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Birch-Type Reductions in Aqueous Media: Benzo[*b*]thiophene and Diphenyl Ether

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The preparative cathodic reductions of benzo[*b*]thiophene and diphenyl ether were investigated. Aqueous and mixed organic–aqueous solutions of tetrabutylammonium salts served as electrolytes, and the cathode was a mercury pool. Experiments were carried out at a constant current and the products were isolated and identified. It was found that benzo[*b*]thiophene is initially reduced to 2,3-dihydrobenzo[*b*]thiophene, which is subsequently reductively cleaved to 2-ethylbenzenethiol. If the amount of charge transferred is controlled, it is possible to form the dihydro derivative or the cleaved benzenethiol as major product. The cathodic product of diphenyl ether was found to be a mixture of bis(2,5-dihydrophenyl) ether (~50%) and phenol (~30%). The first product is of particular interest since phenol and benzene are the only products of diphenyl ether obtained by reductions involving solvated electrons. The mechanism of reduction of the two reactants is discussed, and possible pathways for the formation of the various products are proposed.

We have recently developed an electrochemical method to perform Birch-type reductions in aqueous solutions.[1] This method is of synthetic interest because it does not involve the use of alkali metals and liquid ammonia or amine solvents. Water is obviously preferable as an inexpensive solvent, which with a electrolyte can provide a medium with low electrical resistance. Using these conditions, it is possible to generate and isolate products of the Birch-type, which are unstable and reduced under alkali metal–ammonia conditions.[2,3] Moreover, certain base-sensitive reactants and products, which complicate chemical Birch reductions are stable under these conditions.[2]

From a mechanistic viewpoint, these reactions are intriguing because they seem to belong to a new class of reactions[4] that directly involve the usually inert electrolyte and metal electrode. In this mechanism initial reduction of a tetraalkylammonium electrolyte cation forms a tetraalkylammonium–metal species on the electrode. This species is then responsible for reduction of the organic compound.

The cathodic method has been used primarily for the formation of dihydroaromatic products. The present study, however, grew from an interest in reductive cleavage.[2] It is known that some compounds containing a heteroatom adjacent to an aromatic ring undergo reductive cleavage with alkali metal reductants. The accepted mechanism is given in eq 1. Pertinent examples are the

$$\mathrm{PhXR} + 1\mathrm{e}^- \rightarrow [\mathrm{PhXR}]^{\bullet -} \rightarrow \mathrm{PhX}^- + \mathrm{R}^\bullet \qquad (1)$$

cleavage of diphenyl ether and the cleavage of benzofuran to 2-ethylphenol. Interestingly, we found[3] that benzofuran is not cleaved under the aqueous cathodic conditions described above. This fact has led us to the present investigation of the cathodic chemistry of diphenyl ether and benzo[*b*]thiophene. Our primary interest was investigation of the cleavage/hydrogenation competition.

Table I. Reduction of Benzo[*b*]thiophene, 24 mA cm^{-2}

electrolyte solution	Q, F mol^{-1}	composition of electrolysis mixture, %		
		2a	**3**[b]	**1**[a]
2.1 M aqueous (TBA)OH,[c] divided cell	2	68	15	7
	4	17	64	2
	6	6	77	8
as above, undivided cell	2	36	10	8
	4	8	47	0
(TBA)BF$_4$, THF–H$_2$O (8%),[d] divided cell	2	75	12	4
	4	0	54	8

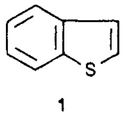
[a] Determined by GC analysis of the basic ether extract with methyl benzoate as an internal standard. [b] Isolated yield. [c] 80 °C. [d] 0 °C.

Results and Discussion

The preparative reduction of benzo[*b*]thiophene (**1**) and diphenyl ether (**4**) in aqueous or mixed organic–aqueous media was investigated. Reductions were carried out with mercury cathodes and tetrabutylammonium (TBA) electrolytes. Since the purpose was to provide a synthetic method, simple conditions were used. Experiments were carried out at a constant current in a large glass tube as the cell. A mercury pool (12 cm^2) at the bottom of the cell was the cathode and a platinum flag was the anode. An extraction thimble suspended from the top of the tube enclosed the anode and served as the anode compartment. Nitrogen was bubbled through the solution to provide an inert atmosphere and stirring.

In a typical experiment 1 mmol of substrate was electrolyzed in 25 mL of the appropriate solution. The electrolyte solutions were 2.1 M (TBA)OH in water or water–THF (20%) and 0.1 M (TBA)BF$_4$ in THF–water (8%). Reductions in the aqueous medium, without a cosolvent, were performed at 80 °C, to ensure some solubility of the reactant. To verify that scale-up of the reactions is possible, some experiments were carried out on samples of 1 g in 35 mL of solution.

Reduction of Benzo[*b*]thiophene (1). Reduction of **1** can be carried out in either aqueous or a mixed THF–water media. The products formed are the dihydro derivative **2** and the cleaved benzenethiol **3**. The solutions



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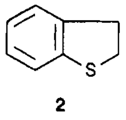

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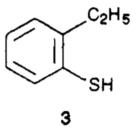

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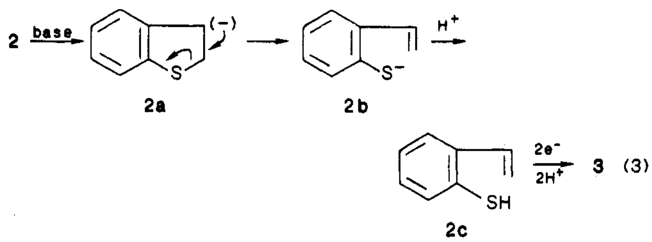
obtained after electrolysis are basic and upon extraction with ether yield a mixture of **2** and unreacted **1**. The mixture was resolved and dihydro derivative **2** was purified by using column chromatography on silica gel. The 2-ethylbenzenethiol (**3**) was isolated by extraction of the remaining catholyte after acidification. Both pure products **2**[5] and **3**[6] were characterized by means of spectroscopic methods (NMR, MS).

The cathodic reduction of **1** was carried out under various conditions. For each set of conditions, the yield of isolated **3** was determined, and the mixture of **2** and unreacted **1** was analyzed by using GC with an internal standard. Product distributions obtained from electrolysis of **1** are shown in Table I. Under all conditions, **2** is the major product obtained by transfer of charge equivalent to 2 F mol^{-1}. Increasing the amount of charge causes an increase in the yield of **3**. The combined yields of the products obtained in an undivided cell are rather low, and it is obvious that under these conditions **1** is consumed in a parallel reaction(s). It is likely that the side reaction(s) takes place at the anode. The electrooxidation of **1** is relatively easy, and it can form monomeric[7] or polymeric[8] products. The results in either water or aqueous THF in a divided cell are more satisfactory and depending on the amount of charge transferred, **2** or **3** is obtained as the major product. Since the separation of **2** from **3** is very simple, cathodic reduction of **1** provides a good method for the preparation of either product.

The benzenethiol **3** is the normal product of metal–ammonia reduction of **1**.[6] But, isolation of **2** from electron-transfer reductions of **1** has not been documented. It seemed therefore of interest to determine the relationship between **2** and **3** in the reduction sequence of **1**. Solely on the basis of the amount of charge transferred, it seems that **2** is initially formed and then it is reduced to **3**. This could involve (a) direct reductive cleavage (eq 2) or (b) a base-catalyzed cleavage of **2** and a consequent reduction of the resulting product **2c**, (eq 3), or (c) a rearranged form of **2** could itself be an intermediate reduction product and give **3** without the intervention of **2** (eq 4).

$$1 \xrightarrow[2H^+]{2e^-} 2 \xrightarrow[2H^+]{2e^-} 3 \tag{2}$$



$$1 \xrightarrow[H^+]{2e^-} 2a \longrightarrow 2b \xrightarrow{H^+} 2c \xrightarrow[2H^+]{2e^-} 3 \tag{4}$$

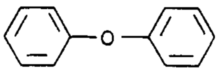
To explore the possibilities described above, we refluxed pure **2** in 2.1 M aqueous (TBA)OH. After 24 h the reactant was quantitatively recovered, indicating that **2** is not isomerized to **2c** as in eq 3. On the other hand, electrolysis of **2** in 2.1 M aqueous (TBA)OH with passage of 2 F mol^{-1} yielded 65% **3** and 22% unreacted **2**. This last experiment establishes that **3** can be obtained by reductive cleavage of **2**. Although the occurrence of the process shown in eq 4 cannot be ruled out, the main reaction pathway for the cathodic reduction of **1** clearly follows eq 2.

Table II. Reduction of Diphenyl Ether (4), Undivided Cell, 24 mA cm^{-2}

electrolyte solution	Q, F mol^{-1}	composition of electrolysis mixture, %		
		5[a]	**6**[b]	**4**[b]
2.1 M aqueous (TBA)OH[c]	5	35	24	32
	10	36	44	11
2.1 M aqueous (TBA)OH 20% THF[d]	10	30	53	6
0.3 M $(TBA)BF_4$ in THF–H_2O (8%)[e]	5	27	52	6
2.1 M aqueous (TBA)OH;[c] 8 mA cm^{-2}	10	55	22	4

[a] Isolated yield. [b] Determined by NMR (details in text). [c] 80 °C. [d] 20 °C. [e] Divided cell, 0 °C.

Reduction of Diphenyl Ether (4). Cathodic reduction of diphenyl ether (**4**) results in mixtures of phenol (**5**) and bis-2,5-dihydrophenyl ether (**6**). Mixtures obtained from electrolysis are basic, and upon extraction with ether (basic extract) yield a fraction containing **6** and unreacted **4**. After acidification, the electrolysis solution was extracted again and phenol (**5**) was isolated. To verify that phenol is the only component of the acidic extract, the extract was analyzed by means of GC with methyl benzoate as an internal standard. The pure phenol was compared (TLC, NMR, IR) with an authentic sample.



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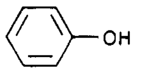

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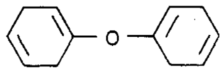

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Purification of the tetrahydro derivative **6** was achieved by chromatography on silica gel, and it was identified with the aid of spectroscopic methods. The ^1H NMR spectrum shows a singlet for the four olefinic protons 3,3′,4,4′ (δ 5.71) and a multiplet for the eight methylene protons 2,2′,5,5′ (δ 2.79). This is in accord with the spectrum of 1-methoxycyclohexa-1,4-diene,[9] which shows absorptions at δ 5.7 for the olefinic and at δ 2.8 for the methylene protons. The UV spectrum of **6** shows no conjugation, and the IR spectrum has strong absorptions at 1695 and 1650 cm^{-1} typical for unconjugated dienes. The high-intensity mass spectrum fragmentations are as expected, *m/e* 174 (M^+), 95 ($C_6H_7O^+$), 79 ($C_6H_7^+$), 77 ($C_6H_5^+$).

Reduction of **4** was carried out under various conditions. The composition of the resulting mixtures was analyzed, and the results are presented in Table II. Each mixture was resolved into a basic and acidic extract fraction. The latter consisted of pure phenol. The basic extracts could not be analyzed by GC since **6** easily reoxidized to **4**. They were analyzed with the aid of NMR spectra. The ratio of **6** to **4** was determined by comparison of the integrals of the olefinic protons [δ 5.71 (s)] of **6** and the aromatic protons [δ 7.15 (m)] of **4**. It was established by chromatographic isolation of both **6** and **4** from several basic extracts that **6** and **4** comprise >95% of the mixture.

Phenol is the product obtained from metal–ammonia reduction[10] of **4**. The accepted mechanism involves a cleavage at the radical anion stage and formation of equimolar amounts of phenol and benzene. Although we did not attempt to look for the benzene component of the

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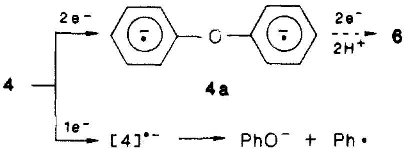
cathodic reduction, it is feasible that the cathodic cleavage of **4** to **5** proceeds by a similar mechanism.

Cathodic formation of the tetrahydro derivative **6** is unprecedented and may have important implications. Examining the data in Table II one observes that **6** is obtained in significant yields in both aqueous and in THF–H_2O. The yield is somewhat higher in the latter. It is noted that, unlike **1**, **4** can be reduced in aqueous (TBA)OH in an individual cell without complications from anodic reactions. An interesting fact that may bear on the mechanism of formation of **6** is that at a lower current density, when 8 mA cm^{-2} is used instead of 24 mA cm^{-2}, more cleavage occurs and **5** is the major isolated product (Table II, last entry). A speculative explanation for the formation of **6** involves the two-electron reduction product **4a** as an intermediate. Thus, one-electron reduction results in cleavage to **5** whereas **6** is formed via **4a**. The increased yield of **5** at lower current density could support this mechanism since less negative potentials favor formation of anion radicals, not dianions. Attempts to increase the yield of **6** by an increase in the current density were unsuccessful. In the range of 24–72 mA cm^{-2} the product composition was the same. Higher currents caused significant loss of material, and the combined yields of the isolated products were rather low (~50%). Nevertheless, the cathodic reduction of **4** by a simple variation of current can be tuned to affect Birch-type cleavage or a novel reduction of the benzene nucleus.



Summary. Reductions of diphenyl ether, benzofuran, and benzo[*b*]thiophene give either hydrogenation or cleavage products. Like benzofuran, benzo[*b*]thiophene first forms the 2,3-dihydro product. This, however, is rather easily reduced with cleavage to give 2-ethylthiophenol, and control over the amount of charge transferred is important. Diphenyl ether gives a mixture of cleavage (phenol) and hydrogenation products. The bis(dihydroaromatic) product **6** is of special interest.

Experimental Section

The reactants benzo[*b*]thiophene (**1**) and diphenyl ether (**4**) from Aldrich and the 55% aqueous (TBA)OH (2.1 M) from Southwestern Analytical Chemicals were used as received. Tetrabutylammonium tetrafluoroborate $(TBA)BF_4$ was prepared by a reported[11] procedure. The silica gel (60–80 mesh) for column chromatography was purchased from Baker. NMR spectra in $CDCl_3$ with Me_4Si as an internal standard were recorded with the aid of a Nicolet 300-MHz instrument. Mass spectra were obtained with a Finnigan 4000 or an AE1 MS-30 mass spectrometer. Cary 17D and Perkin-Elmer 297 spectrophotometers were used to record UV and IR spectra, respectively. A Varian 3700 gas chromatograph (flame ionization detector, helium as carrier gas) with 0.125-in. stainless steel columns and a Perkin Elmer M-2 recording integrator were used for GC analysis.

Electrolysis. Experiments were carried out at a constant current generated by a Hewlett-Packard DC power supply. The electrolysis cell was a 18 cm high cylinder with a diameter of 4 cm. It was immersed in a constant temperature bath. Mercury (15 mL) was added to form the cathode at the bottom (12.5 cm^2) of the cell. An alundum cup (Fisher AN 889) hanging from the top of the cylinder served as the anode compartment, and Pt foil (2 cm^2) was the anode. Electrolyte solution was poured into the cathode (25 mL) and anode (18 mL) compartments. Substrate was added only to the catholyte. The reaction mixture was well stirred by bubbling nitrogen through the solution.

Workup of Electrolysis Mixtures and Isolation of Products. Upon completion of electrolysis, the mercury was separated and water (50 mL) was added to the electrolyte. The solution was repeatedly extracted with diethyl ether (3 × 50 mL). The ethereal layers were washed with 10% aqueous HCl (3 × 50 mL) and water (3 × 50 mL). The organic fraction obtained after drying and removal of the solvent is referred to as the basic fraction, because the solution at the end of electrolysis is basic. The solution remaining after extraction of the basic fraction was made slightly acidic (pH 1 according to pH paper) and extracted with diethyl ether (3 × 50 mL). The etheral extract was washed with water (3 × 50 mL), dried, and after removal of the solvent yielded what is referred to as the acidic fraction.

The Cathodic Products of Benzo[*b*]thiophene (1). The acidic fraction obtained after electrolysis of **1** contains pure 2-ethylbenzenthiol[6] (**3**), which was identified from the following spectroscopic data: ^1H NMR ($CDCl_3$) δ 1.13 (t, 3 H), 2.58 (q, 2 H), 3.18 (s, 1 H), 7.04 (m, 4 H); MS (70 eV), *m/e* (relative intensity) 138 (100), 123 (81), 105 (53), 77 (33), 45 (58).

The basic fraction obtained from **1** consists of 2,3-dihydrobenzo[*b*]thiophene (**2**) and unreacted **1**. Pure **2** was isolated by means of column chromatography on silica gel with hexane as the eluent. It was characterized by comparison of its spectroscopic data (MS, NMR) to published information.[5] The composition of mixtures was determined by means of GC on an 8% OV-17 column (10 ft) on Chromosorb W (80–100 mesh) with methyl benzoate as an internal standard.

The Cathodic Products of Diphenyl Ether (4). The basic fraction obtained from **4** consists of pure phenol, which was compared with an authentic sample. Bis(dihydrophenyl) ether (**6**) and unreacted **4** are the only components of the neutral fraction. Their ratio was determined by integration of the NMR spectrum and comparison of the integrals for the olefinic protons of **6** and the aromatic protons of **4**. Several basic fraction mixtures were resolved with the aid of column chromatography on silica gel with hexane as the eluent. The combined weight of isolated **6** and **4** was 95% of the weight of the mixture before chromatography. Pure **6** is a liquid, and it shows the following spectroscopic properties: IR ν_{max} (neat) 1695, 1650 cm^{-1}; UV (methanol) λ_{max} 206 nm (log ϵ 3.79); ^1H NMR ($CDCl_3$) δ 2.79 (m, 8 H), 5.09 (m, 2 H), 5.71 (s, 4 H); MS (70 eV), *m/e* (relative intensity) 174 (28), 95 (46), 79 (100), 77 (100); HRMS, calcd for $C_{12}H_{14}O$ 174.1045; found 174.1043.

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Registry No. 1, 95-15-8; 2, 4565-32-6; 3, 4500-58-7; 4, 101-84-8; 5, 108-95-2; 6, 103322-55-0.

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