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(c 1.2, 95% ethanol); 92.3% ee, *R*.

The hydroxy ester was converted to its MTPA ester and analyzed by ^{19}F NMR; 92% ee.

Ethyl α-Bromopyruvate (19). The keto ester (8.99 g, 46 mmol) was reduced with 12 mL of 1 (40 mmol). The reaction was very vigorous and had to be controlled by dropwise addition of the reagent at 0 °C. After 0.5 h, α-pinene was pumped off, and the product was isolated by the addition of ethanolamine. The product was readily purified by passing it through a short column of alumina using ether as eluent: yield 9.94 g. Further purification was by distillation (pot temperature 80 °C (0.01 mm)) and preparative GC (20% SE-30, 125 °C, isothermal): $[\alpha]^{23}{}_{D}$ −6.13° (c 2.4, CCl_4); ^{1}H NMR ($CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H), 3.3 (b, 1 H, exchanges with D_2O), 3.71 (d, J = 4 Hz, 2 H), 4.33 (q, J = 7 Hz, 2 H), 4.5 (t, J = 4 Hz, 1 H).

The bromohydrin was converted to its MTPA ester and analyzed by ^{19}F NMR which gave 7.6% ee.

The above reduction was repeated at −78 °C in ~1 M solution of the keto ester in THR. After 18 h at −78 °C, the reaction mixture was warmed up slowly to 25 °C and worked up by the standard method. The product was purified by preparative GC: $[\alpha]^{25}{}_{D}$ −5.44° (c 2.5, CCl_4).

Ethyl Acetoacetate. The keto ester (1.3 g, 10 mmol) was treated with 6 mL of 1 (20 mmol). Initially, an insoluble layer separated (presumably the complex). The reaction mixture became homogeneous in 24 h and the reaction was complete in 48 h. The solution was worked up by the standard method. The product was isolated by bulb-to-bulb distillation: yield 0.650 g (45%); GC showed it to be ~96% pure. Further purification was by preparative GC (10% Carbowax 20M, 110 °C, isothermal): $[\alpha]^{25}{}_{D}$ +21.1° (c 1, $CHCl_3$); 50.6% ee, *S*.[59]

Synthesis of Ubine (12). The bromohydrin (1.0 g) was converted to styrene oxide as described earlier. The styrene oxide (0.6 g) was mixed in a stainless steel bomb with 6 g of dimethylamine and heated to 55 °C. The reaction was complete in 4 h. Dimethylamine was evaporated and the product was isolated by bulb-to-bulb distillation (pot temperature 65 °C (0.01 mm)): yield of amino alcohol, 0.78 g (95%); ^{1}H NMR ($CDCl_3$) δ 2–2.4 (complex with a superimposed singlet at 2.3, 8 H), 4.0 (br, 1 H, exchanges with D_2O), 4.57–4.81 (dd, 1 H), 7.3 (bs, 5 H); ^{13}C NMR ($CDCl_3$) off-resonance δ 44.75 (q, NCH_3), 67.45 (t, $-CH_2N-$), 69.34 (d, CHOH), 124.62 (d), 126.49 (d), 128.19 (d), 142.62 (s); capillary GC (10-m SE-30, 80–260 °C/8°/min/6 min PID) showed it to be a mixture of two isomers, 97.5:2.5.

The compound was dissolved in ether and treated with an equivalent amount of ethereal hydrochloric acid. The mixture was cooled to 0 °C and filtered. The amine·HCl so obtained was dissolved in a minimum quantity of ethanol and ether was added until a turbidity appeared. It was cooled to −18 °C and filtered and dried: mp 114–116 °C [lit. mp 147–148.5 °C for racemic compound,[23] 113.5° for *R*];[59] $[\alpha]^{23}{}_{D}$ −70.2° (c 0.935, ethanol); 88.9% ee, *R*; based on $[\alpha]^{23.5}{}_{D}$ −78.9° (c 0.935, ethanol)].[60] The salt was suspended in ether and decomposed by the addition of aqueous potassium carbonate (or sodium hydroxide) until pH 10. The aqueous layer was extracted with ether twice and ether evaporated to obtain the amino alcohol: 100% pure by capillary GC; overall yield 87%.

Acknowledgment. We thank David N. Whittern for his assistance in obtaining the ^{19}F NMR spectra of MTPA esters on a Varian XL-200 NMR spectrometer (NSF Grant CHE-8004246). We also thank the National Institutes of Health for financial assistance (GM 10937-20). Finally, we thank Dr. Probhakar K. Jadhav for his assistance in carrying out several experiments in the α-keto ester series.

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(61) Originally, we also examined the reduction of acyl cyanides. However, we learned from Professor M. M. Midland that he and his co-workers has also noted the facile reduction of keto esters and acyl cyanides. To minimize the overlap, it was decided that we should explore the keto esters and Midland and his co-workers would explore the acyl cyanides.

Electroreductive Dehalogenation of Fluorobenzenes

Essie Kariv-Miller* and Zlatko Vajtner

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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The electroreduction of 1,3-difluorobenzene and fluorobenzene on mercury cathodes in diglyme was investigated. In preparative experiments using tetrabutylammonium tetrafluoroborate as the electrolyte, fluorobenzene formed benzene and 1,3-difluorobenzene formed a mixture of fluorobenzene and benzene. When dimethylpyrrolidinium (DMP^+) tetrafluoroborate was used, benzene was obtained from fluorobenzene but the electrode potential was less negative. In the reduction of 1,3-difluorobenzene, a similar effect of DMP^+ on the potential was observed. In addition, conditions were found for selective defluorination to fluorobenzene. Results from preparative experiments—products and reaction potentials—and cyclic voltammetry indicate that reductive defluorination in the presence of DMP^+ is catalytic and mercury from the electrode seems to be involved. A possible mechanism is discussed.

We are interested in preparatively useful electrochemical reactions which occur at very negative potentials. Such reactions are not easily performed by any method and we believe the electrochemical approach can give high yields and selectivity. Defluorination is one reaction of this type.

Studies of electrochemical and other reductions of simple fluoroaromatic compounds are rare. One polarographic study[1] of polyfluorobenzenes in DMF did find evidence for fluorine loss from pentafluorobenzene, but no study of less highly fluorinated aromatics was reported. Electrochemical hydrogenation[2] of fluorobenzene on a platinum black electrode gave equal amounts of benzene and cyclohexane. Alkali-metal-promoted $S_{RN}1$ reactions have shown that fluorine can be substituted by a nucleophile.[3] This process presumably involves C–F bond cleavage of

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a fluoroaromatic anion radical.

The attachment of an electron to fluorobenzene is expected to be just slightly easier than attachment to benzene. Thus, in aqueous solution fluorobenzene reacts 6 times faster than benzene with hydrated electrons[4] and in the gas phase it has been shown[5] that the electron affinity of fluorobenzene (−0.89 eV) is less negative than that of benzene (−1.15 eV). Theoretical calculations[6] agree with this finding and it has been suggested that the half-filled orbital of the fluorobenzene anion radical has ^1A symmetry, placing highest electron density on the ortho and meta positions.

In preliminary work[7] some voltammetric evidence was obtained which indicated that fluorobenzene would be reactive. In the present study, it is shown that under certain restrictive conditions carbon–fluorine bond cleavage can be cleanly achieved and, with a judicious choice of a tetraalkylammonium salt as catalyst, selective removal of one fluorine from 1,3-difluorobenzene is possible.

Experimental Section

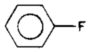
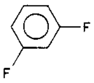
Materials and Purification Methods. Fluorobenzene, 1,3-difluorobenzene, cyclohexane, and benzene were purchased from Aldrich. Tetrabutylammonium (TBA$^+$) tetrafluoroborate[8] and dimethylpyrrolidinium (DMP$^+$) tetrafluoroborate[9] were prepared by reported procedures. Bis(2-methoxyethyl) ether (diglyme), Aldrich, 99%, was used as is, in preparative experiments. It was purified for electrochemical measurements by distillation from sodium benzophenone[10] after standing overnight on KOH (10 g KOH/1 L diglyme). It was stored over lithium under a nitrogen atmosphere.

Preparative Electrolyses. These were performed in a cylindrical cell with a 12 cm^2 mercury pool cathode at the bottom. An alundum cup (Fisher AN 889) dipping into the cell served as the anode compartment and a Pt foil (2 cm^2) was the anode. The reference electrode was a SCE and all potentials reported are vs. SCE. The cell was fitted with a reflux condenser and was immersed in an ice bath. The power supply was a Hewlett-Packard 712C and the coulometer was an Acromag 212 LX 1. A PAR 173 potentiostat was used for constant-potential electrolysis.

Product Formation and Identification. Most preparative experiments were performed by using constant current. In a typical experiment 1 mmol of substrate was dissolved in 20 mL of the appropriate electrolyte solution. The anolyte (5–10 mL) consisted of electrolyte solution only. The potential was measured vs. a SCE placed within 1 mm of the cathode surface and recorded several times during electrolysis. Samples were taken at various electrolysis times and examined by GC using a Varian 3700 gas chromatograph (flame ionization detector, He carrier gas). The composition of the mixtures was determined on a 20-ft column, 20% OV-17 on Chromosorb W, AW-DMCS and cyclohexane served as an internal standard. For unequivocal identification, the products of electrolyses carried out to complete conversion of reactant (for both 1,3-difluorobenzene and fluorobenzene) were isolated and compared (GC and NMR) with authentic samples.

Cyclic Voltammetry. Experiments were performed in a five-necked jacketed cell (20 mL) and the temperature was regulated with a Lauda Brinkman RC-3 recirculating thermostat. The working electrode was a sessile mercury drop[7] (SMDE) of area 0.0215 cm^2 prepared by placing a mercury drop on a pretreated Pt disk.[11] The counter electrode was a Pt wire and the reference was a SCE. Measurements were performed by using a PAR 173 potentiostat, a PAR 175 universal programmer, and a Houston Omnigraphic 2000 X–Y recorder.

Table I. Attempts To Catalyze the Electroreduction of 1,3-Difluorobenzene (0.05 M) Using Various Electrolyte Solutions[a]

	yield, %		
electrolysis conditions			
diglyme–H_2O (3%), 0.20 M (DMP)BF_4[b]	5	0	90
diglyme–H_2O (1%), 0.15 M (DMP)BF_4[b]	8	0	82
diglyme–H_2O (0.5%), 0.10 M (DMP)BF_4[b]	<3	0	96
DMF–H_2O (0.5%), 0.10 M (DMP)BF_4[b,c]	15	0	80
diglyme–H_2O (3%), 0.2 M (TBA)BF_4	60	15	15

[a] I = 0.83 mA cm^{-2}, Q = 2 F mol^{-1}. [b] Gas evolution was visible. [c] 2 °C, all other experiments 20 °C.

Results

Previous studies from this laboratory have shown participation of tetrabutylammonium (TBA$^+$)[12] and dimethylpyrrolidinium (DMP$^+$)[13] cations in electroreductions. Electrolytes containing these cations have been found to catalyze the reduction of organic compounds on mercury. The catalytic activity of DMP$^+$ was observed by voltammetry[7,13] and this work presents a utilization of (DMP)BF_4 as a catalyst for preparative electroreductions.

Initial experiments were performed by using 1,3-difluorobenzene as the substrate, (DMP)BF_4 and (TBA)BF_4 as the electrolytes, and mercury pool electrodes. It was soon apparent that a proton source was needed for the reaction to proceed, and small concentrations of water were usually added for this purpose. Using either DMF or diglyme and controlled-current electrolyses (DMP)BF_4 gave fluorobenzene. (TBA)BF_4 also gave reductive cleavage under these conditions, but mixtures of fluorobenzene and benzene were formed (Table I). This was in accord with our expectation that DMP$^+$ may be more selective than TBA$^+$, since it leads to a catalyst at less negative reduction potentials. Unfortunately, the current efficiencies of the reactions utilizing (DMP)BF_4 as the electrolyte (Table I) are poor.

Catalytic amounts of DMP$^+$ with (TBA)BF_4 as the electrolyte were much more effective. In practice 1,3-difluorobenzene was electrolyzed at −2.65 V by using 0.2 M (TBA)BF_4 and 0.01 M (DMP)BF_4 in diglyme–H_2O (0.5%). The initial current was 5 mA cm^{-2}. It varied and decreased during electrolysis. After transfer of 2 F mol^{-1} the reaction mixture consisted of 83% fluorobenzene and 10% unreacted substrate. In a similar experiment with 0.2 M (TBA)BF_4 (no (DMP)BF_4) the current flow was negligible at this potential and preparative electrolysis was not possible. It seemed that catalytic amounts of (DMP)BF_4 and a constant cathode potential should be used to achieve selective cleavage. Preparative constant-potential electrolyses, however, are tedious because the surface of the mercury is disrupted, black powder separates from the

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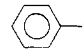
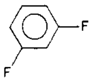
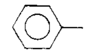
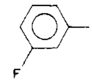
Table II. Effect of the Current Density and R_4N^+ on the Reduction of 1,3-Difluorobenzene in Diglyme-H_2O (0.5%)[a]

				yield, %		
I, mA cm^{-2}	electrolyte composition[b]	E_{init}[c]	E_{end}[d]			
1.25	DMP^+	2.65	2.68	85	0	9
1.25	TBA^+	2.78	2.81	63	3	25
2.08	DMP^+	2.73	2.80	66	6	16
2.08	TBA^+	2.80	2.84	66	8	15
4.16	DMP^+	2.82	2.90	59	13	17
4.16	TBA^+	2.83	2.90	62	18	11
8.33	DMP^+	2.95	3.10	45	30	11
8.33	TBA^+	2.93	3.08	57	23	7

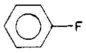
[a] 2 °C, Q = 2 F mol^{-1}. [b] DMP^+ = 0.01 M (DMP)BF_4 and 0.1 M (TBA)BF_4; TBA^+ = 0.1 M (TBA)BF_4. [c] Potential at beginning of electrolysis in −V (SCE). [d] Potential at end of electrolysis in −V (SCE).

Table III. Effect of [DMP^+] and [H_2O] on the Catalytic Electroreduction of 1,3-Difluorobenzene[a]

					yield, %	
	DMP (BF_4), M	H_2O, %	E_{init}[c]	E_{end}[d]		
1	0.1[b]	0.5	2.56	2.59	8	83
2	0.1	0.5	2.58	2.60	8	79
3	0.01	0.5	2.65	2.68	85	9
4	0.001	0.5	2.67	2.76	74	18
5	0.01	0	2.55	2.62	0	98
6	0.01	1	2.52	2.66	67	24
7	0.01	3	2.35	2.65	8	85
8	0.1	5	1.90	2.45	4	90

[a] Diglyme, 0.1 M (TBA)BF_4, 2 °C, I = 1.25 mA cm^{-2}, Q = 2 F mol^{-1}. [b] No (TBA)BF_4 in the solution. [c] Potential at beginning of electrolysis in −V (SCE). [d] Potential at end of electrolysis in −V (SCE).

Table IV. Effect of Reaction Conditions on the Catalytic Electroreduction of Fluorobenzene[a]

						yield, %	
	(DMP)BF_4, M	H_2O, %	I, mA cm^{-2}	E_{init}[b]	E_{end}[c]		
1	0.01	0.5	1.25	2.66	2.70	76	15
2	0.01	0.5	8.33	2.98	3.15	70	23
3	none	0.5	1.25	2.79	2.83	8	85
4	none	0.5	8.33	2.97	3.11	72	14
5	0.01	1	1.25	2.56	2.75	53	43
6	0.1	0.5	1.25	2.61	2.62	0	100
7	0.001	0.5	1.25	2.68	2.80	52	44

[a] Diglyme, 0.1 M (TBA)BF_4, 2 °C. Q = 2 F mol^{-1}. [b] Potential at beginning of electrolysis in −V (SCE). [c] Potential at end of electrolysis in −V (SCE).

surface, and the current flow is erratic. We, therefore, decided to use constant current electrolysis with small amounts of (DMP)BF_4 and (TBA)BF_4 electrolyte, to vary the current density and to measure the potential during electrolysis.

Diglyme has been found[7] to be less reactive than DMF under these conditions and, since it is also a more convenient solvent for organic synthesis, it was used as the solvent. A series of preparative electrolyses of 1,3-difluorobenzene under various conditions were carried out and the results are presented in Tables II–IV. In a typical experiment the catholyte consisted of 1 mmol of substrate in 20 mL of electrolyte solution. The anolyte was 5–10 mL of electrolyte solution only. Samples were taken of the catholyte at various times during electrolysis and analyzed quantitatively by GC with an internal standard.

Table II depicts the effect of the current density. In order to fully understand this effect, each experiment using 0.01 M (DMP)BF_4 as catalyst was repeated with the electrolyte (0.1 M (TBA)BF_4) alone. At current densities above 2 mA cm^{-2} both solutions behaved similarly; similar mixtures of fluorobenzene and benzene were formed with or without DMP^+ and the amount of benzene increased with increasing current density. The potentials measured with or without DMP^+ were also similar (±0.1V) except at 2.08 mA cm^{-2} where the potential measured in the DMP^+ solutions was somewhat lower. The largest difference was observed at the lowest current density (1.25 mA cm^{-2}), where the potential measured in the presence of DMP^+ was −2.65 V as compared to −2.78 V without it. Under this condition the yield of fluorobenzene was maximal (85%) and no benzene was formed.

Using the optimal current density and solutions containing 0.5% H_2O, the effect of the catalyst concentration on the reduction of 1,3-difluorobenzene was investigated (entries 1–4, Table III). The current efficiency for the formation of fluorobenzene increases with decreasing DMP^+ concentration and reaches a maximum at 0.01 M. It decreases slightly when [(DMP)BF_4] = 0.001 M. Lower concentrations were not studied. Benzene was not detected in any of these experiments.

The results obtained when 1,3-difluorobenzene was reduced in the presence of varying amounts of water are shown in Table III (entries 3 and 5–8). The optimum

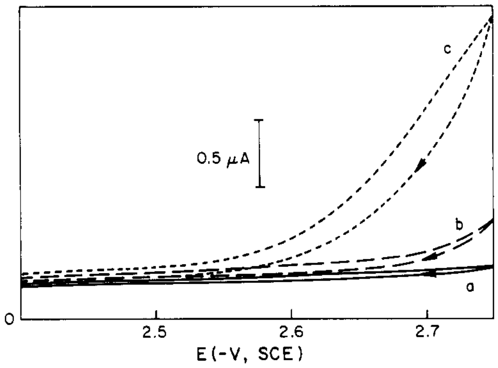


Figure 1. Cyclic voltammograms (20 mV s^{-1}) of fluorobenzene and 1,3-difluorobenzene in dry diglyme or diglyme–H_2O (0.1%): (a) 0.1 M $(TBA)BF_4$; (b) a + 10^{-3} M fluorobenzene; (c) a + 10^{-3} M 1,3-difluorobenzene.

water concentration is about 0.5%. No product is formed in the absence of water, and concentrations greater than 0.5% decreased the efficiency. An experiment with 0.1 M $(DMP)BF_4$ and 5% water was performed to test the possibility that the reaction rate does not depend on the concentration of water but on the ratio of $(DMP)BF_4$ and water. The low yield shows that high water concentrations are not useful even when high $(DMP)BF_4$ concentrations are used (Table III, last entry).

The preparative reduction of fluorobenzene was also investigated and some results are presented in Table IV. In general, the current density, the DMP^+ concentration, and the water concentration have effects similar to those observed for the difluorobenzene. The effect of the current density is presented in the first four entries. At high current densities the potentials measured and the product yields are similar with or without DMP^+ present. At low current density, the potential measured with DMP^+ is −2.66 V, as compared to −2.79 V with TBA^+ only, and the formation of the product is much more efficient. An increase of the DMP^+ concentration from 0.001 M to 0.01 and 0.1 M (entries 1, 6, 7) shows a maximum current efficiency with the intermediate concentration. Increasing the water content from 0.5% to 1% causes the efficiency of the reaction to drop from 76% to 53% (entries 1 and 5).

Experiments under conditions similar to those of preparative electrolyses were made by allowing preprepared DMP^+ "amalgam" to react with the substrate. A solution (20 mL) containing $(DMP)BF_4$ (0.01 M) was electrolyzed until 2 mF of charge were transferred and black precipitate was formed. The current was then disconnected and 1 mmol of 1,3-difluorobenzene was added and allowed to react. The precipitate disappeared and the solution cleared. In one experiment the reactant was added to the dry solvent. In another experiment the difluorobenzene (1 mmol) and water (0.5%) were added to the preelectrolyzed DMP^+ solution. Small amounts of fluorobenzene were formed, 8% in the first experiment and 3% in the second.

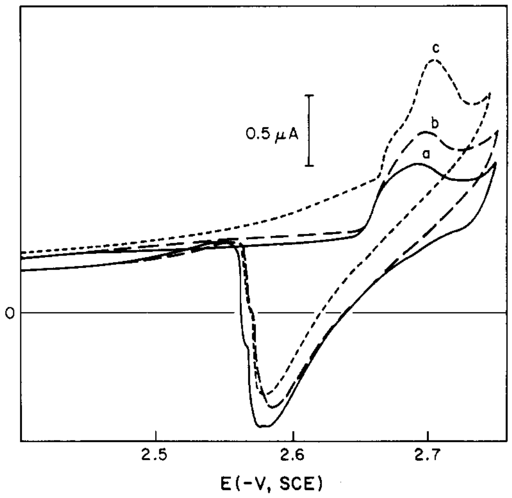


Figure 2. Cyclic voltammograms (20 mV s^{-1}) for the catalytic reduction of fluorobenzene (0.1 M $(TBA)BF_4$): (a) 10^{-3} M $(DMP)BF_4$ in dry diglyme or diglyme–H_2O (0.1%); (b) 10^{-3} M $(DMP)BF_4$ + 10^{-3} M fluorobenzene in dry diglyme; (c) b + 0.1% H_2O.

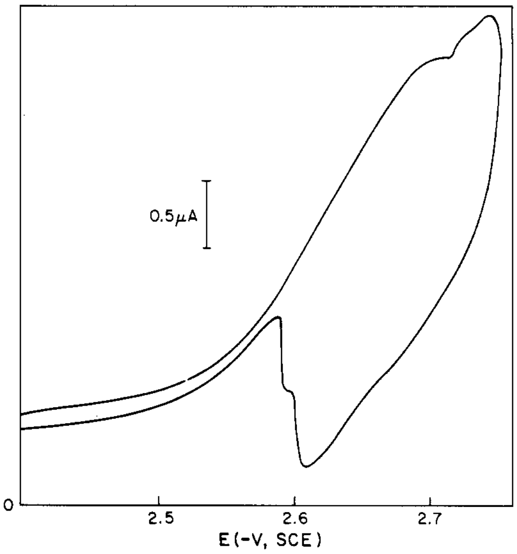


Figure 3. Cyclic voltammogram (20 mV s^{-1}) for the catalytic reduction of 1,3-difluorobenzene: 0.1 M $(TBA)BF_4$, 10^{-3} M $(DMP)BF_4$, 10^{-3} M 1,3-difluorobenzene in dry diglyme or diglyme–H_2O (0.1%).

These preparative results were supplemented by cyclic voltammetry studies on a mercury drop electrode. Cyclic voltammograms were measured by using $(TBA)BF_4$ in diglyme; the potential range was −2.0 V to −3.2 V and the potential sweep rates were varied (10 mV s^{-1}–200 mV s^{-1}). No reduction peaks were observed for either fluorobenzene or 1,3-difluorobenzene, and these curves are not changed by addition of 0.1% H_2O. Voltammograms for both substrates in the range of −2.3 V to −2.8 V are shown as examples in Figure 1. In this potential region the background current is negligible and reduction currents due to the organic substrates can be readily detected. As expected 1,3-difluorobenzene gives much larger currents than fluorobenzene.

It has been previously shown[13] that DMP^+ undergoes a reversible one-electron reduction on mercury. For 10^{-3} M $(DMP)BF_4$ a reduction peak at −2.69 V and a reoxidation peak at −2.58 V are observed (Figure 2a). Addition of either fluorobenzene or 1,3-difluorobenzene to this solution gives an increase in the cathodic charge and a decrease in the anodic charge (Figures 2 and 3).

The cyclic voltammogram of the catalytic reduction of 1,3-difluorobenzene is unaffected by small concentrations of water (Figure 3). The shape of the catalytic cyclic voltammogram for fluorobenzene is altered somewhat when water is present (Figure 2c), but the apparent catalytic current due to fluorobenzene remains the same.

In general the cyclic voltammograms have unusual shapes and meaningful analysis is difficult. This is not surprising since during measurements (as during preparative experiments) the electrode surface becomes black and is visibly disrupted. The voltammograms, however,

Table V. Effect of Fluorobenzene Concentration on the Peak Current and Potential[a]

fluorobenzene, M × 10^3	i_p, μmA	E_p, −V (SCE)
15	7.2	2.75
30	9.1	2.78
60	4.9	2.71
150	6.3	2.74
300	5.0	2.74

[a] 3×10^{-3} M (DMP)BF_4 and 0.1 M (TBA)BF_4 in Diglyme–H_2O (0.5%), ν = 20 mV s^{-1}.

are fully reproducible and a study of the peak current as a function of substrate concentration shows a maximum; the results for fluorobenzene are presented in Table V. It is noted that the peak potential is most negative when the highest currents are observed.

Discussion

The reduction of simple fluoroaromatics has received little attention in general, and to our knowledge there are no studies on their preparative cathodic reduction. Because of the strong fluorine–carbon bond, it was not obvious that reduction would lead to replacement of fluorine by hydrogen and in principle fluorodihydroaromatics could have resulted. In fact, the cathodic cleavage is quite clean and the material yields are high under a variety of conditions. Products are efficiently obtained in diglyme by using (TBA)BF_4 as the electrolyte. Fluorobenzene yields benzene and 1,3-difluorobenzene gives in a mixture of fluorobenzene and benzene. In this study (DMP)BF_4 was also used and it proved superior. It enables defluorination at less negative potentials than (TBA)BF_4. Moreover, it selectively causes monodefluorination of 1,3-difluorobenzene. Primary emphasis then was on understanding how to achieve high conversion and how to selectively remove one fluorine from the difluorobenzene.

The initial experiments (Table I) demonstrated that (DMP)BF_4 as a high-concentration supporting electrolyte in wet diglyme is not suitable. One problem was that hydrogen is evolved from reduction of water. Using DMP^+ as a reagent with (TBA)BF_4 as the higher concentration electrolyte provides a generally useful procedure. In this case some water is required to get reasonable reaction rates. Using difluorobenzene as a reactant the best conditions involve (a) low current density (1.25 mA cm^{-2}), (b) low (DMP)BF_4 concentration (0.01 M), and (c) low water concentration (0.5%). Under conditions which are otherwise the same, higher water concentrations give more and more hydrogen evolution and, therefore, low conversion (Table III). Similarly, if the current density and water concentration are held constant at 1.25 mA cm^{-2} and 0.5%, raising the DMP^+ concentration also leads to lower product yields (Table III). Higher current density gives good conversion but low selectivity. Table II, in fact, demonstrates the correlation of selectivity for monodefluorination with potential. At less negative potentials, selectivity is maintained with DMP^+. At more negative potentials (higher current density), the composition of the product and the potentials measured matches perfectly those obtained without (DMP)BF_4 in the presence of (TBA)BF_4 only. This is indicative that a mechanism pertains at less negative potentials which involves DMP^+.

It is noted that the cathodic potentials measured during the preparative experiments vary not only with the current density and the electrolyte composition but also with the concentrations of DMP^+ and water. DMP^+ has been found[13] to undergo a reversible electron transfer resulting in an insoluble product. In such reactions a positive shift of potential with increasing substrate concentration is expected[14] and was indeed observed here for DMP^+ (Table III). The positive potential shift with increasing water concentration may be due to an increase in the rate of DMP^+-catalyzed hydrogen evolution.

Turning now to the data for fluorobenzene reduction (Table IV), there are exact parallels. As the water concentration or the DMP^+ concentration become too large, the yield goes down because hydrogen evolution intercedes. It is interesting to note that, using either the difluorobenzene or fluorobenzene, the yield is maximal with 0.01 M DMP^+. Since benzene is the sole product of fluorobenzene, the product distribution cannot be used to differentiate between the reaction pathways with and without catalyst. Nevertheless, the reduction potential in the presence of DMP^+ is significantly less negative. Moreover, it has the same value as measured with 1,3-difluorobenzene. This strongly suggests that both fluoro substrates react in a similar way.

The potentials and products observed in these preparative experiments demonstrate that DMP^+ is intimately involved in the reductions, and our previous work[13] demands consideration of the involvement of a putative DMP^+ amalgam in these reactions. An explanation would be that at low current density the potential is mainly determined by the initial reduction of DMP^+ and this "amalgam" gives selective 1,3-difluorobenzene reduction.

$$DMP^+ + e + nHg \rightleftharpoons DMP(Hg)_n$$

$$ArX + DMP(Hg)_n \rightarrow ArX^{-}\cdot + DMP^+ + nHg$$

$$ArX^{-}\cdot \rightarrow Ar\cdot + X^-$$

$$Ar\cdot \xrightarrow[\text{or } DMP(Hg)_n]{e} Ar^-$$

$$Ar^- \xrightarrow{H_2O} ArH$$

DMP^+ forms an "amalgam" by a reversible one-electron process.[7,13] The reactive "amalgam" reduces the fluoro substrate to its anion radical which cleaves,[3] and the resulting phenyl radical is further reduced. Such a mechanism would rationalize the enhanced reaction of the substrates in the presence of DMP^+, the visual observation of the black DMP^+ product, and the reaction with preprepared DMP^+ "amalgam". It does not, however, explain the high reactivity of DMP^+ "amalgam" obtained from high concentration of DMP^+ with water (Table I) nor the decrease of product yield with increasing concentration of catalyst (Table III). Intuitively, these may be somehow connected to the fact that the electrode surface is a reagent.

In principle, voltammetric studies could shed some light on the more detailed mechanistic problems. In fact, the voltammograms are rather complex and interpretations are still unsure. Catalysis is obvious by comparing I_p under various conditions, and the cyclic voltammograms are surprisingly reproducible considering the disruption of the electrode surface. The data in Table V are additional indication for complex kinetics. It indicates again that optimization of preparative results must be done on a somewhat intuitive and empirical basis. The preparative results shown here are nevertheless quite satisfactory, and it should be possible to efficiently and selectively reduce other fluoroaromatic compounds and devise a method to selectively react one function of a polyfunctional molecule.

Reactions performed without (DMP)BF_4 in the presence of (TBA)BF_4 may also be of catalytic nature. They occur at high negative potentials where some reduction of TBA^+

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(14) Meites, L. "Polarographic Techniques"; Interscience: New York, 1967; p 182.

takes place and TBA$^+$ amalgam may be involved. In agreement with this idea, fluorobenzene has only a small effect on the "background" voltammogram obtained by using 0.1 M (TBA)BF$_4$. This can be explained if the reaction rate is controlled mainly by the rate of reduction of TBA$^+$ and the following reaction with fluorobenzene is not fast enough to influence the current. 1,3-Difluorobenzene does increase the "background" voltammogram current. This could arise from a more rapid reaction of 1,3-difluorobenzene with "amalgam" or by competing direct electron transfer to the fluoro compound at mercury.

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Registry No. TBA·BF$_4$, 429-42-5; DMP·BF$_4$, 69444-51-5; fluorobenzene, 462-06-6; 1,3-difluorobenzene, 372-18-9.

Magnetic Isotope Effects in Photochemical Reactions. Observation of Carbonyl ^{17}O Hyperfine Coupling to Phenylacetyl and Benzoyl Radicals. ^{17}O-Enrichment Studies

Nicholas J. Turro,* Mark A. Paczkowski,† and Peter Wan‡

Department of Chemistry, Columbia University, New York, New York 10027

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The photochemistry of ^{17}O-enriched (at C=O) dibenzyl ketone (DBK), benzoin methyl ether (BME), and deoxybenzoin (DB) has been studied on porous silica and in homogeneous solution with the aim of enriching the recovered ketones with ^{17}O [separation of magnetic (^{17}O) from nonmagnetic (^{16}O, ^{18}O) isotopes]. ^{17}O enrichment occurs with modest efficiencies on porous silica ($\alpha \leq 1.12$); photolysis in aqueous micellar solution occurs but is complicated by oxygen exchange with water thereby obviating quanitative analysis of the enrichment. Steady-state ESR spectra are reported in toluene at 165 K. Hyperfine coupling of phenylacetyl and benzoyl radicals to the carbonyl oxygen is observed, with $a(^{17}\text{O}) = 16.1 \pm 0.5$ G.

Introduction

Previous studies from these laboratories[1-4] have shown that ^{13}C may be efficiently separated from ^{12}C in dibenzyl ketone (DBK) (1), and in other ketones,[5] via photolysis in

$$\underset{\textbf{1}}{\text{PhCH}_2\text{C}^*(=\text{O})\text{CH}_2\text{Ph}} \qquad \text{C}^* \text{ encirhced with } {}^{13}\text{C}$$

micellar solution and subsequent recovery of the unreacted ketone. The principle of the method[1-4] involves taking advantage of the difference in hyperfine-induced (hfi) intersystem crossing rates from the triplet radical pair intermediate to a singlet radical pair between ^{13}C ($I = {}^1/_2$; a magnetic nucleus) containing molecules and those molecules that contain only ^{12}C ($I = 0$; a nonmagnetic nucleus) (Figure 1). Those triplet radical pairs possessing a ^{13}C nucleus will have larger intersystem rates (k_{isc}) and will produce the singlet radical pair more efficiently. The latter can than undergo σ-bond formation and hence return to DBK starting material. Under high conversion of the photoreaction, the recovered DBK will be enriched in ^{13}C content, essentially only at the acyl carbon if this carbon is partially enriched in the starting material.

Although a significant number of papers[1-4] have been published concerning the mechanistic detals of ^{13}C enrichment in DBK and related photochemistry, the applicability of the above principle to other nuclear systems has not been exhaustively demonstrated. There are two systems of which we are aware[6,7] that employ these principles in the separation of ^{17}O ($I = {}^5/_2$) from ^{16}O and ^{18}O (both with $I = 0$), but neither of these systems utilizes the simple photochemical behavior provided by DBK and related molecules.

Table I. Oxygen Isotopic Contents of DBK, DB, and BME Starting Materials[a]

ketone	% ^{16}O	% ^{17}O	% ^{18}O
DBK-^{16}*O*[b]	99.76	0.037	0.20
DBK-^{17}*O*[c]	44.8 ± 0.7	34.2 ± 0.5	20.9 ± 0.4
DBK-^{18}*O*	81.0 ± 0.5	0.0 ± 0.05	19.0 ± 0.2
DB-^{17}*O*[c]	51.6 ± 0.5	27.4 ± 0.4	20.9 ± 0.4
DB-^{18}*O*	54.5 ± 0.5	0.0 ± 0.05	45.5 ± 0.5
BME-^{17}*O*[c]	25.6 ± 0.3	41.1 ± 0.4	33.2 ± 0.3

[a] Determined via mass spectral analysis on a Finnigan 3300 GC/MS spectrometer (chemical ionization with methane). [b] Natural abundance material from Aldrich Chemical Co. The percent isotopic oxygen contents are taken from standard tables of isotopic contents of the elements. [c] ^{17}O-Enriched materials must necessarily contain some ^{18}O, since all commercially available H$_2$^{17}O is also enriched in ^{18}O.

Therefore, it was felt that the extension of the above results for DBK-^{13}*C* to the oxygen nucleus of the carbonyl of DBK, and other related molecules, appears to be pertinent and warranted investigation, since a positive result will clearly demonstrate the general applicability of the above principles for isotopic separation to other nuclear systems. In addition, since the magnetic isotope of oxygen

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† Present address: AT&T Bell Laboratories, Whippany, NJ 07981.

‡ Present address: Department of Chemistry, University of Victoria, Victoria, Canada V8W 2Y2.

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