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A Convenient Synthesis of Two Dibenzofurans

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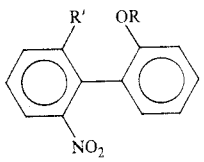
Abstract

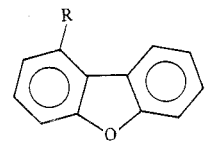
1-Nitrodibenzofuran (4) and dibenzofuran (5) have been prepared in high yield from 2′,6′-dinitrobiphenyl-2-ol (2) and 2′-nitrobiphenyl-2-ol (3), respectively, by a cyclization involving intramolecular displacement of a nitro group.

Introduction

Dibenzofurans substituted in the 2, 3, and 4 positions are available by a variety of methods. However, access to the 1-substituted dibenzofurans is much more difficult through conventional electrophilic substitution reactions.[1] Moreover, in a recent report,[2] Beck has reviewed the synthesis of various heterocyclic systems by displacement of nitro groups in appropriate substances. It seemed likely that the dibenzofuran system would be readily accessible from 2′-nitrobiphenyl-2-ols by analogous reactions. This expectation was realized for 1-nitrodibenzofuran (4) and dibenzofuran (5).



	R	R′
(1)	Me	NO_2
(2)	H	NO_2
(3)	H	H



(4) R = NO_2
(5) R = H

Results and Discussion

In earlier work,[3,4] we described a ready route to 2,6-dinitrobiphenyls by the condensation of 1,3-dinitrobenzene and aryl iodides in the presence of copper(I) t-butoxide. When these conditions were used to couple 2-iodoanisole and 1,3-dinitrobenzene, a good yield of the biphenyl (1) was obtained. Demethylation of the methyl

[1] 'Rodd's Chemistry of Carbon Compounds' (Ed. S. Coffey) 2nd Edn, Vol. 4A, p. 194.
[2] Beck, J. R., *Tetrahedron*, 1978, **34**, 2057.
[3] Cornforth, Sir John, Sierakowski, A. F., and Wallace, T. W., *J. Chem. Soc., Chem. Commun.*, 1979, 294.
[4] Cornforth, Sir John, Sierakowski, A. F., and Wallace, T. W., *J. Chem. Soc., Perkin Trans. 1*, 1982, 2299.

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ether (1) with pyridinium chloride then afforded a moderate yield of the phenol (2). No attempts were made to maximize the yield of this step by use of alternative demethylating reagents.

Conversion of the phenol (2) into 1-nitrodibenzofuran (4) was readily accomplished by treatment with sodium hydride in hexamethylphosphoric triamide at room temperature. The yield was excellent (98%), and isolation of the product proved facile. The present method thus gives a 52% overall yield of 1-nitrodibenzofuran (4) from 1,3-dinitrobenzene. The five-step sequence originally employed by Gilman and Swiss[5] gave the same substance in an overall yield of only 10% from dibenzofuran-4-carboxamide.

In an attempt to extend the scope of the copper-promoted coupling reaction, several substitutes for 1,3-dinitrobenzene (methyl 3-nitrobenzoate, benzene-1,3-dicarbonitrile and 3-nitrophenyl methoxymethyl ether) were tried but their use met with little success.[4] A fuller investigation along these lines is currently under way.[6]

However, the present method does allow access to a number of 1-nitro-substituted dibenzofurans by the choice of appropriately substituted 1,3-dinitrobenzenes and aryl iodides. The nitro group could then serve as a source of other functionalities, namely methoxy,[4] amino, hydroxy, halo and hydrogen, thus leading to a wider range of 1-substituted dibenzofurans.

The phenol (3) is readily available by the method of Colbert *et al.*[7] When this phenol was treated with sodium hydride in hexamethylphosphoric triamide at room temperature for 1 day, poor conversion into dibenzofuran (5) was achieved. However, on heating this mixture at 70° for 16 h, a good yield (82%) of dibenzofuran (5) was obtained.

Thus, from the preliminary results presented above, it is clear that electron-withdrawing substituents on the nitro-containing ring of the nitrobiphenylol will enhance cyclization to the dibenzofuran system.

Experimental

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points were determined on a Kofler hot stage and are uncorrected. Proton magnetic resonance spectra were recorded at 60 MHz on a Hitachi Perkin–Elmer R-24B instrument, with tetramethylsilane as an internal standard. Mass spectra were measured on a Varian MAT-CH7 instrument under the conditions stated in each case. Infrared spectra were recorded on a Perkin–Elmer 337 instrument. Merck Kieselgel GF_{254} was used for analytical thin-layer chromatography. Special conditions used in the purification of reagents and solvents for the condensation of 2-iodoanisole with 1,3-dinitrobenzene are described elsewhere.[4]

Preparation of 2-Methoxy-2′,6′-dinitrobiphenyl (1)

Freshly prepared potassium t-butoxide, from potassium (1·1 g) and t-butyl alcohol (30 ml), was dried at 100°/1 mm for 1 h. Under nitrogen, the white solid was suspended by stirring with freshly purified 1,2-dimethoxyethane (25 ml), cooled in an ice bath; freshly purified, powdered cuprous chloride (2·80 g) was then added over 10 min. The mixture was allowed to stir for 1 h at room temperature, treated with dry pyridine (3·0 ml), then treated with a solution of 1,3-dinitrobenzene (2·78 g, 16·5 mmol) in 1,2-dimethoxyethane (10 ml). After several minutes, 2-iodoanisole (4·25 g, 18·2 mmol) was added, and the stirred mixture heated at 80–90° (bath) for 24 h. The cooled mixture was poured into 5% aq. HCl (400 ml) and extracted with ethyl acetate. The organic

[5] Gilman, H., and Swiss, J., *J. Am. Chem. Soc.*, 1944, **66**, 1884.
[6] Wallace, T. W., personal communication.
[7] Colbert, J. C., Fox, D., and Skinner, W. A., *J. Am. Chem. Soc.*, 1953, **75**, 2249.

phase was separated, dried (Na_2SO_4) and evaporated. The residue was dissolved in warm dichloromethane, and the solution was filtered through a short plug (5 by 3 cm) of neutral alumina. The solid recovered after evaporation of the solvent was recrystallized from dichloromethane/methanol to afford 2-methoxy-2′,6′-dinitrobiphenyl (1) as yellow prisms (3·87 g, 85%), m.p. 146–147° (lit.[8] 146°). ^{1}H n.m.r. δ ($CDCl_3$) 3·65, 3H, s, OMe; 6·70–8·03, 7H, m, ArH. Mass spectrum (50°/70 eV): 274 (M, 100%), 181 (10), 140 (11), 139 (43), 127 (15), 115 (10), 113 (10).

Preparation of 2′,6′-Dinitrobiphenyl-2-ol (2)

An intimate mixture of the methyl ether (1) (0·40 g, 1·46 mmol) and pyridinium chloride (0·50 g, 4·33 mmol, 3 equiv.) was heated at 200–210° (bath) for 3 h. The mixture was cooled and then extracted successively with ethyl acetate and 10% aq. H_2SO_4. The organic phase (100 ml) was separated, washed with water, dried (Na_2SO_4) and evaporated. The residue was taken up in chloroform (*c.* 5 ml), and the mixture was filtered through a short column (2 by 3 cm) of neutral alumina to remove tarry impurities. The solvent was evaporated, and the residue recrystallized from aqueous methanol (charcoal) to afford *2′,6′-dinitrobiphenyl-2-ol* (2) as pale yellow needles (235 mg, 62%), m.p. 154–155° (Found: C, 55·0; H, 3·4; N, 10·5. $C_{12}H_8N_2O_5$ requires C, 55·4; H, 3·1; N, 10·8%). ^{1}H n.m.r. δ [$CDCl_3+(CD_3)_2SO$] 6·60–7·40, 4H, m, ArH; 7·45–7·80, 1H, m, ArH; 7·90–8·15, 2H, m, ArH; 9·55, 1H, s (br), OH, exchanged with D_2O. Mass spectrum (50°/70 eV): 260 (M, 100%), 169 (20), 164 (18), 141 (20), 140 (18), 139 (54), 128 (15), 127 (16), 115 (15), 114 (17), 102 (15). ν_{max} (Nujol) 3410, 1525, 1360 cm^{-1}.

Preparation of 1-Nitrodibenzofuran (4)

A solution of the phenol (2) (420 mg, 1·61 mmol) in hexamethylphosphoric triamide (5 ml) was added to a stirred suspension of sodium hydride (80 mg, 3·33 mmol) in hexamethylphosphoric triamide (2 ml) at room temperature. The deep mauve mixture was stirred for 2·5 h and then poured onto ice containing 0·5% aq. H_2SO_4 (100 ml). The pale yellow solid which precipitated was filtered off, washed with water and dried (vacuum pump). The solid was dissolved in dichloromethane (5 ml), and the solution was passed through a short column (2 by 3 cm) of neutral alumina. The solvent was evaporated, and the residue recrystallized from ethanol (trace of dichloromethane) as pale yellow needles (337 mg, 98%), m.p. 119–121° (lit.[5] 121°). ^{1}H n.m.r. δ ($CDCl_3$) 7·05–7·55, 4H, m, ArH; 7·67, 1H, dd, ArH, J_1 8, J_2 2 Hz; 8·00, 1H, dd, ArH, J_1 8, J_2 2 Hz; 8·40, 1H, dd, ArH, J_1 8, J_2 2 Hz. Mass spectrum (45°/70 eV): 213 (M, 84%), 183 (11), 167 (30), 155 (28), 139 (100), 127 (12), m* 116 (Calc. for 167 → 139: 115·7), 113 (15).

Preparation of Dibenzofuran (5)

A solution of the phenol (3)[7] (215 mg, 1·0 mmol) in hexamethylphosphoric triamide (1·5 ml) was added to a stirred suspension of sodium hydride (48 mg, 2·0 mmol) in hexamethylphosphoric triamide (2 ml), and the scarlet mixture was stirred at room temperature for 24 h. (T.l.c. analysis indicated partial conversion into product.) The mixture was heated at 70° (bath) for 16 h, cooled, and poured into 5% aq. HCl. The aqueous mixture was extracted with ether, and the ethereal phase separated and washed well with water. The organic phase was dried (Na_2SO_4), and the solvent evaporated to afford a cream solid. The solid was taken up in ether, and the mixture was filtered through a short column (2 by 3 cm) of neutral alumina to provide, after evaporation of the solvent, dibenzofuran (5) as colourless plates (138 mg, 82%), m.p. 79–81°. The sample was recrystallized from ethanol to afford plates, m.p. and m.m.p. 80–81° (with an authentic specimen). The synthetic and authentic samples of (5) had identical ^{1}H n.m.r. spectra.

Acknowledgments

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[8] Björklund, C., and Nilsson, M., *Acta Chem. Scand.*, 1968, **22**, 2338.