

Experimental

Melting points were taken as previously described.³

2-Hydroxy-4-nitrobenzenephosphonic Acid.—2-Methoxy-4-nitrobenzenephosphonic acid (15 g.) was refluxed for 28 hours in 75 ml. of 40% hydrobromic acid. The solvent was concentrated *in vacuo* to a volume of 5 ml. and cooled. Aqueous potassium hydroxide (50%) was added until the solution reached approximately pH 2 and the mixture was again cooled. The hemi-potassium salt of 2-hydroxy-4-nitrobenzenephosphonic acid precipitated and was removed by filtration. This salt was dissolved in 10% hydrochloric acid and the solution evaporated to dryness. The phosphonic acid was extracted from the residue with ether, and the ether solution evaporated to dryness. The resulting acid was finally recrystallized from 6 *N* hydrochloric acid. The yield of pale yellow crystals was 4 g., 29%, m.p. 202–204°.

Anal. Calcd. for C₆H₆NO₆P: N, 6.39; P, 14.14. Found: N, 6.37; P, 13.96.

2-Hydroxy-4-aminobenzenephosphonic.—The preceding compound (3.7 g.) was dissolved in 50 ml. of 10% hydrochloric acid and reduced with platinum oxide and hydrogen at 40 lb. pressure in a low-pressure catalytic hydrogenation apparatus. When the reduction was complete, the catalyst was removed and the filtrate was adjusted to pH 3.8 with sodium acetate. The desired amino acid slowly crystallized from solution. The crystals were washed with cold water and dried *in vacuo*. The yield was 2.13 g., 67%, m.p. 210–212°.

Anal. Calcd. for C₆H₈NO₄P: N, 7.41; P, 16.38. Found: N, 7.34; P, 16.00.

2-Methoxy-4-aminobenzenephosphonic Acid.—2-Methoxy-4-nitrobenzenephosphonic acid was suspended in water and sufficient sodium hydroxide added to dissolve the acid (the pH of the solution was 8). The nitro group was reduced with Raney nickel and hydrogen at 40 lb. pressure. The catalyst was removed and the free acid precipitated by acidifying the filtrate to pH 2. The compound was recrystallized from 10% hydrochloric acid containing a trace of sulfur dioxide to prevent oxidation of the amino group. The yield was 86%, m.p. 212–214°.

Anal. Calcd. for C₇H₁₀NO₄P: N, 6.90; P, 15.25. Found: N, 6.69; P, 14.94.

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VENEREAL DISEASE EXPERIMENTAL LABORATORY
U. S. PUBLIC HEALTH SERVICE
SCHOOL OF PUBLIC HEALTH
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.

Reactions of Di-*t*-butoxydiaminosilane¹

By P. D. GEORGE, L. H. SOMMER AND F. C. WHITMORE²
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The reactions of di-*t*-butoxydiaminosilane with water, alcohols, amines and carboxylic acids have been described³ and the preparation of di-*t*-butoxybis-aminoalkoxysilanes through interaction of the diaminosilane with aminoalcohols has been reported.⁴ Some extensions of this work have also been presented.⁵ We now wish to describe the reactions of di-*t*-butoxydiaminosilane with a number of other reagents. The reactions of di-*t*-butoxydiaminosilane with acidic materials ranged all the

(1) Paper 36 in a series on organosilicon compounds. For paper 35 see *THIS JOURNAL*, **75**, 6337 (1953).

(2) Deceased.

(3) (a) C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947); (b) G. W. Pedlow, Jr., and C. S. Miner, Jr., U. S. Patents 2,566,363; 2,566,364; 2,566,365; 2,566,956 and 2,566,957, September 4, 1951.

(4) P. D. George, L. H. Sommer and F. C. Whitmore, *THIS JOURNAL*, **71**, 3254 (1949).

(5) E. Larsson and B. Smith, *Svensk Kem. Tid.*, **62**, 141 (1950).

way from: (1) simple intercondensation of amine groups to form organic polysilazanes, through (2) conversion of the amine groups to chloro substituents, and finally to (3) complete degradation to form *t*-butyl chloride, ammonium chloride and silicic acid. Upon being heated to about 200° in the presence of a little ammonium sulfate the diaminosilane underwent condensation with liberation of ammonia and was converted in high yield to a white crystalline cyclopolysilazane^{3a} which we identified as the trimer, hexa-*t*-butoxycyclotrisilazane.⁵ The diaminosilane reacted readily with a limited amount of hydrogen chloride to form di-*t*-butoxydichlorosilane in good yield. On the other hand the cyclic trimer gave with hydrogen chloride only a small amount of the dichlorosilane together with *t*-butyl chloride arising through cleavage of *t*-alkoxy groups from silicon. With hydrochloric acid the diaminosilane underwent incomplete degradation with the formation of *t*-butyl chloride, ammonium chloride and silicic acid.

The reactions of di-*t*-butoxydiaminosilane with ethylene chlorohydrin and ethylene cyanohydrin proceeded normally with evolution of ammonia and formation of the corresponding mixed orthosilicates bearing functional substituents in the alkyl groups. The compounds so obtained were di-*t*-butoxy-bis-(2-chloroethoxy)-silane and di-*t*-butoxy-bis-(2-cyanoethoxy)-silane.

Substantially no interaction of the diaminosilane occurred at 100° with ethylene oxide, nitromethane or acrylonitrile.

The infrared spectra of (*t*-BuO)₂Si(NH₂)₂, [(*t*-BuO)₂SiNH]₃, (*t*-BuO)₂Si(OCH₂CH₂Cl)₂ and (*t*-BuO)₂Si(OCH₂CH₂CN)₂ were determined and were found to be consistent with the structures presented. Absorption bands are tabulated in the Experimental part.

Experimental⁶

Materials.—The di-*t*-butoxydiaminosilane was obtained from the Minnesota Mining and Manufacturing Company and was redistilled before use, b.p. 96–97 at 32 mm., *n*_D²⁰ 1.4193, *d*₄²⁰ 0.9311.

Anal. Calcd. for C₈H₂₂O₂N₂Si: neut. equiv., 103; *M*R_D 55.68. Found: neut. equiv., 105; *M*R_D, 55.94.

The other reagents were high quality materials of commerce which were used without further purification.

Acidic Condensation.—In a 100-ml., round-bottom flask fitted with a reflux condenser was placed 20.0 g., 0.097 mole, of di-*t*-butoxydiaminosilane and 0.2 g. of ammonium sulfate. The reaction mixture was heated at 230° for one-half hour and ammonia was steadily evolved. Upon cooling the crude product solidified and was purified by recrystallization from a small quantity of acetone. There was obtained 14.4 g., 0.025 mole, 78% yield of white crystalline material m.p. 189–190° which was identified as hexa-*t*-butoxycyclotrisilazane, [(*t*-C₄H₉O)₂SiNH]₃.⁷

Anal. Calcd. for C₂₄H₅₇N₃O₆Si₃: N, 7.40; neut. equiv., 189; mol. wt., 568. Found: N, 7.34, 7.15; neut. equiv.,⁸

(6) Calculated molecular refractions were obtained by use of bond refractions given by K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and by E. L. Warrick, *THIS JOURNAL*, **68**, 2455 (1946); similar results may be obtained by use of the method of R. O. Sauer, *ibid.*, **68**, 954 (1946).

(7) This material was obtained previously in the same manner and was identified as [(*t*-C₄H₉O)₂SiNH]₃.^{4a} The cyclic trimer has also been obtained from the reaction of gaseous ammonia with di-*t*-butoxydichlorosilane in boiling carbon tetrachloride solution.⁶

(8) This value was obtained by allowing a 0.5-g. sample to stand overnight with 50 ml. of 0.1 *N* hydrochloric acid and then back-titrating to a methyl red end-point.

195; mol. wt.,⁹ 579 (Rast in camphor), 598 (ebullioscopic in benzene).

Anhydrous Hydrogen Chloride.—In a two-liter flask surrounded with an ice-bath and equipped with a mechanical stirrer, gas inlet tube, and exit tube protected with anhydrous calcium sulfate was placed 500 ml. of anhydrous benzene and 75 g., 0.36 mole, of di-*t*-butoxydiaminosilane. Passage of anhydrous hydrogen chloride gas for three hours until excess appeared at the exit tube resulted in the formation of a fine white solid. The total weight gain of the reaction mixture was 50 g.; theory for the formation of the dichlorosilane and ammonium chloride was 53 g. The solid was filtered with difficulty, washed with benzene and dried. The total weight was 40 g.; theory for ammonium chloride was 38.5 g. The major portion of crude product solution gelled upon standing at room temperature for 3 days. However, distillation of an aliquot immediately after the reaction had been completed had shown that the major product was 59 g., 0.24 mole, 67% yield of di-*t*-butoxydichlorosilane,³ b.p. 170–190°.

Anal. Calcd. for $C_8H_{18}O_2Cl_2Si$: neut. equiv., 123. Found: neut. equiv., 122.

Hexa-*t*-butoxycyclotrisilazane, 56 g. dissolved in 250 ml. of anhydrous benzene, was also treated with hydrogen chloride in the manner described above. The theoretical amount of ammonium chloride formed. Another product isolated was a liquid b.p. 50°, n_D^{20} 1.38, which contained no silicon and was reactive toward cold aqueous silver nitrate; the 11 g. of this material represented a 17% yield of *t*-butyl chloride—it is probable that much more was formed but was lost during the troublesome vacuum filtration of ammonium chloride. There was also isolated 6 g., 0.03 mole, 10% yield of crude di-*t*-butoxydichlorosilane, b.p. 175–195°.

Anal. Calcd. for $C_8H_{18}O_2Cl_2Si$: Cl, 29.0; neut. equiv., 123. Found: Cl, 27.7; neut. equiv., 129.

Hydrochloric Acid.—In a 200-ml. trident flask cooled in an ice-bath was placed 150 ml. of concentrated hydrochloric acid. The flask was equipped with a mechanical stirrer, dropping funnel and reflux condenser connected to a Dry Ice-cooled trap. Dropwise addition of 34.6 g., 0.17 mole, of di-*t*-butoxydiaminosilane with vigorous stirring gave a pasty reaction mixture from which some organic material distilled on warming. Frothing made it necessary to transfer the reaction mixture with 200 ml. of water to a larger flask from which steam distillation was continued. The total water-insoluble product weighed 17.6 g. after drying with anhydrous potassium carbonate, and it had b.p. 48–52°, n_D^{20} 1.3843. This material constituted a 58% yield of *t*-butyl chloride.

Ethylene Chlorohydrin.—In a 50-ml., round-bottom flask fitted with a reflux condenser protected by a drying tube was placed 15.0 g., 0.073 mole, of di-*t*-butoxydiaminosilane and 11.8 g., 0.146 mole, of ethylene chlorohydrin. A spontaneous reaction set in when the two-phase system was mixed; the temperature rose to 50°, gas was evolved, and there was a 2.1-g. loss due to frothing. The reaction temperature was then raised to 210° over a period of half an hour. At the end of this time the crude product contained no basic nitrogen titratable with hydrochloric acid and methyl red. After having been filtered free of 0.1 g. of discolored solid, the crude product was distilled. There was obtained 12.8 g., 0.038 mole, 53% yield of colorless liquid, b.p. 263–268° at 735 mm., n_D^{20} 1.4250–1.4255, subsequently identified as di-*t*-butoxy-bis-(2-chloroethoxy)-silane.

A second preparation was made with crude di-*t*-butoxydiaminosilane containing about 50% intercondensed silazanes. In this case 65.5 g., 0.80 mole, of ethylene chlorohydrin was added with shaking over a period of 5 minutes to 82 g. of the crude diaminosilane. Ammonia was evolved and the temperature rose to 50°. The temperature was raised to 155° over a period of one hour and the reaction mixture was heated at reflux for one hour more; the weight loss was 11 g. at the end of this time, and heating for an additional half-hour resulted in no further weight loss. After removal of a little discolored solid by filtration, the 122 g. of crude product was fractionally distilled. In addition to unreacted ethylene chlorohydrin there was obtained 48.0 g., 0.14 mole, 72% yield (based on diaminosilane) of

di-*t*-butoxy-bis-(2-chloroethoxy)-silane, b.p. 134–135° at 10 mm., n_D^{20} 1.4250, d_4^{20} 1.067.

Anal. Calcd. for $C_{12}H_{26}O_4Cl_2Si$: Cl, 21.27; mol. wt., 333; R_D 0.2401. Found: Cl, 21.1; mol. wt., 367, 317, 388; R_D , 0.2397.

Ethylene Cyanohydrin.—When 11.0 g., 0.155 mole, of ethylene cyanohydrin was dissolved in 15.0 g., 0.073 mole, of di-*t*-butoxydiaminosilane, the temperature rose somewhat and gas was evolved. During heating to 200° over a period of 10 minutes it was necessary to heat the upper walls of the flask in order to suppress frothing. After 20 minutes heating at 200° the theoretical weight loss for ammonia had been realized, and distillation of the dark orange crude product gave 14 g., 0.045 mole, 60% yield of liquid b.p. 300–302° at 740 mm., n_D^{20} 1.420–1.421, which was subsequently identified as di-*t*-butoxy-bis-(2-cyanoethoxy)-silane.

A second preparation was made from crude di-*t*-butoxydiaminosilane containing about 50% intercondensed silazanes. In this case 57 g., 0.80 mole, of ethylene cyanohydrin was added over a period of 15 minutes with shaking to 82 g. of the crude diaminosilane. The temperature rose to 45° and the rate of addition was controlled by the degree of frothing. The temperature was raised to 195° over a period of one hour and refluxing was continued for one-half hour at this temperature. After this treatment the weight loss was 12 g., and heating for one-half hour more gave no further weight loss. The reaction mixture was filtered with diatomaceous earth, and the resulting 111 g. of clarified crude product was fractionally distilled. There was obtained 34 g., 0.11 mole, 55% yield (based on diaminosilane) of di-*t*-butoxy-bis-(2-cyanoethoxy)-silane, b.p. 126° at 0.3 mm., n_D^{20} 1.4222–1.4225, d_4^{20} 1.0162.

Anal. Calcd. for $C_{14}H_{26}O_4N_2Si$: N, 8.91; mol. wt., 314; R_D , 0.2524. Found: N, 8.9; mol. wt., 373, 324, 367; R_D , 0.2502.

Ethylene Oxide.—Passage of 60 g. of ethylene oxide gas over a period of one hour through di-*t*-butoxydiaminosilane at 100° resulted in no reaction. The ethylene oxide was completely recovered and the diaminosilane showed no gain in weight.

Nitromethane.—Refluxing 11.8 g. of di-*t*-butoxydiaminosilane with 7.0 g. of nitromethane for one-half hour resulted in the recovery of unreacted nitromethane, 4.7 g., 83%, b.p. 98–104°. The diaminosilane was converted to a black solid consisting presumably of silazane condensation products.

Acrylonitrile.—Refluxing 15.0 g. of di-*t*-butoxydiaminosilane with 7.5 g. of acrylonitrile at 90° for one hour resulted in the recovery of 6.9 g., 90%, unreacted acrylonitrile, 7.9 g., 50%, unreacted diaminosilane, and a still residue consisting presumably of silazane condensation products.

Infrared Spectra.—The infrared spectra of the following compounds were determined with a Perkin-Elmer recording spectrophotometer¹⁰: $(t\text{-BuO})_2\text{Si}(\text{NH}_2)_2$, $[(t\text{-BuO})_2\text{Si}(\text{NH})]_3$, $(t\text{-BuO})_2\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_2$ and $(t\text{-BuO})_2\text{Si}(\text{OCH}_2\text{CH}_2\text{CN})_2$. All were done in liquid phase at 0.03 mm. thickness except for the trimeric silazane which was done in 10% carbon tetrachloride and 2% carbon disulfide solutions at 0.10 mm. thickness.

All four compounds exhibited absorption bands at the following wave lengths in μ : 3.38 (vs), 6.80 (m), 6.85 (m), 7.22 (vs), 7.33 (vs), 8.08 (vs), 8.40–8.45 (vs), 9.73–9.78 (vs).

In addition each compound exhibited absorption bands at the following wave lengths in μ :

$(t\text{-BuO})_2\text{Si}(\text{NH}_2)_2$: 2.82(m), 295(s), 5.93(w), 6.45(vs), 9.52(vs), 11.15(vs), 12.80(s), 14.80(s)
 $[(t\text{-BuO})_2\text{Si}(\text{NH})]_3$: 2.93(m), 6.45(s), 8.20(s), 8.55(vs), 9.50(vs), 10.53(vs), 12.09(m), 12.93(m), 14.52(m)
 $(t\text{-BuO})_2\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_2$: 3.46(s), 3.65(w), 7.00(m), 7.68(s), 9.38(vs), 10.43(s), 10.76(vs), 12.00(vs), 12.18(m), 12.40(m), 12.90(s), 13.48(s), 14.28(s), 14.95(m), 15.10(m)
 $(t\text{-BuO})_2\text{Si}(\text{OCH}_2\text{CH}_2\text{CN})_2$: 3.45(vs), 3.63(w), 4.45(m), 7.06(m), 7.52(m), 9.10(m), 9.37(m), 10.72(vs), 11.98(vs), 12.18(s), 12.38(m), 12.92(vs), 13.41(s), 14.28(m)

vs = very strong, s = strong, m = medium, w = weak.

Acknowledgment.—We are grateful to the Min-

(10) The infrared spectra were kindly determined for us by C. A. Hirt of the General Electric Research Laboratory.

(9) The trimeric structure was also supported by cryoscopic determinations in benzene, but the reproducibility was poor; found: 464, 563, 624.

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THE WHITMORE LABORATORY
DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA.

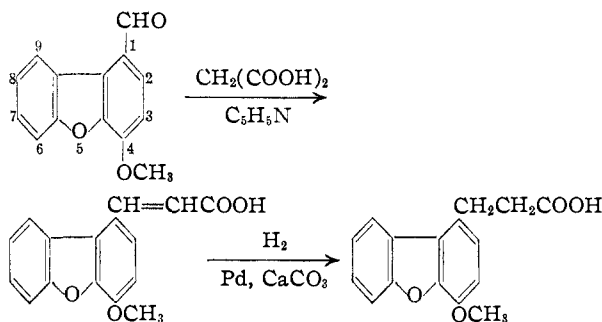
The Preparation of Some Substituted 1-Dibenzofuranpropionic and -Butyric Acids

BY HENRY GILMAN, SOUREN AVAKIAN, JOHN A. HOGG AND
ROBERT G. JOHNSON

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In connection with studies concerning the possible bridging of the 1- and 9-positions of dibenzofuran, we have prepared some previously unreported 1-substituted dibenzofurans. Appropriately substituted dibenzofurans were acylated by means of the Friedel-Crafts reaction employing succinic anhydride¹; several of the keto acids have been reduced to the corresponding dibenzofuranbutyric acids. Acylation was directed to the 1-position² by a methoxyl group in the 4-position as well as by the use of the solvent system, nitrobenzene-tetrachloroethane.³

The introduction of a three-carbon side chain in the 1-position was accomplished by means of the Knoevenagel reaction with 4-methoxy-1-dibenzofuran-carboxaldehyde and malonic acid. The substituted acrylic acid so formed was catalytically reduced to the dibenzofuranpropionic acid.⁴



Experimental⁵

The substituted dibenzofuroylpropionic acids (Table I) were prepared by the procedure previously described² for the synthesis of β -(2-dibenzofuroyl)-propionic acid.

The reductions to the corresponding dibenzofuranbutyric acids (Table II) were carried out by means of a modified Clemmensen reaction.² β -(2-Bromo-4-methoxy-1-dibenzofuroyl)-propionic acid was dehalogenated under conditions of the reduction and yielded γ -(4-methoxy-1-dibenzofuran)-butyric acid.

γ -(3-Nitro-4-methoxy-1-dibenzofuran)-butyric Acid.—A solution of 4.0 g. (0.014 mole) of γ -(4-methoxy-1-dibenzofuran)-butyric acid in 100 ml. of glacial acetic acid was heated on the steam-bath to 40–45°, and 4 ml. of fuming

(1) E. Berliner in R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, Chapter 5.

(2) Dibenzofuran itself yields β -(2-dibenzofuroyl)-propionic acid on treatment with succinic anhydride and aluminum chloride; see H. Gilman, P. T. Parker, J. C. Bailie and G. E. Brown, *THIS JOURNAL*, **61**, 2836 (1939).

(3) Reference 1, p. 241.

(4) The dibenzofuranpropionic and -butyric acids were cyclized to give ketones in good yield. Such cyclization presumably could take place at either the 2- or 9-position. The results of studies on the structures of these cyclic ketones will be reported later.

(5) All melting points are uncorrected.

TABLE I

SUBSTITUTED PROPIONIC ACIDS

-Propionic acid	Empirical formula	Yield, %	M.p., °C.	Analyses, % Calcd.	Analyses, % Found
β -(4-Methoxy-1-dibenzofuroyl)-	C ₁₇ H ₁₄ O ₃	92	224–225	C, 68.45 H, 4.69	C, 68.71 H, 4.98
β -(4,6-Dimethoxy-1-dibenzofuroyl)-	C ₁₈ H ₁₆ O ₄	91	241–242	a	
β -(2-Bromo-4-methoxy-1-dibenzofuroyl)-	C ₁₇ H ₁₃ BrO ₃	71	194–195	Br, 21.22	Br, 21.36

a Calcd.: methoxyl, 18.90, neut. equiv., 328. Found methoxyl, 18.97; neut. equiv., 332.

TABLE II

SUBSTITUTED BUTYRIC ACIDS

-Butyric acid	Empirical formula	Yield, %	M.p., °C.	Analyses, % Calcd.	Analyses, % Found
γ -(4-Methoxy-1-dibenzofuran)-	C ₁₇ H ₁₆ O ₃	81	165	C, 71.83 H, 5.63	C, 71.93 H, 5.81
γ -(4,6-Dimethoxy-1-dibenzofuran)-	C ₁₈ H ₁₈ O ₄	42	197–198	C, 68.79 H, 5.73	C, 68.87 H, 5.89
γ -(3-Nitro-4-methoxy-1-dibenzofuran)- ^a	C ₁₇ H ₁₅ NO ₃	44	169–170	C, 62.00 H, 4.59	C, 61.67; 61.84 H, 4.62; 4.47

a Calcd.: N, 4.25. Found: N, 4.10.

nitric acid (sp. gr., 1.50) was added with stirring. After one hour, the solution was allowed to cool, and the precipitated nitro compound was filtered off. Recrystallization from glacial acetic acid gave 2.0 g. (44%) of pure compound, m.p. 169–170°.

Procedures for Structure Determination.—(a) Oxidation of β -(4-methoxy-1-dibenzofuroyl)-propionic acid with alkaline potassium permanganate solution gave a product which did not depress the melting point when mixed with an authentic specimen of 4-methoxy-1-dibenzofuran-carboxylic acid.²

(b) Four-tenths of a gram (0.0011 mole) of β -(2-bromo-4-methoxy-1-dibenzofuroyl)-propionic acid was suspended in 40 ml. of absolute ethanol with 1.0 g. of palladium-calcium carbonate catalyst⁶ and shaken for 30 minutes at room temperature under a pressure of 35 p.s.i. of hydrogen. After filtration, water was added to the filtrate; the precipitated material melted at 224–225°, both alone and in admixture with a specimen of β -(4-methoxy-1-dibenzofuroyl)-propionic acid prepared as reported above. The yield was quantitative.

(c) Oxidation of β -(4,6-dimethoxy-1-dibenzofuroyl)-propionic acid with alkaline potassium permanganate solution yielded material melting at 297–298° which did not depress the melting point of an authentic sample of 4,6-dimethoxy-1-dibenzofuran-carboxylic acid.⁷

(d) Alkaline potassium permanganate oxidation of γ -(3-nitro-4-methoxy-1-dibenzofuran)-butyric acid gave an acid melting at 269–270°. Decarboxylation⁸ at 200° in the presence of copper powder and quinoline yielded material melting at 194–194.5°. A mixed melting point with an authentic sample of 3-nitro-4-hydroxydibenzofuran⁹ was not depressed.

4-Methoxy-1-dibenzofuran-carboxaldehyde.—A mixture of 7.0 g. (0.035 mole) of 4-methoxydibenzofuran, 9.0 g. (0.059 mole) of freshly distilled phosphorus oxychloride and 9.0 g. (0.067 mole) of N-methylformanilide was heated on the steam-bath for 90 minutes with occasional shaking. The excess phosphorus oxychloride was hydrolyzed with a 10% solution of sodium acetate. The product solidified on cooling and was filtered off. Recrystallization from a 50:50 water-methanol solution gave 5.0 g. (63%) of white needles, m.p. 104–105°.

Anal. Calcd. for C₁₄H₁₀O₃: C, 74.33; H, 4.46. Found: C, 74.56, 74.57; H, 4.55, 4.51.

Neutral potassium permanganate oxidation of the aldehyde gave a 47% yield of 4-methoxy-1-dibenzofuran-carbox-

(6) M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916).

(7) H. Gilman and L. C. Cheney, *THIS JOURNAL*, **61**, 3149 (1939).

(8) A. F. Shepard, N. R. Winslow and J. R. Johnson, *ibid.*, **52**, 2083 (1930).

(9) H. Gilman, A. L. Jacoby and J. Swislow, *ibid.*, **61**, 954 (1939).