Electroreduction of Bicyclic Heteroaromatics.
Selective Product Formation

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The electroreductions of 1-methylindole and several benzofurans were investigated and compared with the corresponding alkali-metal/liquid ammonia reductions. The cathodic reductions were performed using a simple apparatus with aqueous THF as the solvent and were found to be regioselective. Over-reduction and other side reactions were avoided. The possible mechanism of the electroreductions is discussed.

Recently we have developed an electrochemical method to perform Birch-like reductions. The method involves the use of a mercury cathode and a tetrabutylammonium (TBA) electrolyte. Aqueous solutions of TBA,OH were used for the reduction of simple aromatics and 3-methylestradiol [1] and reactions were performed in a heterogeneous mixture at 60-90°. The use of this medium, however, was limited because some solubility of the organic compound in the aqueous layer was necessary. A combination of aqueous THF solvent and TBA,BF$_4$ electrolyte has proven to be of more general use [2]. In this homogeneous medium, products were efficiently obtained at room temperature and no limitation as to substrate reactivity was observed. Isolated benzene rings in several molecules, including steroids, were reduced to the corresponding 1,4-dihydro derivatives. Alkynes were converted to alkenes and even reduction of a terminal alkene was achieved [3].

The cathodic reductions in aqueous THF are performed at ambient temperature, using a simple DC power supply and may be preferable to the use of alkali metal-ammonia for economic reasons or convenience. Solvated electrons, the reductants of the currently used methods, are powerful but nondiscriminating reagents. They are generated in a highly basic medium and a common problem is base originating side reactions. Intrinsic advantages of the electrochemical method over the Birch reduction are: a) The current density and therefore the potential can be controlled, allowing selectivity where more than one functional group is involved or when a reducible product is formed b) using aqueous THF, reactions involving base sensitive reactants, intermediates or products may become possible.

An interesting domain to extend the applicability of the cathodic method and to test its advantages is in the reduction of heterocyclic aromatics. The products isolated from Birch reductions [4] of these substrates indicate that both over-reduction and base originating cleavages may occur during the reduction process. For example, it has been reported [5] that 1-methylindole (1) is reduced by lithium in liquid ammonia to the corresponding 2,3-dihydro derivative 2. The reaction is slow and a large excess of lithium is
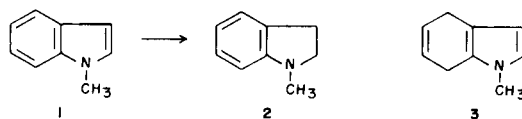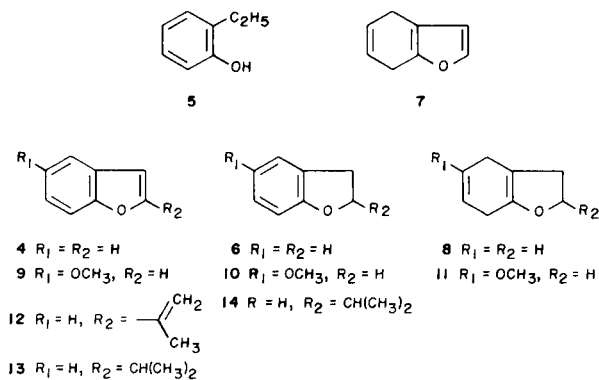

required. Adding methanol to the reaction medium enhances the reaction but a mixture of the two isomers 2 and 3 (32% and 37%) results. The reduction of various benzofurans has also been reported [4]. In general they have been found to undergo reductive cleavage when reduced in dry liquid ammonia [6]. Specifically, under these conditions 2-ethylphenol (5) was formed from benzofuran (4) and the corresponding methoxyphenol was obtained [7] from 5-methoxybenzofuran (9). In the presence of alcohol, the Birch reduction of benzofurans have led to the isolation [7] of the corresponding tetrahydro derivatives and 5-methoxy-2,3,4,7-tetrahydrobenzofuran (11) was obtained from 5-methoxybenzofuran (9) in high yield. No dihydro product was detected.

In this paper, the results obtained from the preparative electroreductions of 1-methylindole and several benzofurans will be presented and compared to the corresponding Birch reductions. It will be shown that the electrochemical method is more selective and eliminates over-reduction or base originating complications.

Results and Discussion.

It was our goal in this work to extend the utility of the Birch-like electroreduction and to specifically address problems of 2,3- *vs.* 4,7-hydrogenation, over-reduction forming tetrahydroproducts and benzofuran cleavage. Attention was given to 1-methylindole (1) and satisfactory yields of 2,3-dihydro product were obtained. Reaction conditions were developed which gave selective formation of 2,3-dihydrobenzofuran (6) avoiding cleavage and formation of the 4,7-dihydro isomer 7. These conditions also gave good yields of 2,3-dihydro-5-methoxybenzofuran (10) and selective hydrogenation of the exocyclic double bond of 12.

The preparative electrolysis experiments were performed at constant current, THF as the solvent and TBA,BF$_4$ as the electrolyte. The cell was a glass cylinder with a cera-

5   **7**

4 $R_1 = R_2 = H$
9 $R_1 = OCH_3$, $R_2 = H$
12 $R_1 = H$, $R_2 = $ (isopropenyl)
13 $R_1 = H$, $R_2 = CH(CH_3)_2$

6 $R_1 = R_2 = H$
10 $R_1 = OCH_3$, $R_2 = H$

8 $R_1 = R_2 = H$
11 $R_1 = OCH_3$, $R_2 = H$
14 $R = H$, $R_2 = CH(CH_3)_2$

mic extraction thimble suspended in it and serving as the anode compartment. Mercury placed at the bottom of the cell served as the cathode.

When 1-methylindole (**1**) was reduced with 2F mol^{-1}, it was consumed completely and two products were formed. Chromatographic separation gave pure 2,3-dihydro-1-methylindole (**2**) (60%) and 4,7-dihydro-1-methylindole (**3**) (10%). NMR analysis showed that variation of the water concentration in the electrolyzed solution, in the range of 2-12% did not significantly change this result, nor did a change in the electrolyte concentration from 0.35 to 0.50 M. In the process of our study we discovered that **3** rearomatizes to **2** upon standing or heating. We therefore did not attempt further optimizaton of conditions for selectivity. Even so the selectivity is better than that reported [5] for the comparable Birch reduction.

Benzofuran **4** was found more suitable for a detailed study. We first repeated its reduction with lithium in anhydrous ammonia and verified the reported [6] results. 2-Ethylphenol (**5**) (70%) was the only product obtained. This product has been rationalized [7] by assuming cleavage of the benzylic anion **4a**. The reduction of **4** with lithium in liquid-ammonia in the presence of alcohol had not been reported and other benzofurans have been found [7] to form tetrahydro and hexahydro derivatives. But, in view of the results obtained with **1**, it was not surprising that upon using sodium and an excess of methanol **4** undergoes a two-electron reduction. The yield of the isolated product was 70% and it consisted (by gc) of almost

Table 1

The Effect of the Current Density on the Reduction of **4**
0.25M TBA,BF$_4$ in THF-H$_2$O (4%) 2F mol^{-1}, 0°C

I [mAcm^{-2}]	6 [%]	7 [%]	unreacted 4 [%]
4	73	5	<1
8	82	6	4
16	89	6	4
24	87	4	11
32	64	5	9

Table 2

The Effect of the Concentration of Water on the Reduction of **4**
0.25M TBA,BF$_4$ in THF, I = 8mAcm^{-2}, 2F mol^{-1}, 0°C

H$_2$O [%]	6 [%]	7 [%]	unreacted 4 [%]
0	2	0	11
0.5	56	0	2
1	79	0	2
2	83	7	0
4	82	6	4
8	71	4	0
12	76	4	9

Table 3

The Effect of the Current Density on the Reduction of **6**
0.25M TBA,BF$_4$ in THF-H$_2$O (4%), 2F mol^{-1}, 0°C

| I [mAcm^{-2}]	8 [%]	unreacted 6 [%]
4	59	25
8	39	60
12	24	71

equimolar amounts of the corresponding 2,3- and 4,7-dihydro derivatives **6** and **7**.

Preparative electrolyses of **4** under various conditions were carried out and the products were analyzed. Reductions in dry THF resulted in electroreductive cleavage and 2-ethylphenol (**5**) was the only volatile product formed. However, due to the low conductivity of the solution and clogging of the separator between anode and cathode (by what seemed as polymeric products) maintaining a current sufficient for a preparative experiment, was tedious. Electrolysis in dry THF to complete conversion of **4** could not be carried out, the yield of **5** was low, and this method is not recommended for synthetic use.

Experiments with aqueous THF and 0.25 M TBA,BF$_4$ were more successful. Benzofuran (**4**) was efficiently reduced without cleavage. Moreover, the 2,3-dihydro derivative **6** was preferentially formed. In a typical experiment the cell was filled with electrolyte solution and 1.25 mmole substrate was added to the catholyte and electrolyzed until an amount of charge equivalent to 2F mol^{-1} was transferred. The composition of samples taken out periodically was determined by gc with an internal standard and it showed that the yield of products is directly proportional to the amount of charge transferred.

The effect of various conditions on the product yields was studied. The current efficiency for the formation of **6** in THF-water (4%) was high at current densities in the range of 8-24 mA cm^{-2} (Table 1). Lower current efficiency and lower combined mass balance resulted at 4 or 32 mA

cm^{-2}. In all experiments with 4% water about 5% 4,7-dihydrobenzofuran (7) was formed and its amount was independent of the current density. The concentration of water in the electrolyte solution had a marked effect on the yield of 6. As seen from Table 2 water concentrations of 2-4% were satisfactory, but, the yield for 6 decreased at higher or lower water concentrations. As noted above cleavage occurs in dry THF and may be the reason for the low yield at low water concentrations. At higher water concentrations, hydrogen evolution competes with the reduction of 4, indeed, in experiments with 12% water, gas evolution was clearly visible. It is noted that when low water concentrations were used, the byproduct 7 was not formed and the exclusive formation of 6 could be achieved. The results obtained with 1% water are of particular importance since pure 6 is obtained at relatively high current efficiency (79%).
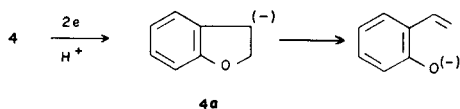
When amounts of charge over 2F mol^{-1} were transferred during the reduction of 4, 2,3,4,7-tetrahydrobenzofuran (8) was obtained. To demonstrate that it is a result of the reduction of the product 6, the reduction of pure 2,3-dihydrobenzofuran 6 was investigated. Using sodium, liquid ammonia and methanol 6 yielded 54% 2,3,4,7-tetrahydrofuran (8) and a small amount (< 5%) of a hexahydro product. Electroreduction in aqueous THF yielded 8 exclusively. In general the current efficiency for the reduction of 6 is lower than that for 4. But, upon transfer of a sufficient amount of charge, the reaction could be carried to completion and pure 8 was isolated. The effect of the water concentration was similar to that observed for 4 and the current efficiency was highest in the presence of 2-4% water. The effect of the current density was very pronounced and the current efficiency was highest at 4 mA cm^{-1}. As shown in Table 3, a change from 4 to 12 mA cm^{-2} dropped the current efficiency substantially.

As stated in the introduction the Birch reduction of some substrates produces tetrahydro or hexahydro products. To test the possibility of limiting the reduction to 2 e using the cathodic method, we chose 9 which has been reported to yield 11 upon Birch reduction and 12 which was of some interest since the isopropenyl substituent is common in naturally occurring benzofurans [8]. It was reasonable to expect that the dihydro derivatives of 12 would be susceptible to the Birch conditions and higher reduction products will result. Indeed, 14 constituted 91% of the isolated product obtained by treatment of 12 with sodium in liquid ammonia and methanol.

Cathodic reduction of both 9 and 12 using the conditions developed for benzofuran (THF-water (4%), 0.25 M TBA,BF$_4$) and 2F mol^{-1}, produced the corresponding dihydro derivatives 10 and 13 in good yield. As determined by nmr, 10 constituted 85% of the isolated product of 9. 2-(1-Methylethyl)benzofuran (13) was identified by comparison with a synthetic sample (gc, nmr). It constituted 85% (by gc) of the isolated product of 12. In the last two reactions some unreacted starting compound (7%) was present in the crude product but no tetrahydro derivatives were detected.

The last examples show that cathodic reductions may be controlled to obtain selective formation of dihydro product. It is likely that even when the dihydro derivatives are reducible their reduction is more difficult than that of the substrate. It seems that electrochemically the more reactive species is depleted first while solvated electrons are nondiscriminating, attacking both substrate and dihydro product while it is formed.

In the cathodic reactions, a mechanistic scheme which is fully analagous to the electron-transfer/protonation routes postulated for Birch reductions may be followed. The simplest mechanism (a) involves initial electron transfer from the electrode to the reactant heterocycle, followed by two protonations and a second electron transfer in some unknown sequence. In this case the potential measured during constant-current reduction should shift to more negative values due to depletion of substrate. When the reaction is complete the potential should be at the background where electrolyte or solvent react.

An alternative mechanism involves initial formation of a "tetrabutylammonium amalgam". This species then, transfers an electron to the reactant followed by appropriate protonations and another electron transfer. This mechanism (b) can be clearly identified [2] if the cathode potential all during the reduction is at the background value (-3.0 V) where TBA is reduced.

Using these criteria it seems that 12 is reduced directly, the reduction of 6 is mediated by TBA (mechanism b) and the results for 1, 4 and 9 are inconclusive. The highly conjugated 12 is expected to accept an electron most readily and it shows an irreversible cyclic voltammetric peak at -2.3 V (SCE). Its reduction potential measured at the beginning of a preparative electrolysis is around -1.8 V and at the end it is -3.0 V. 2,3-Dihydrobenzofuran 6, on the other hand, does not alter the background in cyclic voltammetry and the potential measured during its preparative reduction is -3.0 V throughout the experiment. The other substrates 1, 4 and 9 do not exhibit cyclic voltammetric peaks, but cause shifts of the background current. Their preparative reductions show initial potentials around -2.6 V and end values around -3.0 V. Mechanism (a) may be involved, but the potential range is the one in which TBA forms an amalgam and its intermediacy cannot

be excluded.

Consider now the reasons for regioselectivity. The Birch results for 1-methylindole (**1**) led previous workers [5] to the hypothesis that dianions of **1** formed in ammonia led to **2**, while radical anions, reacting in alcohol containing medium, led to equal mixtures of **2** and **3**. In the present study, electrochemically, **2** was selectively formed even though the medium was protic. This suggests that the dianion, radical anion hypothesis is too simplistic. Indeed, the data in Table 2 show that relative rate of protonation at the benzene *vs.* the heterocyclic ring can be a sensitive function of the proton source used and the medium. In this system where the concentration of other reagents and the reduction rates are quite constant, the change in water concentration from 1% to 2% gives much more **3**.

In conclusion, from a synthesis viewpoint this work has established that the electro-Birch using aqueous THF is a generally useful and selective method for the production of dihydro derivatives of benzofurans and indoles. Again, the electrochemical approach seems attractive in comparison to alkali metal/liquid ammonia reductions.

EXPERIMENTAL

All solvents were Fisher, Baker, or Mallinckrodt except THF which was purchased from Columbus Chemical Industries. The THF was distilled from sodium-benzophenone [10] under nitrogen and used immediately. 1-Methylindole (**1**), benzofuran (**4**), 2-ethylphenol (**5**), 2,3-dihydrobenzofuran (**6**) (all from Aldrich) and ammonia (Matheson) were used as purchased. Mercury (General Refineries) was purified before use. Tetrabutylammonium tetrafluoroborate was prepared [11] from the corresponding bromide. 5-Methoxybenzofuran (**9**) was synthesized by a known procedure [7,12] and 2-(1-methylethenyl)benzofuran (**12**) was prepared [9] in two ways from 2-acetylbenzofuran using a Wittig or a Grignard reaction. During the Grignard reaction much of the starting compound polymerized and the Wittig reaction seems more efficient. 2-Isopropyl benzofuran (**13**) was obtained by catalytic hydrogenation of **12** [9].

The nmr spectra were recorded with a Hitachi-Perkin Elmer R-24B spectrometer. When yields were determined by nmr methylene chloride was used as an internal standard. High resolution mass spectra were obtained with an AEI MS-30 mass spectrometer and ir spectra with a Beckman Acculab 1 spectrophotometer. The gc was performed on a Varian 3700 gas chromatograph with a Hewlett Packard 3390 A Integrator and helium carrier gas. The stainless steel column (10' long, 0.125" diameter) was packed with 6% OV-17 on Chromosorb W-AW-DMCS (80-100 mesh). To calculate yields by gc anisole was used as an internal standard.

Sodium in Ammonia Reduction of Benzofuran (4) in Excess Methanol.

A solution of 1.2 g (10.2 mmoles) benzofuran **4** in 6 ml of methanol was added to 100 ml of liquid ammonia containing 20 ml of anhydrous diethyl ether. The combined solution was treated with 0.82 g (35.6 mmoles) of sodium which reacted very rapidly (10 minutes) as evidenced by disappearance of the blue color. After the ammonia was evaporated the residue was dissolved in 50 ml of water. The aqueous solution was extracted with two 50-ml portions of diethyl ether and the combined ether fraction was dried over anhydrous sodium sulfate. After removal of the solvent the product was analyzed (calibrated gc, and nmr) and it consisted of 34% 2,3-dihydrobenzofuran (**6**) and 36% 4,7-dihydrobenzofuran (**7**). A trace of the starting **4** was also detected (< 2%). Acidification of the water layer with 3N hydrochloric acid and subsequent extraction with

ether, failed to indicate the presence of any volatile products such as 2-ethylphenol (**5**).

Sodium in Ammonia Reduction of Benzofuran (4).

Benzofuran (1.9 g, 16.1 mmoles) was added to 125 ml of liquid ammonia containing 1.04 g (45.2 mmoles) of sodium and 20 ml of anhydrous diethyl ether. After disappearance of the blue color, the ammonia was allowed to evaporate. The residue was treated with 20 ml of methanol and 20 ml of diethyl ether. Analysis (gc) of the resulting solution revealed only a trace amount of unreacted **4** and no dihydro products. After adding 50 ml of water the mixture was acidified with 3N hydrochloric acid and extracted with diethyl ether (2 × 50 ml). The combined ether extract was washed with saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate and the solvent was removed. The resulting brown liquid was identified by comparison with an authentic sample (calibrated gc, nmr and ir) as 2-ethylphenol (**5**). The yield was comparable to the one reported (70%) [6].

Sodium in Ammonia Reduction of 2,3-Dihydrobenzofuran (6).

The procedure was identical to that used for **4** when reduced in the presence of excess methanol. A sample of 0.66 g (55.6 mmoles) of **6** yielded 0.59 g of crude product which by gc and gcms consisted mainly of 2,3,4,7-tetrahydrobenzofuran **8** [13] and a small amount (<5%) of a hexahydrobenzofuran. The product was purified by flash chromatography using hexane-ethyl acetate (10:1) yielding 0.36 g (54%) of pure **8**.

Sodium in Ammonia Reduction of 2-(1-Methylethenyl)benzofuran (12).

The procedure was identical to that used for **6**. The amount of the reactant was 0.1797 g (1.136 mmoles), and 0.104 g (4.513 mmoles) sodium was used. The crude isolated product (61%) was analyzed (by calibrated gc, nmr) and found to contain 91% tetrahydro-derivative **14** and 7% unreacted starting compound.

Preparative Electrolysis, General Procedure.

Preparative electrolyses were perfomed at constant current using a PAR-373 (Princeton Applied Research) galvanostat and an Acromag 212-LX-1 coulometer. The cell was cylindrical with a mercury cathode (12.5 cm²) at the bottom. An alundum extraction cup (Fisher AN 889) dipping into the cell served as the anode compartment and the anode was a platinum flag (2 cm²). Two inlets allowed the passage of nitrogen through the cell during electrolyses.

Electrolyte solution in the appropriate solvent was added to the cell (8 ml catholyte and 5-7 anolyte). The substrate was syringed into the cathode compartment. The solution was stirred throughout the experiment with a magnetic bar placed on the cathode surface. Samples were taken at various reaction times and analyzed. After completion of the electrolysis the products were isolated by extraction. Water (40 ml) was added to the catholyte solution. It was then extracted with ether (4 × 50 ml). The combined ether extracts were washed with water (4 × 50 ml), dried and the solvent was removed.

The potential of the mercury pool was measured crudely during these constant current experiments. The reference electrode was a silver wire. It was placed in a fritted tube filled with electrolyte solution 1-2 mm from the cathode surface. The potential of the silver wire *vs.* an SCE when both were immersed in the electrolysis solution was +5 mV.

Electrolysis of 1-Methylindole (1).

Samples of substrate (400-600 mg) were dissolved in aqueous THF and reduced. Similar results were obtained using 2-12% of water 0.35 or 0.5 M TBA, BF$_4$ and currents in the range of 4-24 mA cm⁻². It was established by gc that after charge transfer of 2F mol⁻¹ the starting compound was completely consumed and the resulting mixture consisted of **2** and **3**. However, the relative amounts of **2** and **3**, as detected by gc, were not reproducible. This was the result of isomerization of **3** to **2**. It was found that **3** rearomatizes to **2** upon prolonged standing in solution or heating. The composition of a sample containing 15% of **3** and 85% of **2** after heating at 130°, or standing in solution for a week changed to 10% of **3** and 90% of **2**. The analysis of the crude electrolysis product of **1** (70%) was therefore made by calibrated nmr integration utilizing the aromatic

protons of **2** (4H, δ 6.3-7.2 ppm) and the vinylic protons of **3** (3H, δ 5.8 ppm). The 2,3-dihydro derivative **2** was the major product and it constituted 85% of the isolated electrolysis product. The two dihydro derivatives **2** and **3** were separated and purified by flash chromatography using hexane-ethyl acetate (15:1) as the solvent.

Electrolysis of Benzofuran (4).

Substrate (1.25 - 8 mmoles) was electrolyzed in aqueous THF containing 0.25 M TBA,BF$_4$. The current-density, and the water concentration were varied. Several samples taken out at various times from each electrolysis were analyzed by gc. The main product obtained was the dihydro derivative **6**. Small amounts of the isomer **7** and some unreacted **4** were also detected and the results are presented in Tables 1 and 2. To determine isolated yield of **6**, it was separated by flash chromatography (hexane-ethyl acetate 10:1) from electrolysis in THF-water (4%) and the pure product was compared to an authentic sample (nmr, ms).

Electrolysis of benzofuran **4** in dry THF led to the formation of 2-ethylphenol (**5**) only and no **4** could be detected. The electroreductive cleavage of **4** to **5** was not quantitated since the high resistance of dry THF solutions does not lead to synthetically meaningful results.

Electrolysis of 2,3-Dihydrobenzofuran (6).

Samples of 1.25 - 4 mmoles were electrolyzed in aqueous THF containing 0.25 M TBA,BF$_4$. The only product was 2,3,4,7-tetrahydrobenzofuran (**8**) and samples were analyzed using calibrated gc as described for **4**. It was possible to carry out electrolysis to completion. After transfer of 3F mol^{-1} 48% pure **8** was isolated. The effect of the current density and the water concentration were studied and the results are shown in Table 3.

Electrolysis of 5-Methoxybenzofuran (9).

Substrate (190-240 mg) was electrolyzed in THF-water (4%) containing 0.25 M TBA,BF$_4$ and using a current of 8 mA cm^{-2}. The crude product isolated after 2F mol^{-1} (80%) was found to contain 86% of the dihydro derivative **10** and 7% unreacted **9**. This was established by calibrated integration of the nmr spectrum. Specifically the aromatic region for **9** and the absorptions of the nonaromatic protons of **10** [δ 3.19 (t, 2H) and 4.56 (t, 2H)], were used.

Electrolysis of 2-(1-Methylethenyl)benzofuran (12).

All conditions were identical to those used for **9**. The isolated product

(62%) was mainly the dihydro derivative **13**, which was identified by comparing its nmr spectrum to published data [15]. Calibrated gc analysis showed that the crude product is 85% pure and it contains 3% starting compound.

Cyclic Voltammetry.

Cyclic voltammograms of all the reduction substrates (**1, 4, 6, 9** and **12**) were measured using an apparatus described elsewhere [14]. Measurements were performed in diglyme-water (0.5%) with 0.1 M TBA,BF$_4$ as the electrolyte and potential scan rates of 50 and 200 mVs^{-1}.

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