Direct Oxidative Acetoxylation of Dibenzoferan with Predominant Attack in the 3-Position†

Lennart Eberson* and Finn Radner

Division of MAX chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden


In a study of the photonitration of dibenzoferan (I), data regarding the reactivity of (dibenzoferan)− toward nucleophiles were needed for a more detailed understanding of the photochemical processes.† Oxidative substitution by cyanide ion was shown to prevail attack at the 3-position of (dibenzoferan)−, as opposed to the characteristic electrophilic reactivity of dibenzoferan at mainly the 2-position. The Shaik–Pross CM model correctly predicts this pattern,3

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in that the regioselectivity of nucleophilic attack upon (dibenzoferan)− should be determined by a combination of the triplet spin density in neutral dibenzoferan and by the LUMO coefficients of (dibenzoferan)−; for a non-alternate system like dibenzoferan this leads to different regioselectivity in the two cases.

Additional information on the reactivity of (dibenzoferan)− 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 dibenzoferan. 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 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 acetoxylolation in HOAc/0.5 M NaOAc, yielding predominately 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)− in HOAc/0.2 M NaOAc at ca. 100°C, silver(I) acetate/peroxydisulfate/2,2′-bipyridyl in HOAc/0.1 M NaOAc at 40°C and ammonium hexanitroborate(IV) in HOAc at 40°C.

The reactivities indicated by the data in Table 1 will be discussed in detail in forthcoming papers.†

Experimental

Materials. Dibenzoferan (Aldrich, 99+ %), 2,4-di-i-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-Amino- dibenzofuran was obtained by Sn/HCl reduction of 3-nitro dibenzofuran. Potassium 12-tungstocobaltate(III) was available from earlier work. All other chemicals were of highest commercial quality available and used as supplied.

Instrumentation. The GLC instrument was equipped with a fused silica column (25 m, OV-1701). GLC/MS and MS spectral analysis were performed as previously reported. 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-
**Table 1. Isomer distributions from the oxidative acetoxylation of dibenzofuran by the anode and various one-electron oxidants.**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Conversion (%)</th>
<th>Isomer distribution</th>
<th>Analyzed as acetates</th>
<th>Analyzed as Me₂Si ethers*</th>
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<td></td>
<td></td>
<td></td>
<td>(1- + 4-)</td>
<td>1- 2- 3- 4-</td>
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<tr>
<td>Anode</td>
<td>10</td>
<td>30  4  66</td>
<td>32  3  62  3</td>
<td></td>
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<tr>
<td>Co⁶⁺W₂O₇⁻</td>
<td>4</td>
<td>46  1  53</td>
<td>42  1  55  2</td>
<td></td>
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<tr>
<td>Co⁶⁺(NO₃)₆²⁻</td>
<td>12</td>
<td>34  2  64</td>
<td>32  2  64  2</td>
<td></td>
</tr>
<tr>
<td>Ag(II)</td>
<td>5</td>
<td>29  1  70</td>
<td>Not determined</td>
<td></td>
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*After hydrolysis of the acetates, followed by trimethylsilylation of the resulting mixture of hydroxydibenzofuran.

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 was treated as above. The conversion was 4%, corresponding to a yield of 20% based upon the Co(III) complex.

With silver(II), 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), 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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References


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