII and XI. Microscopic examination showed the presence of orange and yellow crystals.

Anal. Calcd. for $C_{17}H_9NO_6$: C, 63.2; H, 2.8; N, 4.3. Found: C, 63.0; H, 2.8; N, 4.5.

The above mixture of nitro isomers VII and XI (5 g.) was repeatedly crystallized from benzene. Two fractions were separated. The more soluble fraction (1.8 g.) was recrystallized from the same solvent to give XI as orange needles; m.p. 316–318°.

Anal. Calcd. for $C_{17}H_9NO_6$: C, 63.2; H, 2.8; N, 4.3. Found: C, 63.2; H, 2.7; N, 4.4.

The less soluble fraction (3.1 g.) was recrystallized from *o*-dichlorobenzene to give VII as golden yellow crystals; m.p. 318–320°.

Anal. Calcd. for $C_{17}H_9NO_6$: C, 63.2; H, 2.8; N, 4.3. Found: C, 63.0; H, 2.6; N, 4.4.

The mixed melting point of these two nitro isomers was 274–278°. The infrared spectra are similar up to about 8 μ, both nitro isomers exhibiting the characteristic bands of carbon-carbon double bonds, of the carbonyl and of the nitro groups. A good region for differentiation is 8–15 μ, where the individual isomers present the following bands: isomer VII at 12.25 and isomer XI at 8, 10.85, 11.45, and 13.35 μ.

Oxidative degradation of VII *and* XI. A fine suspension of the above mixture of nitro isomers VII and XI (1 g.) in dilute sulfuric acid, treated with potassium permanganate as described for II, gave, after treatment with acetic anhydride, small shining crystals of m.p. 160–162°. A mixture of this product with an authentic sample of 3-nitrophthalic anhydride (m.p. 162–163°) melted at 162–163°.

7-Amino-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione (VIII). The amine VIII, prepared from the nitro isomer VII

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[10] 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 on Nujol mulls on a Perkin-Elmer Model 21 Recording Spectrophotometer equipped with sodium chloride optics.

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

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

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

as described for the amine III, crystallized from *o*-dichlorobenzene as red crystals of m.p. 282–284°.

Anal. Calcd. for $C_{17}H_{11}NO_4$: C, 69.6; H, 3.7; N, 4.7. Found: C, 69.3; H, 3.7; N, 4.7.

The *N*-*p*-tolylsulfonyl derivative of VIII was obtained by boiling VIII (0.2 g.) for 1 hr. with an excess of *p*-toluenesulfonyl chloride (0.4 g.) in dry pyridine (10 ml.). Orange crystals (0.21 g.) of m.p. 258–260° (acetic acid) were obtained.

Anal. Calcd. for $C_{24}H_{17}NO_6S$: C, 64.4; H, 3.8; N, 3.1; S, 7.1. Found: C, 64.2; H, 3.8; N, 3.3; S, 7.1.

7-Bromo-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione from VIII. A fine slurry of VIII (0.17 g.) in 85% phosphoric acid (30 ml.) was diazotized at 10° with sodium nitrite (0.05 g.). The resulting violet diazonium solution was poured slowly under the surface of 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 formed was filtered off, washed with water and dried. (0.2 g., m.p. 268–270°). Crystallization from acetic acid (Darco) gave 0.15 g. of 7-bromo-3-methoxybenzo[*b*]-naphtho[2,3-*d*]-furan-6,11-dione as orange crystals; m.p. 278°.

Anal. Calcd. for $C_{17}H_9BrO_4$: C, 57.1; H, 2.5; Br. 22.4. Found: C, 57.1; H, 2.5; Br, 21.2.

10-Amino-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione (XII). The amine XII was prepared from the nitro isomer XI following the method described for the isomeric amine III. A 95% yield of XII was obtained as violet-brown crystals of m.p. 278–279°. The mixed m.p. with the isomeric amine VIII (m.p. 282–284°) was 264–266°.

Anal. Calcd. for $C_{17}H_{11}NO_4$: N, 4.7. Found: N, 4.8.

The *N*-*p*-tolysulfonyl derivative of XII crystallized from acetic acid as orange-yellow crystals of m.p. 239–240°. The mixed m.p. with the corresponding derivative of the isomeric amine VIII (m.p. 258–260°) was 236–240°.

Anal. Calcd. for $C_{24}H_{17}NO_6S$: C, 64.4; H, 3.8; N, 3.1; S, 7.1. Found: C, 64.2; H, 3.8; N, 3.3; S, 7.3.

10-Bromo-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione from XII. A solution of the isomeric amine XII (0.1 g.) in 85% phosphoric acid (25 ml.) was diazotized and treated with cuprous bromide (0.6 g.) and 48% hydrobromic acid (12 ml.) as described for the isomeric bromo derivative from VIII. The orange precipitate, after crystallization from acetic acid, yielded scarlet needles (0.08 g.), m.p. 238–240°.

Anal. Calcd. for $C_{17}H_9BrO_4$: C, 57.1; H, 2.5; Br, 22.4 Found: C, 57.8; H, 2.5; Br. 21.8.

Chromatographic separation of the 7- and 10-amino isomers (VIII *and* XII). The mixture of the nitro isomers VII and XI, as obtained in the condensation of 2,3-dichloro-5-nitro-1,4-naphthoquinone with 3-methoxyphenol, was reduced with alkaline sodium hydrosulfite as described for III and the resulting mixture of aminomethoxybenzonaphthofurandiones (m.p. 264–266°) 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 XII, as brown crystals (m.p. 278–280°) and a violet band, which gave VIII as violet crystals (m.p. 282–284°).

Proof of structure of 7-bromo-3-methoxybenzo[b]naphtho[2,3,-d]furan-6,11-dione from VIII. *2-(o-Bromobenzoyl)-6-methoxy-3-benzofurancarboxylic acid* (IX). This acid was prepared from 6-methoxybenzofuran-2,3-dione[14] and *o*-bromophenacyl bromide[15] by a method similar to that described by Chatterjea[16] for the synthesis of 2-(o-toluoyl)-3-benzofurancarboxylic acid. A 92% yield of yellow crystals of m.p. 181° (acetic acid) was obtained.

Anal. Calcd. for $C_{17}H_{11}BrO_5$: C, 54.2; H, 2.9; Br, 21.3. Found: C, 54.2; H, 2.9; Br, 20.2.

7-Bromo-3-methoxybenzo[b]naphtho[2,3-d]furan-6,11-dione (X). Acid IX (6 g.) was converted into the acid chloride by stirring it with thionyl chloride (60 ml.) at room temperature for 16 hr. After removal of the excess thionyl chloride, the residue was dissolved in nitrobenzene (60 ml.) and aluminum chloride (24 g.) was gradually added at 15–20°. After overnight stirring at room temperature, the reaction product was drowned in ice and hydrochloric acid and the nitrobenzene was removed by steam distillation. The residue (5.7 g.) was slurried with an excess of dilute sodium hydroxide solution to remove the unchanged starting material. The alkali insoluble product was purified by vatting to yield 3.4 g. of crude material, m.p. 272–276°, which on crystallization from acetic acid (Darco) yielded 3.2 g. (56% conversion) of X as orange crystals; m.p. 278–279°.

Anal. Calcd. for $C_{17}H_9BrO_4$: C, 57.1; H, 2.5; Br, 22.4. Found: C, 56.8; H, 2.5; Br, 21.1.

The alkaline filtrate upon acidification with concd. hydrochloric acid gave 2.0 g. of unchanged 2-(*o*-bromobenzoyl)-6-methoxy-3-benzofurancarboxylic acid (IX); m.p. 181°

A mixture of X with the bromo compound obtained from VIII (m.p. 278–279°) melted at 278–279°, whereas a mixture with a specimen of the bromo isomer from XII (m.p. 238–240°) melted at 222–228°. The identity of the two bromo derivatives of m.p. 278–279° was further substantiated by comparison of the infrared spectra.

7-(p-Tolylsulfonamido)-3-methoxybenzo[b]naphtho[2,3-d]-furan-6,11-dione. A mixture of X (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 orange crystals (90% yield) of m.p. 258°.

Anal. Calcd. for $C_{24}H_{17}NO_6S$: C, 64.4; H, 3.8; N, 3.1. Found: C, 64.4; H, 3.8; N, 2.9.

The identity of this derivative of X with the *p*-tolylsulfonamide derivative obtained from VIII was established by mixed melting point determinations and infrared spectra.

WILMINGTON, DEL.

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(14) J. N. Chatterjea, *J. Indian Chem. Soc.*, **31**, 198 (1954).

(15) R. L. Lutz and fifteen co-workers, *J. Org. Chem.*, **12**, 664 (1947).

(16) J. N. Chatterjea, *J. Indian Chem. Soc.*, **32**, 265 (1955).