123239-85-0; **12**, 123239-86-1; **13**, 963-74-6; **14a**, 123239-87-2; **14c**, 123239-88-3; **15**, 123239-89-4; **16**, 72670-43-0; **17**, 1158-62-9; **18**, 5885-22-3; **19**, 31687-40-8; **20**, 14222-37-8; **21**, 123239-90-7; **22a**, 123239-91-8; **23**, 123239-92-9; **24**, 123239-93-0; **25**, 5987-29-1; **26**, 25846-17-7; **27**, 123239-94-1; **28**, 32694-25-0; **29**, 123239-95-2; **30**, 123239-96-3; **31**, 112925-02-7; **32**, 123239-97-4.

Supplementary Material Available: Experimental details for the synthesis of **5**, **10**, **14**, **21**, and **22** (4 pages). Ordering information is given on any current masthead page.

Reductive Cyclization of *o*-(3-Butenyl)fluorobenzene at Mercury and Lead Cathodes

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The cathodic behavior of *o*-(3-butenyl)fluorobenzene (**1**) at mercury and lead cathodes in DMF was investigated. Cyclic voltammograms were recorded, and the products of preparative electrolyses were isolated and identified. The reduction products at either cathode were 1-methylindane (**3**) and 3-butenylbenzene (**2**), the first predominating in all experiments with dry solvent. The effects of various reaction conditions on the product composition were studied, and the highest yield of **3** was obtained at a lead cathode at 22 °C (**3**/**2** = 3.8). Dimethylpyrrolidinium (DMP^+) was tested as a possible catalyst for the reduction of **1**. It catalyzed the reaction and increased the proportionate amount of the cyclic product. However the mediated process at lead was very inefficient. The mechanism for the reductive cyclization of **1** at mercury and lead and the mediation by DMP^+ are discussed. It is proposed that tetraalkylammonium–metals are involved in these processes.

Introduction

Reduction of halobenzenes can be accomplished with a variety of reagents, including a cathode. Electrochemical studies have been useful in investigating the mechanisms of reduction of halobenzenes.[2]

Cyclic voltammograms (CV) of halobenzenes at mercury, platinum, or carbon electrodes exhibit a single irreversible reduction peak. The CV peak potentials vary with the halogen and become more negative in the order PhI < PhBr < PhCl < PhF. The cathodic product of halobenzenes is benzene. The reaction is believed to proceed via the mechanism outlined in Scheme I,

Scheme I

$$PhX + 1e^- \rightarrow PhX^{\bullet -}$$

$$PhX^{\bullet -} \rightarrow Ph^{\bullet} + X^-$$

path A:

$$Ph^{\bullet} + 1e^- \rightarrow Ph^-$$

$$Ph^- + ZH \rightarrow PhH + Z^-$$

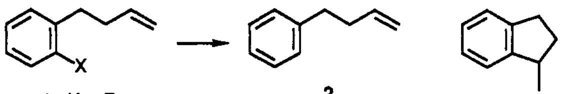
path B:

$$Ph^{\bullet} + ZH \rightarrow PhH + Z^{\bullet}$$

$$Z^{\bullet} + 1e^- \rightarrow Z^-$$

where ZH is the solvent, tetrabutylammonium ion (supporting electrolyte), or residual moisture. Following path A or path B, two electrons per molecule are consumed. Homogeneous catalysts have been used as mediators for the cathodic reduction of halobenzenes, and homogeneous redox catalysis studies[3] have provided thermodynamic and kinetic information about the mechanism in Scheme I. For example, using such techniques, Savéant and co-workers[4] determined that for PhF $E° = -2.97$ V (SCE) and that the rate constant for the cleavage of $PhF^{\bullet -}$ is greater than 10^6 s^{-1}.

Beckwith and co-workers have reported that phenyl radicals with *o*-3-butenyl substituents cyclize, to form 1-methylindane derivatives[5] and have used such cyclizations to probe the mechanisms of reactions which were thought to involve the intermediacy of aryl radicals.[6] Such cyclization reactions have recently been used to investigate the intermediacy of aryl radicals, in the cathodic reduction[7] of **4** and in the reduction of **1**, **4**, and the analogous iodo and chloro compounds by solvated electrons in liquid ammonia.[8]



1, X = F
4, X = Br

2

3

Reduction of tetraalkylammonium ions (R_4N^+) at a variety of electrodes forms tetraalkylammonium–metals (R_4N–metals). R_4N–metals are insoluble composites that contain R_4N^+ cations, metal from the electrode, and electrons.[9] Of particular relevance here are the R_4N–metals derived from dimethylpyrrolidinium (DMP^+) and

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Table I. Constant-Potential Preparative Reductions of 1 at Mercury[a]

$-E$,[b] V (SCE)	[DMP$^+$], mM	Q,[c] F mol^{-1}	product dist: 1, %	2, %	3, %	3/2	current efficiency,[d] %
2.90	0	1	43	12	28	2.3	80
2.90	0	2	11	20	50	2.5	70
2.75	1	1	50	6	29	4.8	70
2.75	1	2	20	11	47	4.3	58
2.75	1[e]	0.5	59	12	9	0.8	84

[a] Electrolyte solution: 0.1 M Bu_4NBF_4 in DMF. Reactions carried out in an ice bath. [b] Current density ranged from 2 to 0.5 mA cm^{-2}. [c] Amount of charge transferred per moles of 1 in solution. [d] Calculated from the total product (2 + 3) yield and Q, assuming 2e$^-$ process. [e] 0.56 M H_2O added.

mercury[10] or lead.[11] DMP$^+$ is reduced reversibly at these metal (M) cathodes to form DMP(Hg$_5$) and DMP(Pb$_5$):

$$\mathrm{DMP^+ + 1e^- + 5M \rightarrow DMP(M_5)} \qquad (1)$$

The products are solids that deposit at the electrode surface. They are strong reducing agents and can, in turn, reduce a variety of difficult to reduce organic molecules. The net effect is that DMP$^+$ can act as a catalyst, and in the presence of small amounts of DMP$^+$ it is possible to reduce compounds at potentials at which the compounds themselves are electroinactive. For example DMP$^+$-mediated reduction of fluorobenzene ($E°$ = −2.97 V (SCE)[4]) at a mercury cathode was achieved at −2.75 V (SCE).[12] Mediation by DMP$^+$ can also redirect the pathway of reduction and cause the formation of products different from those formed in the absence of DMP$^+$. For example,[13] 6-hepten-2-one is reduced at mercury cathodes at −3.00 V (SCE) to 6-hepten-2-ol. In the presence of DMP$^+$, the same substrate is reduced at −2.70 V (SCE), and the sole product is 1,2-dimethylcyclopentanol which results from cyclization at the radical anion stage. This and other examples indicate that DMP$^+$-mediated reductions tend to favor transformations that proceed via a single electron transfer:

$$\mathrm{org + DMP(M_5) \rightarrow org^{\bullet -} + DMP^+ + 5M} \qquad (2)$$

Considering the interest in intramolecular radical cyclizations[14] and the reports on the mediated cathodic reduction of fluorobenzene, it seemed of interest to study the cathodic behavior of *o*-(3-butenyl)fluorobenzene (1). We investigated the reduction of 1 at mercury and lead cathodes, and we probed the effect of catalytic amounts of DMP$^+$ on the reactions. The goals were to determine whether 1 can be reduced at these cathodes, to identify and quantify the reduction products, and to determine whether DMP$^+$ has an effect on the processes or the products.

Results

Experiments were carried out in dimethylformamide (DMF) with tetrabutylammonium (Bu_4N^+) tetrafluoroborate as the supporting electrolyte. The working electrodes were a mercury drop or a lead wire for cyclic voltammetry and a mercury pool or a lead plate for preparative electrolyses. The reference electrode was a SCE, and all potentials are reported vs SCE. The reduction products were isolated and identified by comparison with authentic samples (GC, NMR, MS). The composition of reaction mixtures was determined quantitatively by means of calibrated GC.

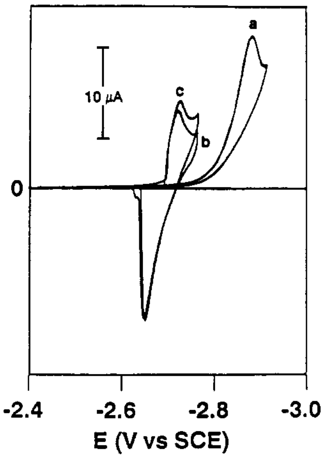

Figure 1. Cyclic voltammetry of *o*-(3-butenyl)fluorobenzene (1); 0.1 M Bu_4NBF_4 in DMF at 25 °C; sessile mercury drop electrode; 50 mV s^{-1}; (a) 2 mM 1, (b) 2 mM $DMPBF_4$, (c) 2 mM $DMPBF_4$ + 10 mM 1.

Reduction at Mercury Cathodes. Cyclic voltammograms (CV) of *o*-(3-butenyl)fluorobenzene (1) showed an irreversible peak at −2.95 V (Figure 1a), close to the solvent-electrolyte decomposition. The reduction of DMP$^+$ is reversible, and its CV (Figure 1b) showed the typical couple of cathodic and anodic peaks. It is noted that the steep rise of the cathodic current and the abrupt decrease of the anodic current, as well as the large peak separation, are characteristic of the deposition and stripping of solids.[10,11] Addition of the organic substrate 1 to solutions of DMP$^+$ caused an increase of the cathodic CV current for DMP$^+$ (Figure 1c). Such an increase is expected in catalytic processes and commonly serves as an indication for catalysis. When the reduced catalyst (in this case DMP(Hg$_5$)) transfers electrons to the substrate (eq 2), its oxidized form (in this case DMP$^+$) is regenerated, increasing its effective concentration and consequently the cathodic peak current.

For comparison, CVs of *o*-fluorotoluene and of DMP$^+$ with this substrate were recorded. The traces were identical with those shown for 1 in Figure 1a,c, correspondingly.

Preparative reductions were performed at a constant potential. The products were 3-butenylbenzene (2) and 1-methylindane (3), and the product distribution at various conditions is presented in Table I. Reduction of the reactant 1 (50 mM) alone took place at −2.90 V. In the presence of DMP$^+$ (1 mM), it was achieved at −2.75 V, a potential at which without the catalyst the current was negligible. The cyclic 3 was the major product in all dry DMF experiments, but its proportional amount was larger in DMP$^+$-mediated reactions. The ratio of yields 3/2 in the presence of DMP$^+$ was about twice of that obtained

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Table II. Constant-Potential Preparative Reductions of 1 at Lead[a]

$-E$,[b] V (SCE)	[DMP$^+$], mM	Q,[c] F mol^{-1}	product dist 1, %	2, %	3, %	3/2	current efficiency,[d] %
2.95	0	1	50	11	25	2.3	72
2.95	0	2	6	19	52	2.7	71
2.75	5	1	85	1	7	7.0	16
2.75	1	1	82	1	9	9.0	20
2.75	5	4	48	4	21	5.3	13

[a] Electrolyte solution: 0.1 M Bu_4NBF_4 in DMF. Reactions carried out in an ice bath. [b] Current density ranged from 1.8 to 1.1 mA cm^{-2}. [c] Amount of charge transferred per moles of 1 in solution. [d] Calculated from the total product (2 + 3) yield and Q, assuming 2e$^-$ process.

Table III. Effect of Temperature on Constant-Potential [E = −2.95 V (SCE)] Preparative Reductions of 1 at Lead[a]

T, °C	measd current, mA cm^{-2}	product dist[b] 2, %	3, %	3/2	current efficiency,[c] %
−18	1.2–0.2	11	25	2.3	72
0	1.8–1.1	11	25	2.3	72
22	2.4–1.6	8	28	3.5	72
60	3.0–2.8	7	25	3.6	64

[a] Electrolyte solution: 0.1 M Bu_4NBF_4 in DMF. [b] The amount of charge transferred, Q, was equivalent to 1 F/mol reactant. The electrolysis mixture contained ~50% unreacted 1. [c] Calculated from the total product (2 + 3) yield and Q, assuming 2e$^-$ process.

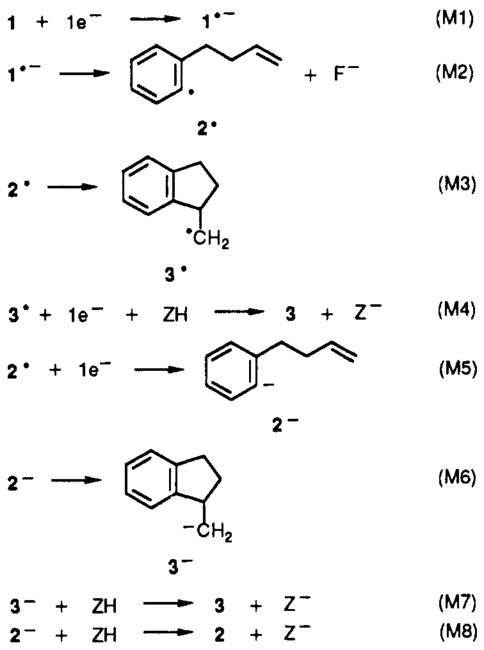
in its absence. During electrolyses with DMP$^+$ the black DMP(Hg$_5$) was visible at the electrode surface, and the catholyte turned green. When H_2O (0.56 M) was added to DMP$^+$-mediated preparative experiments, the amount of cyclic product 3 diminished significantly.

Preparative experiments are easier and cheaper when performed under constant-current conditions. We therefore tested such conditions for the reduction of 1 mediated by DMP$^+$. At constant currents less cyclic product 3 was formed than at constant-potential experiments. After transfer of charge equivalent to 2 F/mol of reactant, the product distribution was at 1.6 mA cm^{-2} 22% of 2 and 37% of 3 (3/2 = 1.7) and at 0.8 mA cm^{-2} 18% of 2 and 50% of 3 (3/2 = 2.8). The current efficiency in these reactions was 59% and 68%, respectively. The potential of the cathode during these reductions was somewhat dependent upon the current and extent of the electrolysis but was near −2.7 V in all cases.

Reduction at Lead Cathodes. CVs of 1 at lead resembled those at mercury and showed a reduction peak close to background decomposition. However, the potentials for both the reduction of 1 and the electrolyte decomposition were about 50 mV more positive at lead than at mercury. The irreversible reduction of 1 at lead was observed at −2.90 V. The CVs of DMP$^+$ at lead which showed a reversible redox couple around −2.6 V were the same with or without 1 in solution. Thus with cyclic voltammetry no catalysis of the reduction of 1 by DMP$^+$ could be detected.

Preparative reductions of 1 at lead cathodes yielded 2 and 3, and the results obtained at various conditions are presented in Tables II–IV. The reduction of the reactant 1 alone at lead was similar to that on mercury. The potentials, product distribution and current efficiencies for both metals were quite close (Table II). In the presence of DMP$^+$ (like at mercury) the reduction of 1 at lead could be affected at −2.75 V, and the relative yield of the cyclic product 3 increased dramatically (Table II). However, the current efficiency for this reaction was very low, rendering it impractical for preparative purposes.

Scheme II



The effect of temperature on reductions at lead was also investigated (Table III). Increasing the temperature increased the reaction current of 1 when it was reduced alone and improved the relative yield of the cyclic product 3. The DMP$^+$-mediated reductions were unaffected in the range −18 to 60 °C.

Reductions of 1 at a constant current were also performed at several temperatures (Table IV). When the current was relatively low (1.6 mA cm^{-2}), the results were similar to those for constant-potential experiments at the same temperature. At higher currents the relative yield of the cyclic product 3 was smaller.

Discussion

The cathodic reduction of *o*-(3-butenyl)fluorobenzene (1) can be accomplished at either mercury or lead elec-

Table IV. Constant-Current Preparative Reductions of 1 at Lead[a]

appl I, mA cm^{-2}	T, °C	measd $-E$, V (SCE)	product dist 1, %	2, %	3, %	3/2	current efficiency,[b] %
1.6	0	2.86–2.90	48	11	29	2.6	80
1.6	60	2.67–2.72	54	7	26	3.7	66
4.8	22	2.91–2.98	52	10	26	2.6	72
1.6[c]	22	2.79–2.97	6	14	53	3.8	67

[a] Electrolyte solution: 0.1 M Bu_4NBF_4 in DMF. The amount of charge transferred, Q, was equivalent to 1 F/mol reactant. [b] Calculated from the total product (2 + 3) yield and Q, assuming 2e$^-$ process. [c] This reaction was carried out to 2 F mol^{-1}.

trodes. Comparison with fluorotoluene and alkenes[15] indicates that C–F *rather than* C=C *is the electroactive* functionality of 1. The reduction products of 1 are 3-butenylbenzene (2) and 1-methylindan (3). The first is the product of hydrodefluorination, which most likely follows steps similar to those shown in Scheme I for the hydrodehalogenation of halobenzenes. The formation of 3 involves cyclization, and a possible mechanism for this process is outlined in Scheme II. The radical $2^{\bullet}$ obtained from 1 after electron transfer (M1) and elimination of F^- (M2) can cyclize (M3). The resulting cyclic radical $3^{\bullet}$ can yield 3 by either path A ($1e^-$, ZH) or path B (ZH, $1e^-$) described in Scheme I. Either way would lead to the same cyclic product 3 with an overall consumption of $2e^-$ per molecule of reactant. Since distinction between path A and path B is not possible, at this stage, they have been combined as step M4. An alternative or an additional pathway to 3 involves reduction of the radical $2^{\bullet}$ (M5) followed by cyclization of the anion 2^- (M6) and protonation of the cyclic anion 3^- (M7). This route requires that step M6 be competitive with step M8, namely, that cyclization of 2^- be faster than its protonation. This seems unlikely under our conditions. The rate constant should be, in principle, large, and the medium contains possible proton sources like residual water (in the DMF) and Bu_4N^+ from the electrolyte.

Reduction of 1 Mediated by DMP$^+$ at Mercury. The preparative reduction of 1 in the presence of DMP$^+$ can be achieved at the reduction potential of the catalyst at which the reactant 1 is electroinactive. This can be rationalized by replacing step M1 in Scheme II with steps M9 and M10. The formation of DMP(Hg_5) takes place

$$\mathrm{DMP^+ + 1e^- + 5Hg \rightarrow DMP(Hg_5)} \qquad \text{(M9)}$$

$$\mathrm{1 + DMP(Hg_5) \rightarrow 1^{\bullet-} + DMP^+ + 5M} \qquad \text{(M10)}$$

around −2.7 V, and therefore the initial electron transfer and all the consecutive steps in Scheme II can occur at this potential. This mechanism is supported by the CV experiments which show increased current at the cathodic E_p for DMP$^+$, when both the reactant and the catalyst are present in solution.

In addition to shifting the reduction potential to a more positive value, DMP$^+$ also affects the products of 1. It enhances cyclization to 3 as compared to simple hydrodefluorination to 2. The proportion between cyclization and hydrodefluorination, 3/2, is obviously a complex function of several factors, including the relative importance of radical (M3) and anion (M6) cyclizations and the rate of escape of the radical $2^{\bullet}$ from the vicinity of the electrode, prior to reduction (M5). The larger value of 3/2 caused by DMP$^+$ seems to indicate that radical cyclization (M3) rather than anion cyclization (M6) is the main route from 1 to 3. This would be in concert with previous reports that DMP$^+$-mediated reductions and reductions mediated by homogeneous redox catalysts[13,16] favor pathways involving additional chemical reactions after single-electron transfer, over pathways involving rapid two-electron transfer. An important example is the reduction of *o*-(3-butenyl)bromobenzene (4), for which it was found[7] that the ratio of yields 3/2 increased from 1 to 8 by adding a homogeneous redox catalyst to the system. The assumption of a radical cyclization pathway is strengthened further by the results of preparative electrolyses in solutions containing 0.56 M H_2O. Under these conditions, which are bound to enhance protonation of 2^- (M8) at the expense of its cyclization (M6), about 40% of the product of 1 is the cyclic 3 (Table I). In the reduction of the bromoderivative 4,[7] under conditions at which cyclization of 2^- was the predominant pathway to 3, addition of 0.40 M H_2O to the electrolysis solution diminished the yield of the cyclic product 3 to only 5%. The reason for the preference of DMP$^+$-mediated reduction to proceed via radical cyclization ($1e^-$) rather than hydrodehalogenation ($2e^-$) is unclear. It could be associated with eliminating slow kinetics at the electrode surface (M1), which necessitate −2.9 V for electron transfer, replacing it with fast catalytic electron transfer (M9, M10) at −2.7 V. It could be that at the less negative potential of the mediated processes, the rate of reduction of $2^{\bullet}$ (M5) is slower, allowing for more cyclization (M3) to occur. It is also possible that DMP(M_5) exerts some unknown surface effect on the product distribution. Surface effects have been used to explain[7] the difference in the yield ratio 3/2 obtained from 4 which was equal to 1 at mercury and 2 at platinum electrodes.

Reduction of 1 Mediated by DMP$^+$ at Lead. The effect of DMP$^+$ on the preparative reduction of 1 at mercury and lead is qualitatively similar. The reduction potential is less negative in the presence of the catalyst, and more cyclization to 3 relative to hydrodefluorination to 2 takes place. According to one of the hypotheses presented above, to explain the effect of DMP$^+$, it was assumed that at the more positive potential of the catalyzed reaction the reduction of $2^{\bullet}$ (M5) is slower, allowing for more cyclization (M3). This hypothesis could also explain why proportionally more 3 is formed at lead than at mercury since the potential for DMP(Pb_5) in a step equivalent to (M9) is more positive than that for DMP(Hg_5).

The major differences between mediated reductions at lead and mercury are that the current efficiency for preparative reductions at lead is extremely low and that no catalysis is detected by cyclic voltammetry at this cathode. These differences probably originate in the different reducing power of DMP(Pb_5) and DMP(Hg_5). DMP(Pb_5), which is a milder reducing agent,[17] reacts slowly with 1 (a step equivalent to M10). The rate of this reaction could be such that the amount of DMP$^+$ regenerated at the time scale of the CV is not sufficient to affect the CV peak current. On the preparative time scale some of the DMP(Pb_5) reacts with 1, to generate 3; however, the very slow reaction allows for competing pathways and is expressed in the very low current efficiency.

Reduction of 1 at Mercury and Lead. Without an added catalyst, the cathodic behavior of 1 is very similar at mercury and lead cathodes. An irreversible CV reduction peak is observed at high negative potentials, and preparative experiments yield comparable mixtures of cyclic and acyclic products. Although these reactions could involve "simple" electron transfer from electrode to substrate, some doubts arose when the results presented here on the reduction of 1 at mercury were compared with the published[7] information on the reduction of the corresponding bromo derivative 4 under the same conditions. The product yield ratio 3/2 from 1 is around 2.3–2.5, while that from 4 is 1.0. We hypothesize that the larger proportionate amount of 3 from 1 as compared to that of 3 from 4 indicates that the reduction of 1 is (at least in part) mediated. According to this hypothesis 4, which displays a discrete reduction wave away from the background, is reduced by direct electron transfer from the cathode. On the other hand, the reduction of 1, which occurs at high

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negative potentials, is (at least in part) mediated by Bu_4N–metals which are formed at the same potential range. The CV peaks for 1 appear only as a shoulder on the background and clearly indicate that 1 and Bu_4N^+ react at the same potentials. Although information on Bu_4N–metals is sparse, they could in principle act as their DMP^+ analogues. The composition of $Bu_4N(Hg_4)$ has been proposed[18] for the mercury derivative and the formation of a lead derivative was reported.[9] Bu_4N^+ has been shown to mediate reduction of otherwise electroinactive compounds at mercury,[15] and Bu_4N–metals have been proposed as the intermediates.

An alternative, or an additional, cause for more cyclization in the reduction of 1 as compared to the reduction of 4 could be the rate of the dehalogenation step (M2). Although the actual rates of cleavage for $\mathbf{4}^{\bullet-}$ and $\mathbf{1}^{\bullet-}$ are unknown, it is known[3] that the relative rates of cleavage for the radical anions of halobenzenes are $PhI^{\bullet-} > PhBr^{\bullet-} > PhCl^{\bullet-} > PhF^{\bullet-}$. The rate of dehalogenation of $\mathbf{1}^{\bullet-}$ should be slower than that of $\mathbf{4}^{\bullet-}$, allowing $\mathbf{1}^{\bullet-}$ to escape more efficiently from the electrode prior to cleavage. The radical $\mathbf{2}^{\bullet}$ originating from 1 would then be formed in the bulk solution, further from the electrode, where it cannot be reduced and has a greater chance to cyclize. Similar arguments have been made to explain different **3**/**2** product distributions during reduction of *o*-(3-butenyl)halobenzenes with sodium in liquid ammonia.[8] The importance of the reducing power of the environment where $\mathbf{2}^{\bullet}$ is generated by defluorination of $\mathbf{1}^{\bullet-}$ (M2) is reflected in the results of preparative electrolyses of 1 at a constant current. Higher currents result in less cyclization. At higher currents the concentration of $\mathbf{1}^{\bullet-}$ is higher in the bulk solution, and it could act as a reducing agent for $\mathbf{2}^{\bullet}$ to decrease cyclization. Such disproportionations have been identified by Savéant and co-workers.[19]

To summarize, reduction of *o*-(3-butenyl)fluorobenzene (**1**) can be achieved at either mercury or lead electrodes. The products are 1-methylindane (**3**) and 3-butenylbenzene (**2**). The most convenient conditions to produce **3** are constant-current electrolysis at lead at room temperature. Indications exist that **3** is obtained by cyclization of *o*-(3-butenyl)phenyl radical and that R_4N–metals are involved in the process.

Experimental Section

The cell, electrodes, and instruments for cyclic voltammetry have been described elsewhere.[10,11] GC analysis was performed on a Varian Model 3740 gas chromatograph modified to accommodate a fused silica capillary column, Carbowax 20M (0.32 mm × 25 m). GC/MS was conducted with a VG 7070E-HF interfaced to a Hewlett-Packard 5890 gas chromatograph equipped with a J & W Scientific 30-m DB-5 capillary column. NMR spectra were recorded with either an IBM AC-200 or AC-300 spectrometer.

Materials. *N,N*-Dimethylformamide (DMF, Burdick and Jackson) was distilled under vacuum (60–65 °C, 30 Torr). The middle 60% was collected and stored over activated 4-Å molecular sieves. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4)[20] and dimethylpyrrolidinium tetrafluoroborate ($DMPBF_4$)[21] were prepared by reported procedures. Standard solutions of 0.1 M Bu_4NBF_4 were prepared under a nitrogen atmosphere by using a cannula. The DMF was passed through a column of activated alumina into a volumetric flask containing Bu_4NBF_4 that had been purged with nitrogen. The solution was then transferred through another column of activated alumina into a nitrogen purged storage container.

The substrate, *o*-(3-butenyl)fluorobenzene (**1**) was prepared from (*o*-fluorobenzyl)magnesium chloride and allyl bromide.[8] 1-Methylindan (Dixon Fine Chemicals) and 3-phenylbutene (Aldrich) were used for identification of the electrolysis products, and 4-phenylpentane (Wiley) served as a standard for GC.

Preparative Electrolysis. Electrolyses were carried out at a constant current with an Electronic Instruments power supply and at constant potential with the same instrument coupled with an Electrosynthesis 412 potentiostatic controller. The cathode was a mercury pool (12.5 cm^2) or a lead plate (12.5 cm^2), and the reference electrode was an SCE. All potentials reported are vs SCE. The counter electrode was a platinum flag (2.25 cm^2). It was enclosed in a glass cylinder, with a glass frit bottom, which dipped in the cell and served as the anode compartment. The cell was a 12-cm-high cylinder with a 14.0-cm^2 base. In a typical electrolysis 15 mL of 0.1 M BU_4NBF_4 in DMF was introduced with a syringe into the cathode and anode compartments (about 12 and 3 mL, respectively). The catholyte was then purged with dry nitrogen for about 15 min. About 0.1 g of 1 was drawn into a 250-μL syringe. The syringe was weighed, and the substrate was then injected into the catholyte. The syringe was reweighed to determine the exact mass of 1 transferred. Electrolyses were carried out with stirring under constant-current or constant-potential conditions at various temperatures and concentrations of catalyst as indicated in the tables.

Upon completion, the reactions were quenched with 1 mL of ethanol, and 2 mL of 25 mM 4-phenylpentene in DMF was added as an internal standard. The resulting solution (100 μL) was diluted with 1 mL of ethanol, and this mixture was analyzed by GC. From several reactions the products were isolated and compared (spectroscopy) with authentic samples.

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