TABLE I

POLYMERIZATION OF TETRAHYDROFURAN AND SUBSTITUTED TETRAHYDROFURAN

Monomer	Catalyst	Mole, %	Reaction Time, Hr.	Reaction Temp.	Monomer Recovered
Tetrahydrofuran	$SbCl_5$	1.2	24	12–20	8
2-Methyltetrahydrofuran	$SbCl_5$	2.8	168	12–20	100
2,5-Dimethyltetrahydrofuran	$SbCl_5$	3.3	24	12–20	96
Tetrahydrofuran	BF_3-etherate	20	24	12–20	76
2-Methyltetrahydrofuran	BF_3-etherate	27	168	12–20	100
2,5-Dimethyltetrahydrofuran	BF_3-etherate	32	192	12–20	100

TABLE II

TEMPERATURE RISE WHEN BF_3-ETHERATE[a] WAS ADDED TO TETRAHYDROFURANS

	Temperature Rise
Tetrahydrofuran	16
2-Methyltetrahydrofuran	14
2,5-Dimethyltetrahydrofuran	11

[a] 10 g. of boron trifluoride etherate to 20 g. of compound.

medium upon addition of a boron trifluoride catalyst.

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2,4-Dimethyldibenzofuran

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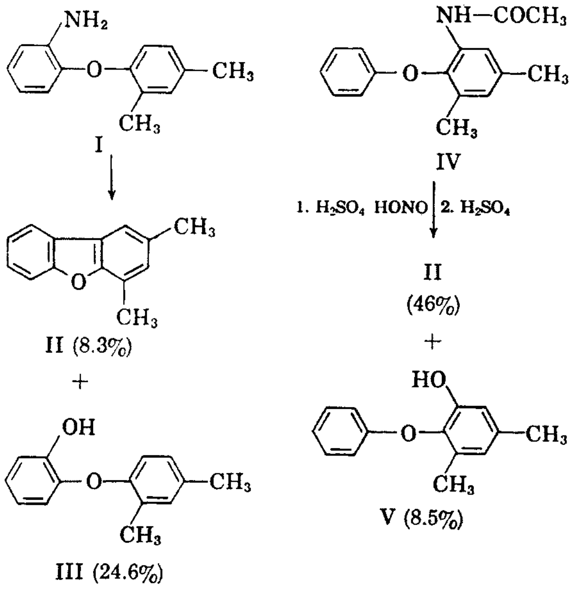
Previous studies[2] have led to the conclusion that the synthesis of 4-substituted dibenzofurans from *o*-aminodiphenyl ethers, by diazotization and subsequent intramolecular coupling of the resulting diazonium salt, must be effected on diphenyl ethers that have the amino group in the same ring as the group which will ultimately occupy the 4-position in the resulting dibenzofuran. While there appears to be no apparent theoretical justification, there is considerable experimental data to support this concept.[3] Thus far success has attended every synthesis in which these conditions were fulfilled, and every attempt in which these conditions were not met has ended in failure. We have reexamined this procedure as applied to the synthesis of 2,4-dimethyldibenzofuran (II), and the synthesis of II, several nitro derivatives of II, and a variety of new diphenyl ethers, constitutes the subject of this report.

Reaction of the diazonium salt derived from 2 aminophenyl 2,4-xylyl ether (I) with hot dilute sulfuric acid (1:1) afforded a mixture, from which 2,4-dimethyldibenzofuran (II, 8.3%) and 2-hydroxyphenyl 2,4-xylyl ether (III, 24.6%) were isolated. Treatment of the isomeric 6-amino-2,4-xylyl phenyl ether, (derived from IV), in a similar manner, afforded 2,4-dimethyldibenzofuran (II, 46%) and 6-hydroxy-2,4-xylyl phenyl ether (V, 8.5%). These results definitely establish that ring closure to a dibenzofuran from a diphenyl ether possessing an *ortho* amino group in either ring is possible, despite the fact that the resulting product contains a substituent in the 4-position. There was, however, a marked difference in the proportion of products formed in the two cases, and the results generally support previous experience relative to yield.



Oxidation experiments were conducted in an effort to produce dibenzofuran-2,4-dicarboxylic acid. Potassium dichromate was used in 1:1 sulfuric acid, but only a trace of white acidic solid was obtained. Potassium permanganate was used as the oxidizing agent in three attempts in which the solvents were dilute sodium hydroxide, acetone, and water. Again, only traces of acidic materials were isolated.

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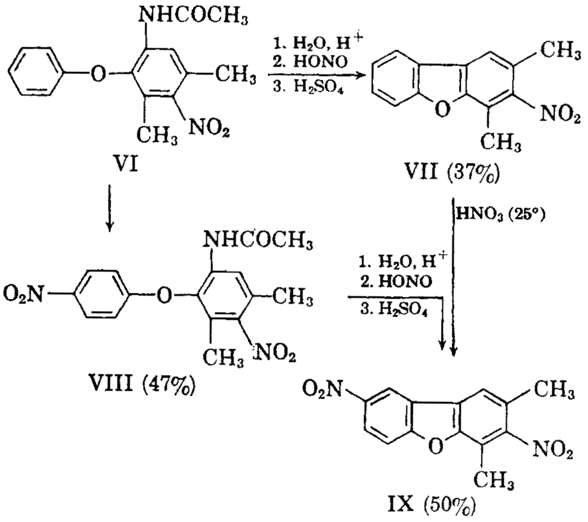
(1) From the Ph.D. Thesis of Roger W. Strassburg, the University of Minnesota, 1950.

(2) H. Gilman, M. W. Van Ess, and D. M. Hayes, *J. Am. Chem. Soc.*, 61, 643 (1939).

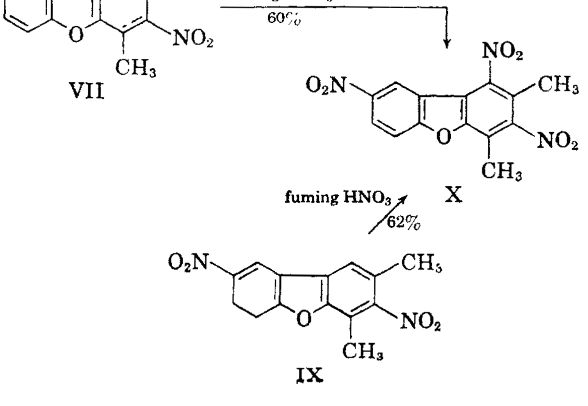
(3) *Heterocyclic Compounds*, Vol. 2, R. C. Elderfield, ed., Wiley, New York, 1951, p. 125.

Two additional derivatives of II (VII and IX) were prepared by direct ring closure of the appropriate diphenyl ether.



6-Acetamido-3-nitro-2,4-xylyl phenyl ether (VI) was prepared in 84% yield by nitration of 6-acetamido-2,4-xylyl phenyl ether with fuming nitric acid in acetic acid. An isomer of VI, of undetermined structure, was isolated in 4% yield. 6-Acetamido-3-nitro-2,4-xylyl 4-nitrophenyl ether (VIII) was prepared in 47% yield by further nitration of VI; a smaller amount of an isomer of VIII, of undetermined structure, was also isolated. Both VI and VIII were new; their structures were determined by deamination to the corresponding diphenyl ethers, which were compared with authentic samples prepared by independent methods. Details are found in the Experimental section.

The product obtained by nitration of 3-nitro-2,4-dimethyldibenzofuran (VII) with concentrated nitric acid at room temperatures was a mixture containing at least two dinitro derivatives. The isomer which appeared to be present in greatest amount (isolated 25% pure, m.p. 231°) was 3,8-dinitro-2,4-dimethyldibenzofuran (IX)–identical in every respect to IX, prepared from VIII. A second isomer (m.p. 245°), was isolated in smaller amounts and was not obtained analytically pure.



The dinitration of 3-nitro-2,4-dimethyldibenzofuran (VII) occurred smoothly in fuming nitric acid at room temperature to give a single trinitro derivative (m.p. 254°) in 60% yield. This same trinitro derivative was also formed in 62% yield by nitration of 3,8-dinitro-2,4-dimethyldibenzofuran (IX); thus, this product is most probably 1,3,8-trinitro-2,4-dimethyldibenzofuran (X).

The nitration of 2,4-dimethyldibenzofuran (II) was also studied. With fuming nitric acid at 0–25°, X was isolated and appeared to be a major product. Nitration of II with concentrated nitric acid gave a mixture of mononitro derivatives which was not resolved; however a dinitroderivative, isomeric with IX, was isolated in low yield from this mixture.

EXPERIMENTAL[4]

6-Nitro-2,4-xylidine. Impure 6-nitro-2,4-acetoxylidide[5] (m.p. 148–170° from ethanol, 75% from 2,4-acetoxylidide,[5] 390 g., 1.87 moles) was dissolved in 6 l. of ethanol. Crystallization was induced by seeding with pure 6-nitro-2,4-acetoxylidide (m.p. 174–176°, reported 172°[5]), and allowing the solution to cool slowly over a period of 12 hr. The crystalline product (161 g.) was dissolved in concentrated sulfuric acid (200 ml.), and the acid solution was heated for 3 hr. on the steam bath and then poured onto ice. The red solid was washed with water until free of acid and air dried; weight 125 g., m.p. 68–70° (reported[5,6] m.p. 70, 76°). The alcohol filtrate was reduced to dryness and hydrolyzed with sulfuric acid (200 ml.) as described above. The dilute acid solution, after adding ice, was steam distilled (2 l. of distillate per hr.). From 36 l. of distillate there was collected 90 g. of product melting at 72–74°. The total yield of 6-nitro-2,4-xylidine obtained was 215 g. (69% based on impure starting material).

The acidic solution from the steam distillation was neutralized and the black solid was recrystallized from ethanol.

5-Nitro-2,4-xylidine (19.5 g., m.p. 120–122°, reported[7,8,9] 123°) was obtained and characterized by conversion to the acetate (m.p. 160–161°, reported[7] m.p. 162°) and the benzenesulfonate (m.p. 146–148°, reported[10], m.p. 148.5°).

4-Iodo-5-nitro-m-xylene was prepared from 6-nitro-2,4-xylidine essentially as previously described; yellow plates, 62% yield, m.p., 102–104° (reported,[5] m.p. 105°).

4-Bromo-5-nitro-m-xylene. 6-Nitro-2,4-xylidine (50 g., 0.301 mole) was diazotized in 34% hydrobromic acid (174 ml.) in water (150 ml.). The diazonium salt was treated with cuprous bromide (from 81.0 g., 0.231 mole of copper sulfate pentahydrate) at ice temperature, and the mixture was allowed to stand overnight at 25°. The crude product was purified by steam distillation from 4% aqueous sodium hydroxide. 4-Bromo-5-nitro-*m*-xylene was obtained as bright yellow crystals, m.p., 53–56° (reported,[5] m.p. 56°).

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(4) Melting points are corrected and were taken on a brass melting-point block.

(5) M. J. J. Blanksma, *Rec. trav. chim.*, **25**, 179 (1906).

(6) F. Ullmann and P. Sponagel, *Ann.*, **350**, 87 (1906).

(7) E. Noelting, A. Braun, and G. Thesmar, *Ber.*, **34**, 2253 (1901).

(8) E. Noelting and A. Colling, *Ber.*, **17**, 265 (1884).

(9) R. Fitting, W. Ahrens, and L. Mattheidas, *Ann.*, **147**, 18 (1868).

(10) G. T. Morgan and F. M. G. Micklewait, *J. Chem. Soc.*, **89**, 1296 (1889).

6-Nitro-2,4-xylenol, m.p. 70–72° (reported[11] m.p. 72°) was recovered from the alkaline residue.

4-Chloro-5-nitro-m-xylene was prepared from 6-nitro-2,4-xylidine (10 g., 0.061 mole) as described for the preparation of *o*-chlorotoluene.[12] Yellow crystals (10.0 g., 89% yield) recovered from the steam distillate melted at 49–50° after recrystallization from ethanol and water (reported[5,13] m.p. 52°, 51°).

6-Nitro-2,4-xylyl phenyl ether. 4-Bromo-5-nitro-*m*-xylene (39.5 g., 0.172 mole) was added to a solution of sodium phenoxide prepared from phenol (260 g., 2.75 moles) and potassium hydroxide (28.9 g., 0.515 mole). The resulting mixture was heated at vigorous reflux for 3 hr. during which time water was allowed to escape from the top of the air condenser. The mixture was allowed to stand overnight, sodium hydroxide (89 g.) and water (300 ml.) were added and the resulting mixture was distilled with steam. Unchanged starting halide (1.2 g.) was recovered from the distillate. The basic solution was cooled and 35.6 g. (88% yield) of yellow solid, m.p. 52–54°, was collected. The 6-nitro-2,4-xylyl phenyl ether was further purified by recrystallization from ethanol; light tan cubic crystals, m.p. 54–55°.

Anal. Calcd. for $C_{14}H_{13}O_3N$: C, 69.10; H, 5.39. Found: C, 69.30; H, 5.56.

Attempts to prepare 6-nitro-2,4-xylyl phenyl ether by condensation of 4-chloro-5-nitro-*m*-xylene with sodium phenoxide gave a red oil (40%), which did not crystallize, together with 60% recovery of unchanged halide. When copper acetate was added as catalyst only 11% of starting halide was recovered; however, the red oily product (82%) did not crystallize. Similar results were obtained when 4-iodo-5-nitro-*m*-xylene was employed. Only small amounts (10–20%) of red oily products were obtained, together with large quantities of unchanged starting halide (18–90%).

6-Acetamido-2,4-xylyl phenyl ether (IV). 6-Nitro-2,4-xylyl phenyl ether (26 g., 0.15 mole) in methanol (200 ml.) was reduced with hydrogen using 0.4 g. of platinum oxide catalyst. The red oil obtained from the methanol was dissolved in benzene containing acetic anhydride (12 ml.). The resulting mixture was allowed to stand overnight and was then treated with solid sodium carbonate. The light pink solid (26.3 g., 88%, m.p. 106–107°) obtained from the benzene was purified by recrystallization from ethanol. The white amide melted at 107–108°.

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71. Found: C, 75.22; H, 6.72.

2,4-Dimethyldibenzofuran (II) *and 6-hydroxy-2,4-xylyl phenyl ether* (V). A mixture of 6-acetamido-2,4-xylyl phenyl ether (5 g., 0.0194 mole) and aqueous sulfuric acid (15 ml., 1:1) was heated to reflux; the resulting solution was cooled, treated with ice (4 g.) and diazotization was accomplished by the addition of a cold solution of sodium nitrite (1.47 g., 0.0213 mole) in water (5 ml.). The resulting clear red solution was added dropwise to 100 ml. of refluxing 1:1 sulfuric acid-water. The acid solution was steam distilled to remove both II and some V. The oily product was dissolved in ether, the ether was removed, and the residue was steam distilled from 5% aqueous sodium hydroxide. The yellow oily distillate (2.40 g.) was not free of phenol. The oil was dissolved in petroleum ether (b.p. 30–60°) and extracted with 5% sodium hydroxide until no phenolic precipitate was obtained by acidification of the basic extract. Evaporation of the dried petroleum ether solution gave 1.75 g. (46%) of light yellow 2,4-dimethyldibenzofuran. This material gave white crystals, m.p. 42–43°, from ethanol.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.88, 86.10; H, 6.69, 6.41.

6-Hydroxy-2,4-xylyl phenyl ether (V, 0.35 g., 8.5%) was obtained from the basic extracts, and was purified by sublimation at atmospheric pressure; fine white needles, m.p. 83–85°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.74; H, 7.29.

2,4-Xylyl 2-nitrophenyl ether was prepared from potassium 2,4-xylenoxide (0.375 mole), and *o*-chloronitrobenzene (57.5 g., 0.365 mole) at 200–210°, essentially as previously described.[14] The tarry product was distilled with steam to remove unchanged *o*-chloronitrobenzene (~5 g.). The residue from the steam distillation was extracted with benzene, and the red solid obtained from the benzene extract was purified by recrystallization from ethanol. 2,4-Xylyl 2-nitrophenyl ether (51.5 g., 64%) was obtained as tan plates melting at 61–62° (reported m.p. 61–62°[14]).

2,4-Xylyl 2-aminophenyl ether (I) was prepared by a modification of a method previously described.[14] 2,4-Xylyl-2-nitrophenyl ether (20 g., 0.0825 mole) was reduced with hydrogen in a Parr shaker in methanol (200 ml.) using platinum oxide (0.5 g.) as catalyst. The calculated pressure drop (20 lb.) was observed in 15 min. The amine was isolated as a red oil which formed a white hydrochloride melting at 177–179°.

2,4-Dimethyldibenzofuran (II) *and 2-hydroxyphenyl 2,4-xylyl ether* (III). 2-Aminophenyl 2,4-xylyl ether (13.1 g., 0.0616 mole) was diazotized in 30% sulfuric acid (150 ml.) at 0° by the addition of sodium nitrite (4.67 g., 0.0675 mole) in water (16 ml.). The resulting mixture was added dropwise to refluxing 1:1 sulfuric acid (300 ml.), and the mixture was processed as previously described in this report. There was obtained 1.00 g. (8.3%) of 2,4-dimethyldibenzofuran, (mixed melting point from that obtained from IV was 42–43°), and 3.25 g. (24.6%) of 2-hydroxyphenyl 2,4-xylyl ether [III, m.p. 66–67° from petroleum ether (b.p. 30–60°)].

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.47; H, 6.90.

6-Acetamido-3-nitro-2,4-xylyl phenyl ether (VI). A solution of fuming nitric acid (4.5 ml., 0.1 mole) in glacial acetic acid (5.5 ml.) was added slowly to a solution of 6-acetamido-2,4-xylyl phenyl ether (5.0 g., 0.0194 mole) in glacial acetic acid, and the reaction mixture was stirred at 60° for 2 hr. The resulting mixture was poured into water and the solid was collected, washed free of acid, and dried. The crude product (5.40 g.) was dissolved in a minimum of hot ethanol (27 ml.), and the red solid (4.00 g., 68% yield, m.p. 142–143.5°) which separated from the cooled solution was collected. This material was subsequently proved to be 6-acetamido-3-nitro-2,4-xylyl phenyl ether (VI, orange cubic crystals, m.p. 144–145° from ethanol).

Anal. Calcd. for $C_{16}H_{16}O_4N_2$: C, 63.99; H, 5.37. Found: C, 64.04; H, 5.08.

The mother liquor was concentrated, and the residual solid was chromatographed on alumina with benzene. Two products were obtained: additional 6-acetamido-3-nitro-2,4-xylyl phenyl ether (0.89 g., total yield 84%), and an isomer of VI (0.25 g., 4% yield, m.p. 203–203.5° from ethanol).

Anal. Calcd. for $C_{16}H_{16}O_4N_2$: C, 63.99; H, 5.37. Found: C, 64.21; H, 5.51.

Proof of structure of 6-acetamido-3-nitro-2,4-xylyl phenyl ether (VI). *1. Deamination of 3-nitro-2,4-xylyl phenyl ether.* A mixture of 6-acetamido-3-nitro-2,4-xylyl phenyl ether (3.00 g.) and 7% aqueous hydrochloric acid (25 ml.) containing ethanol (2 ml.) was refluxed for 1 hr., and the acid solution was neutralized by the addition of excess solid sodium acetate. The solid crude amine (2.65 g.) was collected and washed with water. Crude amine (2.00 g.) was dissolved in a solution containing concentrated hydrochloric acid (3 ml.) and water (6 ml.). A solution of sodium nitrite (1 g.) in water (3 ml.) was added to the acid solution, and the cold (0°) mixture was stirred for 0.5 hr. A cold solution of hypophosphorous acid prepared from sodium dihydrogen hy-

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(11) B. Francke, *Ann.*, **296**, 199 (1897).

(12) L. Fieser, *Experiments in Organic Chemistry*, Heath, N. Y., 1935, pp. 213–216.

(13) A. Klages, *Ber.*, **29**, 311 (1896).

(14) J. D. C. Mole and E. E. Turner, *J. Chem. Soc.*, **1720** (1939).

pophosphite (10. g.) and a 1:1 mixture (20 ml.) of concentrated hydrochloric acid and water, was added to the diazonium salt and the mixture was stored at 10° for 24 hr. The precipitate (1.90 g.) was recrystallized from ethanol to give yellow crystals of 3-nitro-2,4-xylyl phenyl ether, m.p. 60–61°. This material was identical (melting point and mixed melting point) with authentic 3-nitro-2,4-xylyl phenyl ether, prepared as described below.

2. *Authentic 3-nitro-2,4-xylyl phenyl ether.* A mixture prepared from phenol (42.5 g., 0.45 mole), potassium hydroxide (6.00 g., 0.09 mole) and copper acetate (0.60 g., 0.003 mole) was dried by distilling 3.0 g. of phenol and water. 4-Bromo-2-nitro-*m*-xylene (6.90 g., 0.03 mole) was added, and the resulting mixture was heated at the reflux temperature for 1 hr., and at 25° for 3 days. Water was added, and the warm solution was treated with a solution of sodium hydroxide (15.0 g., 0.375 mole) and water (200 ml.). The resulting solution was distilled with steam to remove unchanged halide (1.53 g.) and the residue from the distillation was extracted with ether. Crude 3-nitro-2,4-xylyl phenyl ether (5.09 g., 70%) was recovered from the ether solution, and the pure product melted at 60–61° after several recrystallizations from ethanol. This material caused no depression in melting point when admixed with the product described in the preceding section.

Anal. Calcd. for $C_{14}H_{13}O_3N$: C, 69.13; H, 5.39. Found: C, 69.02; H, 5.51

3-Nitro-2,4-dimethyldibenzofuran (VII). The conversion of 6-acetamido-3-nitro-2,4-xylyl phenyl ether (VI, 4.0 g., 0.0133 mole) into 3-nitro-2,4-dimethyldibenzofuran (VII) was carried out by a procedure essentially identical to that described for the conversion IV to II, previously described. The product VII was recovered from the steam distillate and, subsequent to recrystallization from ethanol was obtained as yellow needles (1.20 g., 37% yield, m.p. 107–108°).

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60. Found: C, 69.56; H, 4.80.

6-Acetamido-3-nitro-2,4-xylyl 4-nitrophenyl ether (VIII). 6-Acetamido-2,4-xylyl phenyl ether (5.0 g., 0.0194 mole) was added in portions to an ice cold mixture of fuming nitric acid (12 ml.) and concentrated nitric acid (2 ml.). After 1 hr. the nitration mixture was added to ice, and the solid (6.57 g., m.p. 153–167°) was recrystallized from ethanol to give 3.16 g. (47% yield) of tan needles melting at 176–181°. The melting point of VIII was 177–180° after further recrystallization of the product from ethanol.

Anal. Calcd. for $C_{16}H_{15}N_3O_6$: C, 55.56; H, 4.38. Found: C. 55.81; H, 4.76.

The red oil obtained from the mother liquor was dissolved in benzene and chromatographed on a 6-in. column of alumina; benzene was used to develop and elute the column. Small amounts of VIII (> 0.5 g.) were eluted first, followed by a small amount (0.21 g., m.p. 179–180° after recrystallization from benzene; mixed melting point with VII was depressed) of an isomer of VIII.

Anal. Calcd. for $C_{16}H_{15}N_3O_6$: C, 55.65; H, 4.38. Found: C, 55.87; H, 4.59.

Proof of structure of 6-acetamido-3-nitro-2,4-xylyl 4-nitrophenyl ether (VIII). 1. *Deamination of* VIII *to 3-nitro-2,4-xylyl 4-nitrophenyl ether.* The amide VIII (2.45 g., 0.0071 mole) was hydrolyzed to the corresponding amine by action (15 min.) of a hot (reflux) mixture of 1:1 aqueous sulfuric acid (10 ml.). The resulting solution was treated with nitrous acid, and subsequently with hypophosphorous acid, essentially as previously described for the deamination of VI. The resulting solution was allowed to stand in an ice chest for 2 days, and crude 3-nitro-2,4-xylyl 4-nitrophenyl ether (1.65 g., 80% yield, m.p. 81–85°) was collected, and purified by several recrystallizations from ethanol. 3-Nitro-2,4-xylyl 4-nitrophenyl ether was obtained as yellow monoclinic crystals melting at 90–91°; a mixture melting point with a sample prepared as described below was 90–91°.

Anal. Calcd. for $C_{14}H_{12}N_2O_5$: C, 58.34; H, 4.19. Found: C, 58.47; H, 4.29.

2. *Authentic 3-nitro-2,4-xylyl 4-nitrophenyl ether.* a. *3-Nitro-2,4-xylidine.* The reduction of 2,4-dinitro-*m*-xylene[15] (19.6 g., 0.10 mole, m.p. 82–84°, reported 83–84°) in methanol (150 ml.) was carried out with sodium hydrosulfide[16] (from sodium sulfide nonahydrate, 14.0 g., 0.166 mole in methanol and water, 230 ml.) by a procedure similar to that described[17] for the reduction of *m*-dinitrobenzene. The mixture was heated at reflux for 1 hr., methanol (200 ml.) was removed by distillation, and the residue was added to cold water (500 ml.). The crude, yellow crystalline solid (15.1 g., 91%, m.p. 64–77°) was purified by recrystallization from ethanol. Pure 3-nitro-2,4-xylidine (53% yield) melted at 80–81° (reported[15] m.p. 81–82°) and was further characterized by conversion to the acetate (m.p. 147–148°, reported m.p. 149°,[18] 147°[5]).

b. *3-Nitro-2,4-xylenol.* A cooled slurry prepared originally from 3-nitro-2,4-xylenol (50 g., 0.30 mole) and hot 1:1 aqueous sulfuric acid (150 ml.) was diazotized in the usual manner when a solution of sodium nitrite (24.0 g., 0.35 mole) in water (50 ml.) was added below the surface of the stirred mixture over a period of 1 hr. The clear diazonium salt solution was added slowly to refluxing aqueous sulfuric acid (1:1, 300 ml.), and reflux was maintained for 1 hr. The tar, which separated from the cold solution, was treated with aqueous (200 ml.) sodium hydroxide (17.0 g., 0.03 mole) to separate phenolic material, and the alkaline filtrate was acidified. The phenolic precipitate, containing inorganic salts, was extracted with benzene. The extract was treated with Darco, filtered, and cooled. 3-Nitro-2,4-xylenol (22.0 g., 44% yield, m.p. 100–104°) separated as a tan precipitate and melted at 108–109° after further recrystallization from benzene.

Anal. Calcd. for $C_8H_9NO_3$: C, 57.48; H, 5.43. Found: C, 57.40; H, 5.73.

The p-nitrobenzoate of 3-nitro-2,4-xylenol was prepared in the usual way and recrystallized from benzene; white needles, m.p. 147–148°.

Anal. Calcd. for $C_{15}H_{12}O_6N_2$: C, 56.96; H, 3.83. Found: C, 57.36; H, 4.10.

c. *3-Nitro-2,4-xylyl 4-nitrophenyl ether.* The solid, obtained by evaporation of water from a mixture of 3-nitro-2,4-xylenol (5.0 g., 0.03 mole) and aqueous potassium hydroxide (containing 2.00 g., 0.03 mole of potassium hydroxide), was dried at 160°. Copper acetate (0.5 g.) and *p*-chloronitrobenzene (9.5 g., 0.06 mole) were added, and the mixture was maintained at 190–200° for 1 hr. The mixture was distilled with steam to remove unchanged starting halide (5.1 g.), and the residue was dissolved in benzene and decolorized with Norite. 3-Nitro-2,4-xylyl 4-nitrophenyl ether (1.18 g., 14%, m.p. 90–91°) was recovered from the benzene solution, which was identical to the sample prepared, as described above, from VIII.

Mononitration of 3-nitro-2,4-dimethyldibenzofuran (VII). Concentrated nitric acid (10 ml.) was cooled (0–5°) in an ice bath and VII (0.60 g., 0.0025 mole) was added. The acid solution was removed from the ice bath, allowed to stand at 25° for 20 hr., and then poured into water. The resulting solid was washed free of acid and dried; 0.65 g., m.p. 182–192°. Recrystallization of this product from benzene afforded 0.18 g. (25% yield) of material melting at 231–232°.

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 59.18, 58.69; H, 3.98, 4.10.

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(15) E. Noelting, A. Braun, and G. Thesmar, *Ber.*, **34**, 2260 (1901).

(16) H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 242 (1948).

(17) H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 1316 (1949).

(18) E. Grevingk, *Ber.*, **17**, 2426 (1884).

The melting point of a mixture of this solid and authentic 3,8-dinitro-2,4-dimethyldibenzofuran (IX) (m.p. 231-232°) was 231-232° (micro-melting stage).

The solid (0.55 g.) recovered from the mother liquor of recrystallization was recrystallized using the James method[19]; however, no analytically pure isomers were obtained. Additional quantities of IX were separated, together with a small amount of (0.08 g.) of a product melting at 226-227° which depressed the melting point when admixed with IX. A second product, m.p. 245-246°, seemed to be present in significant amounts, and the analysis suggests that it is an isomer of IX.

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 59.27; H, 3.46.

Dinitration of 3-nitro-2,4-dimethyldibenzofuran. 3-Nitro-2,4-dimethyldibenzofuran (0.60 g., 0.0025 mole) was added to cold (ice bath) fuming nitric acid (6 ml.). The ice bath was removed, and after 1 hr. at room temperature, the mixture was added to 50 ml. of water and ice. The resulting white solid was washed free of acid, dried, and recrystallized from benzene. There was obtained 0.49 g. (60%) of colorless tetragonal crystals, which melted at 250-252°. The melting point was raised to 254-255° by additional recrystallization from benzene.

Anal. Calcd. for $C_{14}H_9O_7N_3$: C, 50.76; N, 2.73. Found: C, 51.05; H, 2.77.

The analysis establishes this product to be a trinitro derivative, and subsequent experiments suggest structure X.

Mononitration of 3,8-dinitro-2,4-dimethyldibenzofuran. 3,8-Dinitro-2,4-dimethyldibenzofuran (IX, 0.10 g., 0.00029 mole), derived from VIII, was nitrated as described above. The crude product (m.p. 250-251°) was recrystallized from benzene, and 0.07 g. (62%) of colorless tetragonal plates, m.p. 253-254°, was obtained. A mixture melting point of this material and that described above was 254-255°.

Nitration of 2,4-dimethyldibenzofuran with fuming nitric acid. (a). 2,4-Dimethyldibenzofuran (II, 0.60 g., 0.0036 mole) was added slowly (5 min.) to cold (ice bath) fuming nitric acid (6 ml.). The mixture was allowed to stand for 5 min., was poured onto ice, and the solid was collected and washed free of acid. Recrystallization of this product from benzene gave 0.24 g. (25% yield) of nearly colorless, tetragonal crystals melting at 245-246°. The melting point was raised to 253-254° (0.16 g. recovery) after further recrystallization from benzene. This material was identical to the trinitro isomer (m.p. 254-255°, mixture m.p. 254-255°) designated structure X, obtained by dinitration of VII or mononitration of IX.

The residue from the mother liquor was recrystallized from ethanol (James[19] method), and a second trinitro derivative was isolated. This product melted at 210°.

Anal. Calcd. for $C_{14}H_9O_7H_3$: C, 50.71; H, 2.73. Found: C, 50.90, 51.23; H, 3.15, 2.94.

(b) In another experiment impure II (0.480 g.), containing some phenol V was nitrated essentially as described above. The principal product, insoluble in 80 ml. of boiling ethanol, melted at 231-232°, and was identified as 3,8-dinitro-2,4-dimethylbenzofuran (IX, m.p. and mixture m.p. 231-232°).

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 58.41 3.57.

Nitration of 2,4-dimethyldibenzofuran with concentrated nitric acid. Nitration of II (0.60 g., 0.0036 mole) with concentrated nitric acid (10 ml.) was carried out at ice bath temperature and the mixture was allowed to stand at 25° for 12 hr. The product (0.85 g.) melted at 106-136° and was not resolved by crystallization (benzene). A new dinitro derivative (colorless needles, 0.05 g., 6%, m.p. 251°) of II was isolated.

Anal. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52. Found: C, 58.78; H, 3.52.

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[19] C. James, *J. Am. Chem. Soc.*, 30, 184 (1908).

Neighboring Group Reactions. III. Structural and Stability Relationships between Two Geminally-substituted γ-Lactones

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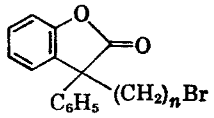
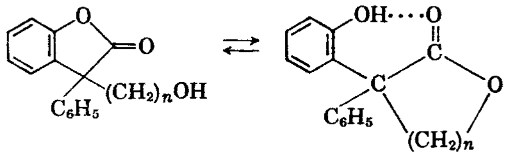
During the study of the chemical behavior of the two bromides Ia,b (and the corresponding chlorides), there was isolated from each homolog a product with elementary composition corresponding to the replacement of the halogen by hydroxyl.[1] The product obtained from Ia was a solid m.p. 159-161°, and the one derived from Ib (or the corresponding chloride) was an oil, b.p. 193-195° (1 mm.), n_D^{25} 1.5830. The main purpose of this work was to show by both chemical and spectral means that the solid product has structure IIIa and the liquid, structure IIb. Semiquantitative infrared studies were also carried out to provide an estimate of the interconvertibility within these two lactone systems.



Ia. $n = 2$.
Ib. $n = 3$.



IIa, $n = 2$.
IIb, $n = 3$.
IIIa, $n = 2$.
IIIb, $n = 3$.

The chemical evidence merely serves to show that the products are indeed lactones, and that no skeletal rearrangements have occurred during their formation. Thus, treatment of IIb with methanolic potassium hydroxide gave a potassium salt of an acid which on acidification yielded an unstable hydroxy acid that slowly reverted to the original lactone; and, by the action of hydrobromic acid, IIb was readily converted to the bromide Ib. Treatment of IIIa with hydrobromic acid likewise

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(1) H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, 26, (1961).