modification was also induced by KCl, KBr, $KClO_4$, and potassium phosphate (Figure 2), but unlike the fluoride salts, these latter salts did not promote the related model transformation of **1** under comparable conditions. The nature of the duplex structure formed by **4** + **5** then likely stimulated a secondary salt dependent process (now under investigation) that also provided a suitable electrophile for selective alkylation.

Aqueous application of the silyl phenol described here illustrates an extremely intriguing principle by which a variety of new therapeutic and diagnostic reagents may be designed. DNA alkylation in this report was controlled by the ionic nature of the medium. Perhaps future compounds may be designed to decompose within a unique microenvironment established by a particular nucleotide sequence or conformation.[9]

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Supplementary Material Available: Experimental details for the syntheses of **1**, **3**, and **4**, reaction of **1**, and preparation of oligonucleotides (6 pages). Ordering information is given on any current masthead page.

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Electrochemical Detection of Fulleronium and Highly Reduced Fulleride (C_{60}^{5-}) Ions in Solution

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With the truncated icosahedral structure of buckminsterfullerene (C_{60}), as originally proposed by Smalley et al.,[1] now established by X-ray crystallography,[2] one of the important unresolved possibilities posed by this molecule is that C_{60}^{+} may explain the origin of the diffuse interstellar lines.[1,3] With this possibility in mind, the present work employs electrochemistry to probe the oxidation of C_{60} and its related fullerene, C_{70}. This study also describes the first electrochemical generation of C_{60}^{5-} in benzene and presents new electrochemical data on the stepwise electrogeneration of stable C_{60}^{n-} and C_{70}^{n-} (n = 1 to 4) ions in benzonitrile.[4a] Fulleride chemistry of this nature has recently acquired new importance with the advent of C_{60}-based superconducting materials.[5]

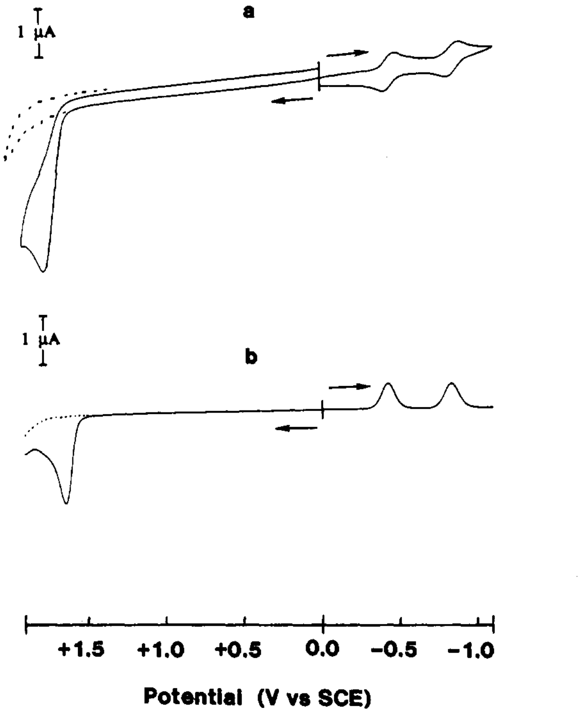

Figure 1. (a) Cyclic voltammogram (100 mV/s) and (b) differential pulse voltammogram (10 mV/s) of C_{70} in PhCN, 0.1 M $[(n\text{-Bu})_4N](PF_6)$. The dotted lines show the background current in the absence of C_{70}.

Cyclic voltammograms of C_{60} and C_{70} in benzonitrile exhibit a single, irreversible oxidation at E_{ox} = +1.76 V vs SCE (+1.30 V vs Fc/Fc^+) at a scan rate of 0.1 V/s (Figure 1a for C_{70}).[6] Both oxidation peak currents rise well above the base line and are much larger than for any of the reversible one-electron reductions. This oxidation remains irreversible at scan rates up to 50 V/s and at temperatures down to −15 °C.

Differential pulse voltammograms also exhibit well-defined anodic peaks associated with these irreversible oxidations (Figure 1b). The peak current intensities are about 4 times that of each of the one-electron reductions. Rotating disk voltammograms show these oxidations to be diffusion controlled at rotation rates between 300 and 3000 rpm, and the ratios of maximum diffusion currents between the single oxidation and the first reduction are 4:1. Controlled-potential coulometry of both fullerenes at +1.90 V vs SCE gives $n = 3.9 \pm 0.1$ to confirm that four electrons are abstracted.[6] As expected, no significant current is recorded upon returning the potential to 0.00 V. Both oxidized solutions are orange, stable toward air, and EPR silent at −150 °C.[6] These data indicate that the oxidations of C_{60} and C_{70} proceed via overall four-electron transfers which are followed or accompanied by one or more chemical reactions to render the overall electrochemical oxidations irreversible. The behavior of C_{60} and C_{70} upon oxidation is consistent with that of other polyaromatic hydrocarbon molecules which often exhibit irreversible electrooxidations due to chemical reactions of the electrogenerated species.[7]

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(6) Experimental conditions are as previously reported (ref 4). The stationary working electrode had a diameter of 1 mm. The reference electrode was used without the fritted-glass bridge in benzene to avoid additional potential drop between the reference and the working electrodes. Repeated oxidative scans passivated the working electrode, and thus it was cleaned with tissue paper before each scan to ensure reproducibility.

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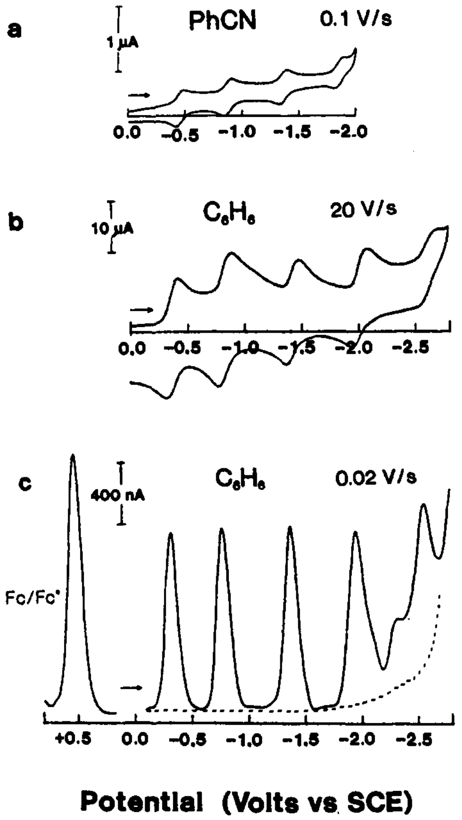

Figure 2. Reduction of C_{60} by (a) cyclic voltammetry in PhCN, 0.1 M $[(n\text{-Bu})_4N](PF_6)$ at 22 °C, and (b) cyclic voltammetry and (c) differential pulse voltammetry (80-mV pulse, 50-ms pulse width, 300-ms period) of C_{60} in C_6H_6 containing $[(n\text{-}C_6H_{13})_4N](ClO_4)$ (0.55 g in 1 cm^3) at 45 °C. The dotted line shows the background current in the absence of C_{60}.

Theory suggests that the LUMO of C_{60} can accept six electrons to form diamagnetic C_{60};[6-8] however, observation of more than four electroreductions of C_{60} or C_{70} has been hindered by the lack of a solvent in which they are soluble and which has a reduction potential window that extends beyond −2.0 V vs SCE.[4,9,10] To circumvent this problem, this study utilizes benzene, which has one of the widest known reduction windows.[11] Figure 2 shows cyclic and differential pulse voltammograms of C_{60} in benzene containing $[(n\text{-}C_6H_{13})_4N](ClO_4)$ at 45 °C.[12] Under these conditions, five reductions occur at $E_{1/2} = -0.36, -0.83, -1.42, -2.01$, and −2.60 V vs SCE (−0.83, −1.29, −1.89, −2.48, and −3.07 V vs Fc/Fc^+). A small peak between the fourth and fifth reductions in the differential pulse voltammograms (Figure 2c) and a similar peak in the cyclic voltammograms at sweep rates below 10 V/s appear to arise from a side reaction of C_{60}^{4-} in benzene. This side reaction is not observed by high scan rate CV, where all five reductions are reversible (Figure 2b).

Differential pulse voltammograms indicate that electrogenerated C_{70}^{3-} and C_{70}^{4-} ions are less stable in benzene than their C_{60} counterparts. Thus, several new peaks appear after the fourth reduction, none of which can be unambiguously assigned to C_{70}^{5-}.

C_{60}^{3-}, C_{60}^{4-}, C_{70}^{3-}, and C_{70}^{4-} can be observed electrochemically in methylene chloride at high scan rates, but are unstable by bulk electrolysis in that solvent.[4a] It is possible, however, to generate C_{60}^{3-} and C_{60}^{4-} by bulk electrolysis using 0.1 M $[(n\text{-Bu})_4N](PF_6)$ in benzonitrile.[4b] Similarly, C_{70}^{3-} andC_{70}^{4-} can be observed by CV at slow scan rates in benzonitrile and are also likely to be stable after bulk electrolysis.

In conclusion, this work presents the first reported observation for an electrochemical oxidation of C_{60} and C_{70} in solution. The overall four-electron oxidation is accompanied by one or more chemical reactions that consume the fulleronium ions. No conclusion can be reached as to whether the initial cation is multiply or singly charged. This report also presents the first reversible generation of C_{60}^{5-} in benzene. The third and fourth reductions of C_{60} give unstable species in CH_2Cl_2,[4] but in benzonitrile the highly reduced fulleride ions appear quite stable. Advantage is being taken of this stability for the electrosynthesis, isolation, and study of new fulleride-containing materials.

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(12) $[(n\text{-}C_6H_{13})_4N](ClO_4)$ (0.55 g) was dissolved in 1 cm^3 of benzene freshly distilled from sodium. The elevated temperature solubilizes and dissociates the supporting electrolyte.

Photochemical Activation of Racemic Mixtures in Biological Matrices

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Optical activation of racemic mixtures by preferential photoconversion of one antipode is a long-known process.[1] This process is to be expected when one antipode is preferentially excited by light of a selected circular polarity or when it is excited (deexcited) by means of energy-transfer processes from (to) a chiral sensitizer (quencher) under irradiation with achiral light. In the case of circularly polarized light (CPL), the enantiomeric excess (ee) obtained depends on Kuhn's dissymmetry factor, *g*,

$$g(\lambda) = 2(\epsilon_l - \epsilon_r)/(\epsilon_l + \epsilon_r) = \Delta\epsilon(\lambda)/\epsilon(\lambda)$$

and on the extent of substrate photodestruction. For reasonably large ees, almost complete photodestruction of the substrate is required, because *g*, in general, is small (0.01–0.001) at optical frequencies.[1a,c] The main scope of CPL photolysis probably rests on the determination of *g*, and hence of enantiomeric $\Delta\epsilon$, from both the measured circular dichroism signal induced on residual substrate and the extent of the photodestruction. This technique has been used in selected instances.[1a,2] With chiral photosensitization processes, optical activation is generally low, and spectroscopic quantities, such as $\Delta\epsilon$, cannot be deduced.[1a]

Herein it is reported that (*S*)-(−)-1,1′-bi-2-naphthol, (−)-**1**, is photoconverted with a large preference over (+)-**1**, so that *with moderate photodestruction*, high ees are obtained in residual **1**. This fact is related to the differences in the absorption spectra of the antipodes when they are complexed with the transport

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