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Selective Reduction of Saturated Perfluorocarbons

John A. Marsella, Andrew G. Gilicinski, Anne M. Coughlin, and Guido P. Pez*

Air Products and Chemicals, Inc., 7201 Hamilton Blvd, Allentown, Pennsylvania 18195-1501

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Perfluorocycloaliphatic compounds are reduced by solutions of the sodium benzophenone radical anion to give perfluorinated and highly fluorinated aromatic compounds. Perfluorocycloalkanes containing tertiary carbon centers are much more reactive than perfluorocyclohexane. Reduction of perfluoroalkanes and perfluorocycloalkanes that contain perfluoroalkyl substituents proceeds easily; however, it appears that overreduction occurs and no organofluorine products are obtained with these substrates. The selectivity and reactivity of several radical anion reducing agents are strongly correlated with the electrochemical behavior of the reducing agents, the perfluoroalkanes, and the observed perfluoroaromatic reduction products. Direct electrochemical reduction of saturated unsubstituted perfluoroalkanes on an analytical scale was observed for the first time in this work.

Introduction

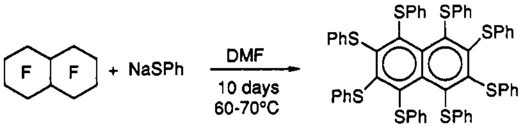
The reaction chemistry of "inert" fluorocarbons has recently received increased attention, owing in large part to the growing concern over the impact of chlorofluorocarbons (CFC's) on the upper atmosphere. In the laboratory, of course, the C–Cl bonds in CFC's offer a site for reactivity. In contrast, perfluoroalkanes offer no such weak point, and the reactivity of these materials is therefore much lower. Recent reports of the activation of C–F bonds in highly fluorinated aromatics[1] and perfluoroolefins[2] by low oxidation state organometallic complexes further demonstrate the contrast between the reactivity of perfluoroalkanes and that of other highly fluorinated organic compounds. In an effort to arrive at higher value fluoroorganic chemical intermediates, we have investigated the possibility of a selective reduction and functionalization of saturated fluorocarbons.

It has long been recognized that perfluoroalkanes react vigorously and even explosively with strong reducing agents such as alkali or alkaline earth metals.[3] Indeed, such reactions are very important in the analytical chemistry of organofluorine compounds and have been accepted as a destructive means of "mineralizing" analytical samples.[4,5] Sodium in soluble forms has also been utilized for quantitative fluorine analysis in organic chemistry, either as an ammonia solution[6] or as a biphenyl radical anion complex in dimethoxyethane.[7] Very recently, the sodium radical anion of naphthalene has been used to completely defluorinate 1,2,3,4-tetrafluorobenzene and perfluorotoluene.[8] Similarly, perfluorohexane and hexafluorobenzene react spontaneously with lithium amalgam to give a Li-containing, oxygen-reactive, polymeric carbon.[9]

The selective reduction of perfluoroalkanes without further reducing the products is a challenge analogous to that of achieving alkane functionalization by selective oxidation chemistry. In contrast to the extreme modes of reaction cited above, the activation of perfluoroalkanes by controlled reduction chemistry is relatively unexplored. The defluorination of cyclic perfluoroalkanes to perfluoroaromatics at high temperature[10a] by iron metal is the best known work of this type and was practiced on an industrial scale in the fifties.[10b] More recently, a similar defluorination was reported at slightly lower temperatures (380 °C) using a material derived from "exhausted" CsCoF$_4$—presumably CsCoF$_3$.[11] Carbon has also been used at high temperatures to defluorinate perfluoroalkanes.[12]

Only very recently have lower temperature techniques for the selective transformation of saturated perfluorocarbons been reported. Stable perfluorocarbon radicals form when perfluoroalkanes are irradiated at room temperature and below,[13a] which are similar to those observed in the fluorination of hydrocarbons.[13b] Perfluoroalkanes and alkenes[14a] as well as fluorinated surfactants[14b] (after subsequent reactions) have been obtained by radiochemical degradation of polytetrafluoroethylene (PTFE). Although not a synthetic technique, a gas-phase defluorination of C$_2$F$_6$ with [Mn(CO)$_3$]$^-$ has been described.[15]

MacNicol and Robertson[16] have shown that sodium phenylthiolate slowly reacts with cyclic perfluoroalkanes that contain tertiary carbon centers to completely defluorinate and aromatize the molecules (eq 1). Perfluorocyclohexane and perfluorohexane were both unreactive. Despite the fact that complete defluorination occurred, the mild conditions under which the perfluoro-



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alkane was reduced are noteworthy. Indeed, the reactivity observed led them to speculate that these materials might not be inert under biological conditions—an important consideration since perfluoroalkanes are used in a number of biomedical applications.

Also relevant to this present work is the report that the benzoin dianion can be used to derivatize the surface of PTFE.[17] Much of the fluorine at the surface was lost in order to form the functional groups desired for surface modification, but again, the reactions were performed under mild conditions, apparently with high efficiency. Similarly, by the action of lithium in liquid ammonia, samples of bulk PTFE were reduced to high-density polyethylene.[18] An electrochemical reduction of PTFE has also been reported.[19]

Reported here are the results of our efforts to find reducing agents that not only react with perfluoroalkanes at near-ambient temperatures but also lead to products that still contain fluorine. The observed selectivity and reactivity of the reducing agents with various perfluoroalkanes are strongly correlated with the electrochemical properties of the reducing agents, the perfluoroalkanes, and the observed perfluoroaromatic reduction products.

Experimental Section

General Information. Fluorine-19 NMR spectra were recorded at room temperature using an IBM SY-200 FTNMR spectrometer operating at 188.3 MHz. Chemical shifts are referenced to $CFCl_3$ with resonances upfield from this standard being assigned negative values. Perfluoroalkanes were obtained from Alfa Chemicals, Fluorochem LTD, Aldrich, and Air Products and Chemicals. They were dried over activated molecular sieves (4A) overnight, thoroughly degassed by at least four freeze/thaw cycles, vacuum distilled, and then stored under N_2. Tetrahydrofuran (Fisher-HPLC grade) was refluxed overnight over CaH_2 and distilled under N_2. It was then further dried and deoxygenated by treatment with the disodium complex of benzophenone dianion. Octafluoronaphthalene (Alfa), octafluorotoluene (Alfa), hexafluorobenzene (Aldrich), pentafluorobenzene (Aldrich), and 2,3,5,6-tetrafluorophenol (Fluorochem Ltd.) were obtained as indicated. The latter was also prepared by a literature method.[20] Chromatographic analyses were run using a capillary column (SPB-5) and FID detector.

Screening Reactions. The following description using perfluorodecalin, sodium, and benzophenone is representative of procedures used to screen reactions of various perfluoroalkanes with radical anion reducing agents. *Caution: Addition of perfluorocarbons to large amounts of alkali metals and other strong reducing agents can result in highly exothermic and uncontrolled reactions.* A vessel equipped with a vacuum Teflon stopcock was placed in an N_2-filled glovebox and charged with 8 mg of Na (0.35 mmol) and 75 mg of benzophenone (0.41 mmol). A separate vessel was charged with 85 μL of perfluorodecalin ($d = 1.95$ g/mL, 0.17 g, 0.36 mmol). Both vessels were sealed and brought out of the glovebox. The vessel containing Na and benzophenone was attached to a vacuum line, evacuated, and frozen in liquid N_2, and ca. 10 mL of THF was vacuum distilled into it. Upon thawing and stirring, the blue color due to the radical anion formed. Stirring was continued for ca. 2 h to assure that all of the sodium had reacted. The blue solution was then placed in a cold bath maintained at ~ -60 °C. The vessel containing the perfluorodecalin was then attached to the vacuum line, and this too was vacuum distilled into the cold mixture. The reaction solution was allowed to slowly warm, with stirring. After warming to room temperature (~ 1 h elapsed time), stirring was continued for 1-2 h. During the warming period, the solution color changed from deep blue to red-brown.

The reaction vessel was then opened to air, and a sample of the reaction mixture was analyzed by GC. All volatiles were then stripped in vacuo and collected for analysis by GC and ^{19}F NMR. The involatile solids were then extracted with D_2O for purposes of analyzing for F^-. The remaining residue, wet with D_2O, was then dissolved in acetone-d_6 for further NMR and GC analyses.

Preparation of Perfluoronaphthalene. A 100-mL glass vessel was charged with 0.5 g of Na (22 mmol) and 5.2 g of benzophenone (29 mmol) in a nitrogen-filled glovebox. Approximately 100 mL of THF was vacuum distilled into the vessel to form the blue radical anion solution. After the solution was stirred for 2 h, the flask was placed in a cold bath (−70 °C) and 0.9 mL perfluorodecalin (1.74 g, 3.8 mmol) was added via syringe through a septum-sealed side arm. The reaction mixture was allowed to warm to room temperature over a period of 1.5 h, during which time the color changed to dark red-brown. The flask was opened in air, and the THF was removed under a stream of nitrogen, leaving a brick-red solid.

Column chromatography afforded 0.37 g (62% based on sodium) of a fluffy white crystalline solid (mp 83–4 °C (lit.[21] 87–8 °C). Gas chromatographic analysis of the solid indicated a purity of 94% by area %. Mono- and dihydroperfluoronaphthalene were identified as the byproducts by GC/MS.

Preparation of Perfluorophenanthrene. The procedure described above for perfluoronaphthalene was repeated with perfluoroperhydrophenanthrene instead of perfluorodecalin. After separation by liquid chromatography, perfluorophenanthrene[22] was obtained in 84% purity with mono-, di-, and trihydroperfluorophenanthrene being present as impurities (22% yield based on sodium).

Electrochemical Studies. Cyclic voltammetry experiments were run in a nitrogen drybox in a polarographic cell. The working electrode was a 3-mm-diameter Pt disk and was polished prior to each experiment. Platinum wire served as the counter electrode, and a Ag/0.010 M $AgClO_4$ reference was used (measured at +0.292 V vs saturated calomel electrode). The THF solvent was distilled over either NaBzph or CaH_2 and degassed prior to use. Tetrabutylammonium perchlorate (Southwest Analytical) was dried under vacuum overnight at 60 °C and used in 0.10 M concentration as an inert electrolyte. Solution concentrations of perfluorocarbons were typically 3×10^{-3} M. Experiments were run using a BioAnalytical Systems 100A electrochemical analyzer. Resistance compensation was used, and approximately 95% of solution resistance was compensated in a typical experiment (10 kΩ average resistance, 500 Ω average uncompensated). All results were obtained at ambient temperature (about 22 °C).

Results

Reactivity Trends. Aromatic radical anions offer the opportunity to control the reducing power of active metals in solution.[23] With this in mind, various solutions of radical anions were treated with perfluorooctane at low temperature (ca. −60 °C). The colors of the resulting solutions were observed as the temperature was slowly raised. The temperature at which the characteristic color of the radical anion solution faded was noted, and the results are summarized in Table I. Although organic products were not identified, a clear reactivity ordering is evident. The radical anion from benzil did not fade in color even when heated to 65 °C for several hours, while NaNp reacted almost immediately on mixing at −58 °C.

An ordering of reactivity can also be assembled based on fluorocarbon substrate. Again, by monitoring the

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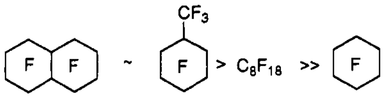
Table I. Reactivity of n-C_8F_{18} with NaA, Half-Wave Potentials ($E_{1/2}$) for One-Electron Reductions, and Relative Reactivity (Rel Rate) of $A^{\bullet-}$ with Alkyl Halides

A	temp of onset of reduction with NaA (°C)	$E_{1/2}$ $A/A^{\bullet-}$ (V vs Ag/0.010 M $AgClO_4$)	rel rate[b]
naphthalene (Np)	−58	[a]	10^{11}
anthracene (Anth)	>−58	−2.65	8×10^5
naphthacene (Npcn)	∼−25	−2.27	–
benzophenone (Bzph)	∼20	−2.50	10^3
benzil (Bnzl)	>65	−1.86	11

[a] Reduction potential was below the accessible range (<−3.3 V). Value vs the Ag/0.10 M $AgClO_4$ reference has been reported as −3.32 V.[24] [b] Approximate relative rate of reaction of radical anion ($A^{\bullet-}$) with alkyl halides in dioxane.[25]

temperature at which the color of the radical anion fades, the following reactivity order with NaBzph was observed:

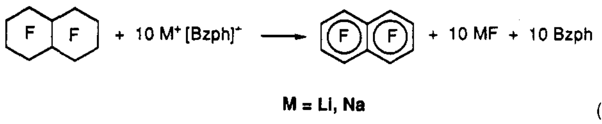


(2)

Perfluorocyclohexane is extraordinary in that the deep blue color of NaBzph persists in its presence even at 50 °C for several hours. Despite the lack of color change, however, some reaction had occurred and was evident upon spectroscopic examination.

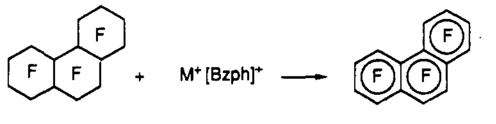
Reactions of Perfluorooctane. A large number of reactions were run attempting to selectively reduce n-C_8F_{18} with sodium naphthalide (NaNp). Color changes were observed and seemingly clear reaction solutions were obtained, suggesting that soluble, discrete products were forming. However, since the reaction mixtures exhibited a distinct Tyndall effect, it was apparent that metastable colloidal suspensions of carbon and NaF were being produced that could be precipitated by admission of air, thus mimicking the behavior of air-sensitive solutions. The solid products obtained in these reactions were clearly physical mixtures of NaF, C, and H_2O (from atmospheric workup). Fluorine-19 NMR spectra were obtained showing broad, odd-shaped peaks at high field (<−200 ppm). This is in the region of CH_2F groups,[26] but the broadness of the peak ($w_{1/2} \approx 1000$ Hz) limited any further interpretation of this feature. It should be noted that this resonance was observed with and without exposure of the reaction products to air.

Reactions of Perfluorocycloalkanes. Reactions of perfluoromethylcyclohexane and perfluorodecalin with NaNp appeared to proceed entirely to carbon and NaF. On the other hand, the reduction of perfluorodecalin with NaBzph or LiBzph proceeded smoothly to perfluoronaphthalene. Yields by GC for NaBzph ranged from 60 to 86% (based on Na) in small-scale reactions and an isolated yield of 62% was obtained for a larger scale reaction. Even when a deficiency of Na was used, no products were observed that were less reduced than perfluoronaphthalene. In these cases, unreacted perfluorodecalin was present along with the reduced products. While the selectivity to perfluoronaphthalene was good and no partially reduced intermediates such as fluoroolefins were observed, ^{19}F NMR indicated that small amounts of 2-[H]perfluoronaphthalene[27] were sometimes observed as a contaminant. Reductions run in THF-d_8 showed partial (about 30%) incorporation of deuterium into the heptafluoronaphthalene byproduct. Quenching the reaction with D_2O in regular THF without exposure to air gave no appreciable deuterium incorporation. The use of a stoichiometric amount of NaBzph (10:1 based on eq 3) did not appreciably alter the yield based on Na, and in this case a yield of 61% was observed based on both reagents.



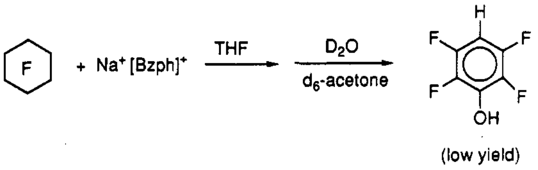
(3)

In a similar manner, perfluoroperhydrophenanthrene was reacted with NaBzph (eq 4) to give perfluorophenathrene in 22% isolated yield. The synthetic parameters were not optimized; however, GC yields of 40–56% were obtained in small scale reactions.



(4)

Heating to ca. 50 °C was necessary in order to effect any reaction with perfluorocyclohexane, and the main reaction product after exposure to air and D_2O/acetone-d_6 workup (^{19}F NMR and GC/MS data) was 1,2,4,5-tetrafluorophenol. The identification of the tetrafluorophenol as the hydrogen and not deuterium derivative is based on both GC–MS data and the fact that the splitting pattern in the ^{19}F spectrum is identical to that seen for an authentic sample prepared by a literature route.[20]



(5)

As with perfluorodecalin, further reduction beyond simple reductive defluorination is taking place. An additional experiment where the products were analyzed without exposure to air showed the presence of tetrafluorobenzene. Because of the low reactivity seen with perfluorocyclohexane, this reaction was not examined further; however, both C_6F_6 and C_6HF_5 were reduced with NaBzph under identical conditions and both fluorocarbons were found to be more reactive than perfluorocyclohexane. Although the products were not analyzed quantitatively, among the products of hexafluorobenzene reduction was pentafluorobenzene. Analysis of the volatile products from the reduction of C_6HF_5 by ^{19}F NMR showed a resonance at −140 ppm in addition to unreacted C_6HF_5, which corresponds to that reported for 1,2,4,5-tetrafluorobenzene.[28] Analysis of the hydrolyzed (with D_2O) residues of these reactions by ^{19}F NMR showed F^- to be present as well as 1,2,4,5-tetrafluorophenol.

No identifiable organic products were obtained from perfluoromethylcyclohexane, even though there is a driving force for forming an aromatic product. Similarly, perfluoroisopropyldecalin and perfluoro(2-butyl)decalin reacted at low temperatures, but again, no identifiable organic products were obtained. Clearly, ring substitution is affecting the course of these reactions.

Electrochemistry. To understand the observed reactivities, thermodynamic data from perfluorocycloalkane reductions and corresponding data from organic reducing agents were desired. A series of cyclic voltammetry experiments were done in THF to provide data for the or-

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Table II. Peak Reduction Potentials (E_{PC}) of Perfluorocycloalkanes and Perfluoroaromatics (V vs Ag/0.010 M $AgClO_4$)

perfluorocycloalkane	E_{PC}	perfluoroaromatic	E_{PC}
perfluoroperhydrophenanthrene	−2.40	decafluorophenanthrene	−2.33
perfluorodecalin	−2.60	octafluoronaphthalene	−2.58
perfluoroisopropyldecalin	−2.65		
perfluoro(2-butyl)decalin	−2.66		
perfluoromethylcyclohexane	−2.9[a]	perfluorotoluene	−2.75
perfluorocyclohexane	<−3.0[b]	hexafluorobenzene	−2.85

[a] Poorly defined peak potential (close to cathodic limit). [b] Reduction occurred below cathodic limit.

ganic reducing agents. Results are listed in Table I. The half-wave potential $E_{1/2}$ was taken as the average of reduction and oxidation peak potentials. These data are in agreement with similar data reported in the literature.[24] In addition, peak reduction potentials of perfluorocycloalkanes and their aromatic reduction products were measured. Results from this study are listed in Table II.

Discussion

The reactivity order for the reduction of n-perfluorooctane shown in Table I roughly corresponds to the reducing power of the aromatic radical anion as measured by its reduction potential ($E_{1/2}$). However, sodium benzophenone (NaBzph) seems to be less reactive than expected. A closer correlation with our results is available from work done with other alkyl halides. Warhurst and co-workers[25,29] extensively studied such reactions, and comparative data is available for a large number of cation/radical anion/alkyl halide combinations, though not for naphthacene. Solvation effects based on solvent and cation size play a key role in determining the reactivity of radical anions.[30]

The ordering of reactivity based on fluorocarbon substrate as shown in eq 2 indicates the importance of structure on the susceptibility of the fluorocarbons to reduction. The trend shows that substrates with tertiary carbon centers are more reactive than those with only secondary carbon centers. The greater reactivity of n-C_8F_{18} relative to C_6F_{12} may be due to reaction of the NaBzph with branched impurities in the commercial C_8F_{18}.[31]

A similar relation between structure and reactivity was noted by MacNicol and Robertson in the total reductive defluorination of cyclic perfluoroalkanes with sodium arenethiolates.[16] They noted that neither n-perfluorohexane nor perfluorocyclohexane reacted with these nucleophilic reducing agents while perfluorodecalin and perfluoromethylcyclohexane reacted with comparable ease. These observations are all consistent with the first step of both reduction reactions (sodium phenylthiolate and NaBzph) being a single electron transfer (SET) to the fluorocarbon. The reactivity exhibited toward perfluoroalkanes by aryl thiolates is the subject of a recent theoretical study.[32]

In this work, only three of the fluorocarbon substrates were reduced to discrete fluoroaromatic products with NaBzph as the reducing agent. Others were overreduced to fluoride and various forms of carbon indicating that the initial fluoroaromatic intermediates are also susceptible to reduction by NaBzph.

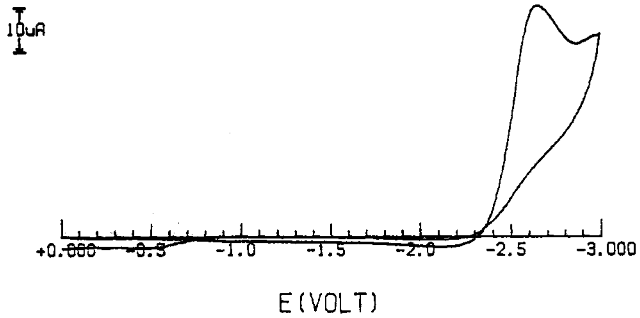

Figure 1. Cyclic voltammogram of perfluorodecalin in tetrahydrofuran, with 0.10 M tetrabutylammonium tetrafluoroborate electrolyte, at a platinum working electrode. Background current was substracted. Scan rate was 0.10 V/s. The peak reduction potential (E_{PC}) was measured to be −2.60 V vs Ag/0.010 M $AgClO_4$ reference.

The $E_{1/2}$ for reduction of perfluoroperhydrophenanthrene is by definition more positive than its E_{PC} of −2.40 V. NaBzph ($E_{1/2}$ = −2.50 V) should therefore reduce it initially to the $C_{14}F_{24}^{\bullet-}$ anion radical with successive reductions (accompanied by defluorinations) to the major observed aromatic product, perfluorophenanthrene. Since the E_{PC} for perfluorophenanthrene (−2.33 V) is more positive than that of the initial perfluoroalkane, some overreduction may be expected and was observed. Similarly, perfluorodecalin's $E_{1/2}$ is more positive than its peak reduction potential of −2.60 V; therefore, it should be susceptible to NaBzph reduction. Since the E_{PC} of perfluoronaphthalene (−2.58 V) is slightly more positive than that of perfluorodecalin, some overreduction (but less than with perfluorophenanthrene) may be expected and was observed.

The fluoroalkyl ring substituted compounds, perfluoroisopropyldecalin and perfluoro(2-butyl)decalin are reduced by NaBzph but yield no discrete organofluorine products. Electrochemical data predicted the reducibility; however, no data were available for the aromatic products so we could not use the same analysis to understand the overreduction. It is known that upon the substitution of fluorine in perfluorobenzene and perfluoronaphthalene by fluorocarbon groups there is a large increase in the rate of displacement of the aromatic fluorine atoms by nucleophiles.[33] If electron transfer reactions follow the same trend we would expect that any perfluoroisopropylnaphthalene that is formed would be very rapidly degraded by successive defluorination reactions.

In the case of perfluoromethylcyclohexane (E_{PC} = −2.9 V), the initial reduction is clearly less favorable than for all the previous substrates. However, its aromatic product, perfluorotoluene, is more easily reduced (E_{PC} = −2.75 V), leading to an anticipated overreduction reaction, which was observed. In addition, perfluorotoluene might be expected to be more easily reduced for kinetic reasons than perfluorobenzene.[33]

The reduction of perfluorocyclohexane is more difficult than with the polycylic substrates, but it does give, albeit in low yield, tetrafluorobenzene and (via subsequent reactions) tetrafluorophenol. The expected reduction product, perfluorobenzene, was not seen despite having only a slighly more positive reduction potential than

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perfluorocyclohexane. In fact, its hydrogenated derivative C_6HF_5 is observed. Rodionov and Furin[33] report that substitution of $C_6H_2F_4$ with an H atom decreases the rate of nucleophilic substitution at a fluorine-containing carbon atom; hence, the introduction of H may reasonably be considered to have a stabilizing effect. *n*-Perfluorooctane ($E_{PC} < -3.0$ V) is reduced with greater difficulty than the polycyclic perfluoroalkanes, and no organofluorine products are seen. This is presumably due to a lack of adequate resonance stabilization in potential fluoroolefin products.

Finally, it is interesting to compare our fluorocarbon reduction results with those of MacNicol and Robertson[16] in terms of electrochemical potentials. Clearly, thiolates are weaker reducing agents than the radical anions we used. Nichols and Grant report a value of −0.514 V vs SCE (−0.81 V vs Ag/0.010 M $AgClO_4$) for phenylthiolate in acetone/water.[34] While solvent effects limit a direct comparison, it is safe to say that the reduction potentials of PhS^- and perfluorodecalin differ by at least 1 V. We feel that the reducing ability observed for the sodium phenylthiolate reduction of perfluorodecalin is due to the driving force of NaF precipitation in anhydrous DMF (solubility ~2 ppm[35]), coupled with the very high nucleophilicity of phenylthiolate. It seems unlikely that these driving forces would persist in biological systems, where water and strong hydrogen bonding effects are present. Indeed, MacNicol and Robertson saw no reaction between perfluorodecalin and phenylthiolates in aqueous environments.[16]

Conclusion

The controlled reduction of saturated fluorocarbons has been achieved under near-ambient conditions. Direct electrochemical reduction of perfluoroalkanes has been observed for the first time, and electrochemical studies have provided valuable insight into the parameters and reagents needed for obtaining organofluorine products. The observed reactivity has been correlated with reduction potentials of the perfluoroalkane substrate, the organofluorine reduction product, and the organic reducing agent. The most favorable reduction chemistry is expected when the order of electrochemical reduction potentials is substrate ⩾ reducing agent ≫ product. The most favorable reduction chemistry we observed was that of polycyclic perfluoroalkanes that contain tertiary carbon centers but no perfluoroalkyl substituents.

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Registry No. Benzophenone, 119-61-9; perfluorodecalin, 306-94-5; perfluoronaphthalene, 313-72-4; monohydroperfluoronaphthalene, 30998-48-2; dihydroperfluoronaphthalene, 36445-33-7; perfluoroperhydrophenanthrene, 306-91-2; perfluorophenanthrene, 1580-20-7; monohydroperfluorophenanthrene, 139565-02-9; dihydroperfluorophenanthrene, 139565-03-0; trihydroperfluorophenanthrene, 139565-04-1; naphthalene, 91-20-3; anthracene, 120-12-7; naphthacene, 92-24-0; benzil, 134-81-6; perfluorooctane, 307-34-6; perfluoro(methylcyclohexane), 355-02-2; perfluorocyclohexane, 355-68-0; sodium benzophenone, 3463-17-0; lithium benzophenone, 16592-10-2; 2[H]-perfluoronaphthalene, 784-00-9; tetrafluorobenzene, 28016-01-5; hexafluorobenzene, 392-56-3; pentafluorobenzene, 363-72-4; 1,2,4,5-tetrafluorobenzene, 327-54-8; perfluoroisopropyldecalin, 136286-31-2; perfluoro(2-butyldecalin), 119107-96-9; perfluorotoluene, 434-64-0; 1,2,4,5-tetrafluorophenol, 769-39-1.

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