

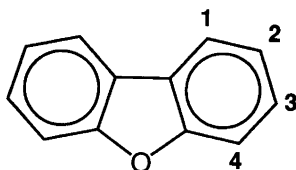
Direct Oxidative Acetoxylation of Dibenzofuran with Predominant Attack in the 3-Position[†]

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In a study of the photonitration of dibenzofuran (**1**),¹ data regarding the reactivity of (dibenzofuran)^{•+} toward nucleophiles were needed for a more detailed understanding of the photochemical processes.² Oxidative substitution by cyanide ion^{2a} showed prevalent attack at the 3-position of (dibenzofuran)^{•+}, as opposed to the characteristic electrophilic reactivity of dibenzofuran at mainly the 2-position. The Shaik–Pross CM model correctly predicts this pattern,³



in that the regioselectivity of nucleophilic attack upon (dibenzofuran)^{•+} should be determined by a combination of the triplet spin density in neutral dibenzofuran and by the LUMO coefficients of (dibenzofuran)^{•+}; for a non-alternant system like dibenzofuran this leads to different regioselectivity in the two cases.

Additional information on the reactivity of (dibenzofuran)^{•+} can be obtained from another well established oxidative substitution process, *viz.* acetoxylation, in which an electron transfer oxidant is used to oxidize a substrate in acetic acid in the presence of acetate ion. Here we report results from anodically, 12-tungstocobaltate(III)-, silver(II)- and cerium(IV)-induced acetoxylation of dibenzofuran. The results are given in Table 1. As required in this type of study, the degree of conversion was kept low (4–12 %) in order to avoid isomer distributions that might be distorted by over-oxidation. Two sets of GLC analyses are presented because 1- and 4-acetoxydibenzofuran could not be separated on any of the columns tried. The reaction mixtures were, instead, hydrolyzed to phenols and the latter converted into trimethylsilyl ethers in order to afford

separable derivatives. Authentic hydroxy- and acetoxydibenzofurans were prepared as described in the Experimental.

The first entry of Table 1 is anodic acetoxylation in HOAc/0.5 M NaOAc,⁴ yielding predominantly the 3-isomer (62 %), with 1-acetoxydibenzofuran as the second most abundant isomer (32 %). Almost identical results were obtained with the typical one-electron metal-ion oxidants, 12-tungstocobaltate(III)⁵ in HOAc/0.2 M NaOAc at ca. 100 °C, silver(I) acetate/peroxydisulfate/2,2'-bipyridyl⁶ in HOAc/0.1 M NaOAc at 40 °C and ammonium hexanitratocerate(IV)⁷ in HOAc at 40 °C.

The reactivities indicated by the data in Table 1 will be discussed in detail in forthcoming papers.^{1,8}

Experimental

Materials. Dibenzofuran (Aldrich, 99+ %), 2,4-di-*t*-butylphenol (Merck, 98+ %) and chlorotrimethylsilane (Fluka, 99+ %) were used without further purification. Dichloromethane (*Merck zur Rückstandsanalyse*), acetic acid (Baker, 100 %), acetyl chloride (Janssen, 98 %) and pyridine (Merck, 99 %) were used as supplied. 3-Aminodibenzofuran was obtained by Sn/HCl reduction of 3-nitrodibenzofuran.¹ Potassium 12-tungstocobaltate(III) was available from earlier work.⁵ All other chemicals were of highest commercial quality available and used as supplied.

Instrumentation. The GLC instrument² was equipped with a fused silica column (25 m, OV-1701). GLC/MS and MS spectral analysis were performed as previously reported.² Electrolyses were run at constant current (0.5 A) in a non-divided cell (Pt anode and cathode, physically separated by a polypropylene gauze). Column chromatography was performed on Silica Gel 60 (Merck) using pentane/dichloromethane as the eluent.

Synthesis of authentic acetoxydibenzofurans. 1-Acetoxydibenzofuran. 1-Hydroxydibenzofuran (prepared from 2,4-

[†] Part IV in a series on photonitration by tetranitromethane. For Part III, see Ref. 2b.

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Table 1. Isomer distributions from the oxidative acetoxylation of dibenzofuran by the anode and various one-electron oxidants.

Oxidant	Conversion (%)	Isomer distribution						
		Analyzed as acetates			Analyzed as Me ₃ Si ethers ^a			
		(1- + 4-)	2-	3-	1-	2-	3-	4-
Anode	10	30	4	66	32	3	62	3
Co ^{III} W ₁₂ O ₄₀ ⁵⁻	4	46	1	53	42	1	55	2
Ce ^{IV} (NO ₃) ₆ ²⁻	12	34	2	64	32	2	64	2
Ag(II)	5	29	1	70	Not determined			

^aAfter hydrolysis of the acetates, followed by trimethylsilylation of the resulting mixture of hydroxydibenzofurans.

di-*t*-butylphenol via bromination, oxidative coupling and removal of the *t*-butyl groups⁹) was heated for 10 min with a large excess of acetyl chloride. After evaporation, the residue was dissolved in dichloromethane, washed with water, dried and evaporated to yield 1-acetoxydibenzofuran as colorless crystals, m.p. 75–76 °C (hexane), lit.¹⁰ 76 °C. ¹H NMR (CDCl₃): 7.84 (dd, 1 H), 7.58 (d, 1 H), 7.47 (m, 3 H), 7.35 (dt, 1 H), 7.15 (M, 1 H), 2.52 (s, 3 H).

2-Acetoxydibenzofuran. 2-Hydroxydibenzofuran was prepared from 2,4-di-*t*-butylphenol as described¹¹ and converted into 2-acetoxydibenzofuran as described above. Colorless crystals, m.p. 139.5–140.5 °C (hexane), lit.¹² 115–116 °C. ¹H NMR (CDCl₃): 7.90 (dd, 1 H), 7.69 (d, 1 H), 7.56 (m, 2 H), 7.48 (t, 1 H), 7.31 (t, 1 H), 7.18 (dd, 1 H), 2.37 (s, 3 H).

3-Acetoxydibenzofuran. 3-Aminodibenzofuran was converted into the corresponding diazonium hydrogensulfate as described,¹³ and then treated with boiling aqueous copper(II) sulfate/copper(I) oxide to yield 3-hydroxydibenzofuran which was acetylated as before. Colorless needles, m.p. 118–118.5 °C (ethanol), lit.¹⁴ 111–115 °C. ¹H NMR (CDCl₃): 7.92 (d, 1 H), 7.91 (s, 1 H), 7.57 (d, 1 H), 7.45 (dt, 1 H), 7.35 (m, 2 H), 7.10 (dd, 1 H), 2.36 (s, 3 H).

4-Acetoxydibenzofuran. 4-Hydroxydibenzofuran was obtained via direct lithiation of dibenzofuran,^{15,16} followed by bubbling of oxygen into the suspension of 4-lithiodibenzofuran. The yield was low (10%) but sufficient for the purpose at hand; higher yields have been reported after conversion into the organomagnesium derivative.¹⁶ Acetylation (see above) gave 4-acetoxydibenzofuran as colorless plates, m.p. 101–102 °C (hexane), lit.¹² 99–100 °C. ¹H NMR (CDCl₃): 7.95 (dd, 1 H), 7.83 (dd, 1 H), 7.59 (dd, 1 H), 7.48 (dt, 1 H), 7.36 (m, 2 H), 7.23 (dt, 1 H), 2.47 (s, 3 H).

Acetoxylation of dibenzofuran. Anodic acetoxylation.⁴ Dibenzofuran (1.0 g, 6 mmol) was electrolyzed in 200 ml of 0.5 M NaOAc/HOAc until 10% of the starting material had been consumed (GLC). The mixture was poured into dichloromethane (100 ml) and water (1000 ml) and the organic layer was separated, washed with water, dried

(MgSO₄) and analyzed by GLC (Table 1). On a preparative scale, electrolysis followed by column chromatography readily provided large amounts of pure 1-acetoxy- (eluting first) and 3-acetoxy-dibenzofuran. Hence anodic acetoxylation, followed by hydrolysis, constitutes a convenient route to these hydroxydibenzofurans.

With 12-tungstocobaltate(III).⁵ Dibenzofuran (0.42 g, 2.5 mmol) and potassium 12-tungstocobaltate(III) (1.65 g, 0.5 mmol) were refluxed overnight in 25 ml of 0.2 M KOAc/HOAc. The mixture was poured into dichloromethane (100 ml) and water (500 ml), and the organic layer treated as above. The conversion was 4%, corresponding to a yield of 20% based upon the Co(III) complex.

With silver(II).⁶ Silver(I) acetate (0.083 g, 0.5 mmol) was added to a solution of dibenzofuran (1.68 g, 10 mmol), 2,2'-bipyridyl (0.156 g, 1.0 mmol), and potassium peroxydisulfate (1.35 g, 5 mmol) in 20 ml of 0.1 M NaOAc/HOAc. The mixture was stirred at 40 °C for 20 h and then worked up as before. The conversion was 5%.

With ammonium hexanitratocerate(IV).⁷ Dibenzofuran (1.68 g, 10 mmol) and ammonium hexanitratocerate(IV) (2.74 g, 5 mmol) in 50 ml of HOAc were stirred at 40 °C for 16 h. Work-up was performed as before, the conversion being 12%.

Transformation into trimethylsilyl ethers. Samples of the four hydroxydibenzofurans were separately treated with a fivefold excess of pyridine in dichloromethane, followed by a fivefold excess of chlorotrimethylsilane. After 30 min the mixtures were filtered and washed with water and the organic extracts analyzed by GLC. Baseline resolution was obtained for a mixture of all four trimethylsilyloxydibenzofurans. Samples of the crude acetoxylation product mixtures were heated with 2 M sodium hydroxide for 1 h and subsequently cooled, filtered, extracted with dichloromethane and acidified (HCl). The hydroxydibenzofurans were taken up in dichloromethane, washed with water, dried (MgSO₄) and evaporated to give a crude mixture which was trimethylsilylated as above and analyzed by GLC.

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