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Synthesis of Annulated Dioxins and their Use as Donors for Cation Radical Salts.

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Abstract: The synthesis of a series of new alkoxylated annulated dioxins is described together with their cyclovoltammetric behaviour.

The search for new organic materials with interesting electrical and/or magnetic properties is a continuing "trial and error" process, where systematic and careful variation of the substitution pattern in the constituent molecular donors/acceptors is a basic and necessary strategy.[1] In our continuing program for synthesizing materials with very narrow ESR-signals, we have previously presented cation radical salts with alkoxylated dibenzofurans[2] and naphthalenes.[3]

Halogenated dibenzodioxins are a notorious class of compounds, infamous for their ecotoxicity. Less is known about more electron rich derivatives although the stability of the corresponding cation radicals had been noted quite early.[4] This stability and the planarity of the dibenzodioxine system[5] prompted us to synthesize a series of substituted dibenzodioxines for evaluation of this class of compounds as potential donors for cation radical salts. We now present the synthesis of four new annulated dioxins **7**, **8**, **9** and **11** together with a new synthesis of the known dinaphthodioxin **10**, and their cyclovoltammetric behaviour.

Recent strategies of dibenzodioxine synthesis are either aimed at preparing electron-poor halogenated structures[6] or use carcinogenic HMPA as solvent.[7] Low yields are common when the substrate is not activated towards nucleophilic aromatic substitution.[8]

Our approach is a modification of the Ullman ether synthesis.[9] Readily available[10] diiodinated substrates **2**, **3**, **4** and **6**, (2,3-diiodonapthalene, **5**, has been synthesized by an independent route)[11] were reacted with commercial 2,3-dihydroxynaphthalene, **1**, in the presence of copper(I)iodide with the non-carcinogenic[12] 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) as solvent. By this procedure we were able to isolate the four new dioxins **7**, **8**, **9** and **11**,[13] in modest yields after chromatography. Dinaphthodioxin, **10**,[14] has been described previously, but mostly as a byproduct in minor amounts.

A further advantage is the possibility to vary the substituents from sterically demanding (in **9**), to electron donating (in **7**), and unsubstituted "slim" (in **10**). The yields are all in the same range, 20-25 % (except for **11**), indicating that demethylation of **2** is not an important side reaction. Compound **11** is an exception in several senses, being both alkoxylated and sterically demanding, and could be isolated only in a miniscule yield of 1.5%.

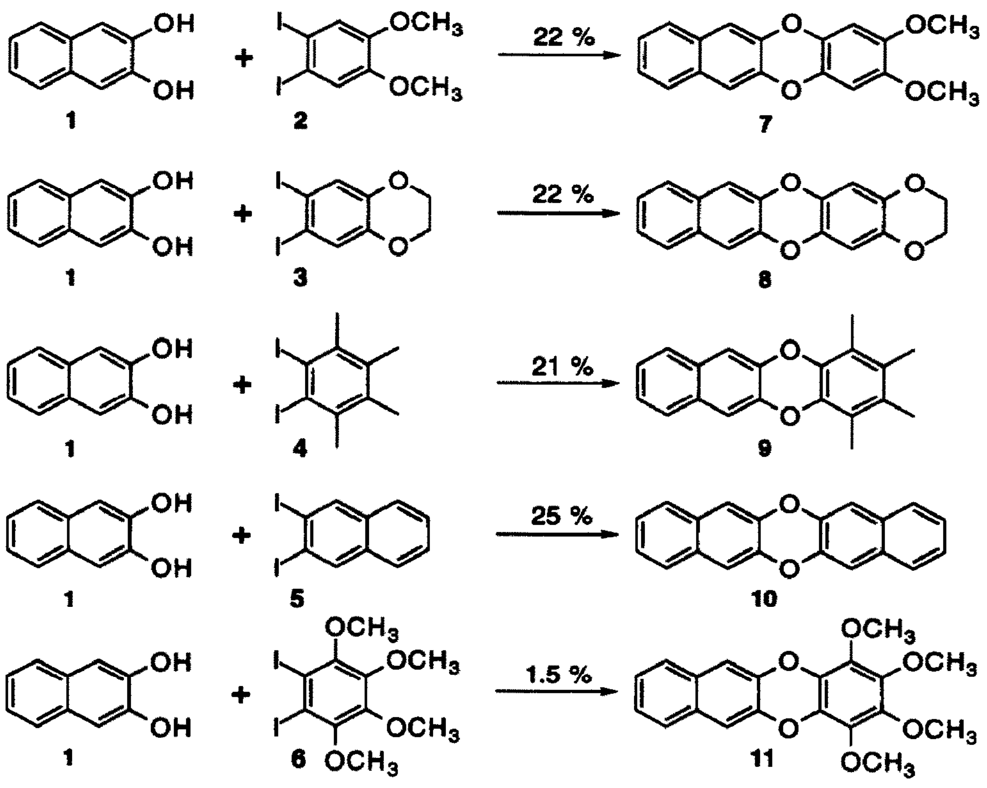
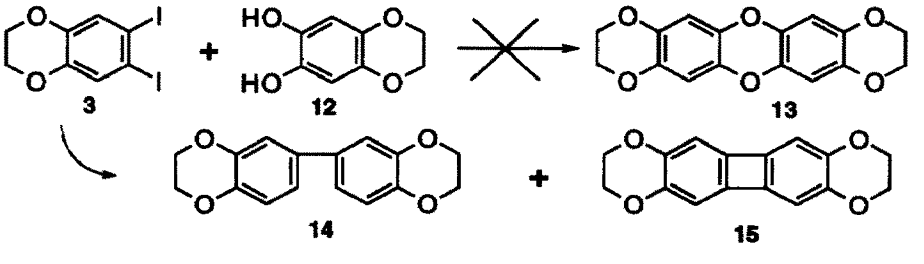


Figure 1: Dioxins synthesized in this study. Conditions: 2.1 equiv NaH, 2 equiv CuI, DMPU, 150 °C. Yields are for isolated, NMR-pure material.

Interestingly, this method fails when 6,7-dihydroxybenzo(1,4)dioxan, **12**,[15] is allowed to react with 6,7-diiodobenzo(1,4)dioxane, **3**, in an attempt to synthesize the highly symmetric dioxin **13**. In this system, the copper(0) generated *in situ* directs the reaction path to the dimer **14** (main product) along with traces of **15**.



A typical procedure is as follows: Sodium hydride (1.26 g, 80% purity, 42 mmol) was cautiously added to 2,3-dihydroxynaphthalene, **1**, (3.2 g, 20 mmol), dissolved in DMPU (200 ml) under nitrogen. After hydrogen evolution had ceased copper(I)iodide (7.62 g, 40 mmol) was added together with 1,2-diiodo-3,4,5,6-

tetramethylbenzene, **4**, (9.0 g, 20 mmol) and the resulting dark solution warmed to 150 °C during 21 h. The bulk of the solvent was then distilled under pump vacuum. The tarry residue was treated with 2M HCl, the precipitate filtered off and dissolved in dichloromethane with the aid of an ultrasonic bath. This solution was once again filtered, the filtrate washed with 2M sodium hydroxide, dried and evaporated. The crude product so obtained was treated with ethanol from which the product precipitated. Gradient chromatography (hexanes/dichloromethane) of these crystals gave 1.073 g of NMR-pure **9**. A further 158 mg could be isolated from the ethanol filtrate by chromatography. Combined yield: 21 %, m.p. 180.5-183 °C. An analytically pure sample was obtained after recrystallization from toluene/ethanol and sublimation.

Cyclovoltammetry was measured at 25 °C in dichloromethane at 100 mV/s with Bu_4NPF_6 as electrolyte and measured vs SCE. All donors except **10** gave quasireversible one electron oxidation halfwaves (Table 1). These are rather high values compared with common TTF-systems, i. e. BEDT-TTF shows under similar conditions 0.44 V. Compound **10** fails to show any significant oxidative behaviour under these circumstances. The very low solubility of **10** in dichloromethane at 25 °C prompted us to scan the CV trace at 80 °C in both 1,2-dichlorobenzene and 1,4-dioxane, but inert behaviour was the single result, which lead us to the conclusion that **10** has a $E_{1/2}$ >1.6 V.

Compound:	**7**	**8**	**9**	**10**	**11**
$E_{1/2}$ (V vs SCE)	1.02	1.12	1.24	(>1,6)	1.24

Table 1. Cyclovoltammetric data for dioxines synthesized in this study.

Even though a low oxidation potential stabilizes the corresponding cation radical, a relatively high energy cation radical (as in these systems) can be stabilized by proper design of the accompanying donor molecule. Alkoxylation serves here the double purpose of lowering the oxidation potential by donating to the aromatic π-system, and of blocking the aromatic nucleus against attack by nucleophiles. A comparison between **10** and **7** is a good example of this effect. However, contrary to what could be expected, tetramethoxylated **11** shows a substantially higher $E_{1/2}$ than the dimethoxyderivative **7**, indicating that the electron-releasing ability of the methoxy groups is in this system not only saturated, but reversed, probably due to the steric crowding present in the methoxy periphery of **11**.

Well formed crystals can be achieved by constant current electrocrystallization in the presence of a suitable tetrabutyl ammonium salt, and so far $(\mathbf{8})_2AsF_6$ and $(\mathbf{7})_{1.1-1.2}(AsF_6)$ have been isolated. Further studies of the properties of the cation radical salts (conductivity, structure, ESR-properties) are under investigation and will be reported in due course.

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