(5) The spectra were obtained on the DuPont instrument at the University of North Carolina. Results on silylated carbon electrodes are reported independently, C. M. Elliott and R. W. Murray, *Anal. Chem.*, in press.

(6) The basal surface is not a prefect planar sheet. It is, therefore, possible to bind at dislocations as well as adsorb. This can account for the nitrogen signal.

(7) B. Firth and L. L. Miller, *J. Am. Chem. Soc.*, following paper in this issue.

(8) Optical yields are lower using the edge surface than the spectroscopic rods. The reason(s) for this is under investigation, but most likely involves differences in the surfaces.

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Oxidations on DSA and Chirally Modified DSA and SnO_2 Electrodes

Sir:

The chemical modification of electrode surfaces has recently come under investigation in our laboratories. Our goal is to produce interfacial regions which can be used to perform specific and unique reactions. Initial approaches have concentrated on synthesizing chiral electrode surfaces by binding electroinactive, chiral compounds to conductors. Such chiral electrodes are then used to perform asymmetric electrode reactions. This approach was selected because asymmetric synthesis requires a chiral reagent. It, therefore, provides a sensitive probe for a successful modification which remains intact and "active" during use. The first reported example is the preparation of "(*S*)-C_{el}PheM" involving binding (*S*)-(−)-methyl phenylalanate to a carbon electrode via the surface oxides.[1,2] This material was used to produce optically active alcohols by the reduction of ketones.[1]

In the present study we have prepared chiral surfaces from DSA[3] and SnO_2 electrodes and used them for preparative, asymmetric oxidations. Evidence is available which indicates that meta oxides can be chemically modified by silylation,[4,5] but these materials have not been used for preparative electrolysis. It was hoped that "active" and stable surfaces could be prepared which would be useful for anodic synthesis.

To our knowledge DSA electrodes have not been previously used for preparative organic electrochemistry and we have, therefore, investigated the use of this material without surface modification. It is found that the onset of background in CH_3CN containing 4% H_2O is about 1.8 V vs. Ag|$AgNO_3$ in CH_3CN. The surface is quite stable in this solvent at 1.5 V, and very high current densities are supported. Several reactions, e.g., cyclization of laudanosine[6] and conversion of 1-anisylethanol to *p*-methoxyacetophenone, proceed with yields equivalent to those obtained using platinum. Therefore, these electrodes seem to be a promising addition to the limited list of useful anodes.

Modification of antimony doped SnO_2 on a glass backing and DSA on a titanium backing was achieved by the following procedure. The electrode (general dimensions 30 × 80 mm) was placed in 100 ml of dry benzene (distilled from CaH) containing 3 ml of γ-aminopropyltriethoxysilane. The electrode was transferred after 30 min[7] to a dry benzene solution of (−)-camphoric anhydride (2 g in 100 ml). After 24 h the electrode was removed, washed with acetone, and was ready for use.[8] In the case of the DSA electrodes the titanium backing was covered with Dow Corning Silastic 732 RTV after functionalization.

Table I. Optical Purity of Sulfoxides[a]

Electrode	Reactant	Potential (V)[b]	Enantiomeric excess −2 (%)
Modified DSA	**1a**	1.4	0.9[c]
	1a	1.1	0.8
	1b	1.1	0.3
Modified SnO_2	**1a**	1.8	1.4

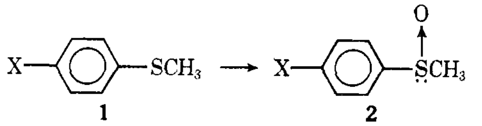
[a] Oxidations performed as described in text. [b] Measured vs. Ag|$AgNO_3$. [c] Average of four runs. Deviation of α_{589} ±0.1°. α_{obsd} −0.045 (*c* 3, $CHCl_3$).

There are to our knowledge no reports of asymmetric, anodic reactions. The anodic process chosen for study was the conversion of an aryl methyl sulfide to the sulfoxide. This reaction is relatively simple and proceeds in high chemical yield.[9] The sulfoxide molecules are chiral and the production of optically enriched product constitutes the test of successful modification.

The oxidation was carried out in a three-compartment cell using Ag|0.1 M $AgNO_3$ in CH_3CN as a reference electrode. The electrolyte consisted of 15 g of tetraethylammonium fluoroborate in 140 ml of acetonitrile and 10 ml of water.[9] In a typical experiment on DSA the potential was held at 1.4 V, background current was 20 mA, initial current from 500 mg of **1a** was 150 mA and after passage of 2 faraday/mol the final current was 30 mA. On SnO_2 at 1.8 V a typical background was 1 mA, initial current from 500 mg of **1a** was 28 mA and final current 2 mA. The products were isolated by evaporation of the anolyte, followed by addition of 100 ml of water and extraction with two 100-ml portions of ether. Rotary evaporation after drying the ether over anhydrous $MgSO_4$ gave the crude sulfoxide (~350 mg, current yield 65%) which was purified by chromatography on silica gel using $CHCl_3$ as elutent or by preparative TLC using a 1:1 mixture of chloroform and ethyl acetate as developer. All oxidations were run at room temperature under air (no change was observed if the reaction was run under argon or nitrogen) with the solution stirred with a magnetic stirrer.

The enantiomeric excesses shown in the table are of a low magnitude,[10] but they are quite reproducible and further purification by chromatography gave sulfoxide with an unchanged rotation. Crystallization gave material with higher rotations as is common for such compounds.[11] Rotations were taken at four wavelengths. Partially resolved material was compared to the electrolysis product and direct proportionality between all readings was obtained. The optical purity of the product was established by NMR using tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III). The methyl signal of a partially resolved sample split into a doublet and allowed the specific rotation of pure **2a** to be assigned as $\alpha^{20}{}_{589}$ 167°. The rotation of optically pure **2b** is $\alpha^{20}{}_{589}$ 146°.[12] Although the selectivity is not useful for asymmetric synthesis, it is comparable to the results obtained in similar conversions using chiral chemical reagents.[11] We have made a specific comparison using **1a** with (+)-percamphoric acid[13] which produced **2a** with enantiomeric excess +1.4.

To test the possibility that an adsorbed chiral reagent would be effective, a comparison experiment was conducted by oxidizing **1a** under the same conditions as above except that an unmodified DSA electrode was used and (+)-camphoric acid (equimolar with **1a**) was added to the anolyte. An electrode which had only been silanized was used in separate experiments with and without camphoric acid. In each case **2a** was isolated but was optically inactive. An attempt was also made to directly bind (+)-camphoric anhydride to DSA by soaking the electrode in a benzene solution of the anhydride for 24 h. The resulting material was used under the usual conditions to convert **1a** to **2a**. The product was again optically inactive.



a, X = NO$_2$
b, X = CH$_3$

Other experiments showed that the modified DSA electrode gave identical optical yields in three consecutive runs and that there was little dependence of optical yield on the potential used. There are, however, differences in the voltammograms of **1a** on modified and unmodified surfaces. These will be reported on and analyzed in a full publication.

Acknowledgment. Support by the National Science Foundation is gratefully acknowledged. Materials were supplied by Professor T. Kuwana, Dr. R. Neale, and Electrode Corporation. Stimulating discussions with Professor Kuwana and Dr. Neale are also acknowledged.

References and Notes

(1) B. Watkins, J. Behling, E. Kariv, and L. L. Miller, *J. Am. Chem. Soc.*, **97**, 3549 (1975).
(2) The accompanying communication reports on the use of C$_{el}$PheM in asymmetric sulfoxide synthesis. A variety of amino acids have been attached to carbon. Unpublished work of M. Mitani from this laboratory.
(3) These DSA electrodes contain tantalum and iridium oxides. They were supplied by Electrode Corporation, Chardon,Ohio.
(4) N. R. Armstrong, A. W. C. Lin, M. Fujihara, and T. Kuwana, *Anal. Chem.*, **48**, 741 (1976).
(5) P. R. Moses, L. Wier, and R. W. Murray, *Anal. Chem.*, **48**, 1882 (1975).
(6) L. L. Miller, F. R. Stermitz, and J. R. Falck, *J. Am. Chem. Soc.*, **93**, 5941 (1971).
(7) This is essentially the procedure used by Murray and co-workers for SnO$_2$. It was originally suggested to us by R. Neale, Union Carbide Corporation. In the present work it was found that a 24-h reaction period gave an electrode which passed very little current under the usual conditions. This is presumably due to polymer formation.
(8) Although there is some logic in this selection of reagents, it is deficient in two aspects. The use of camphoric anhydride means that two diastereomeric products could result. Second, it has been very recently suggested by R. W. Murray, based on ESCA measurements, that only a fraction of the amine groups on "γ-aminopropylated-SnO$_2$" are available for reaction.
(9) V. D. Parker in "Organic Electrochemistry", M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973, p 551.
(10) A control experiment in which **1a** was oxidized in the presence of partially resolved **2a** established that the latter was partially racemized during the oxidation. This apparently takes place at the surface of the polarized electrode since there is no racemization in solution without electrolysis.
(11) J. D. Morrison and H. S. Mosher in "Asymmetric Organic Reactions", Prentice Hall, Englewood Cliffs, N.J., 1971, p 335.
(12) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).
(13) J. F. Collins and M. A. McKervey, *J. Org. Chem.*, **34**, 4172 (1969).
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Carbanion Chemistry. A Room Temperature Retro-Diels–Alder Reaction

Sir:

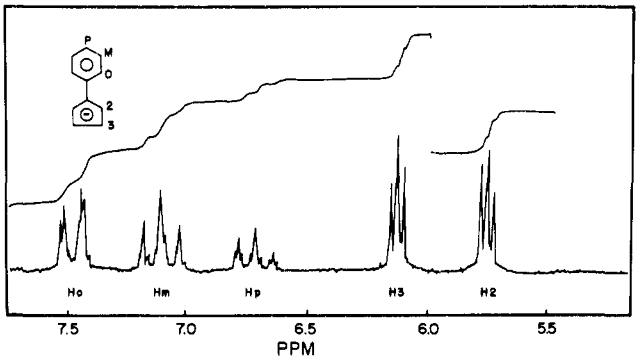
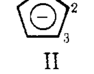


Figure 1. The 100-MHz ^{1}H NMR spectrum of phenylcyclopentadienide ion in DME-d_{10}. Chemical shifts are shown in δ units from internal Me$_4$Si.

The retro-Diels–Alder reaction commonly requires temperatures of 150 °C or more for convenient reaction.[1,2] The extensive chemistry of norbornene and norbornadiene provides ample demonstration of the resistance to thermolysis.[3] In striking contrast we now report that the 7-phenylnorbornenyl anion I undergoes the retro-Diels–Alder reaction within 30 min at room temperature. When a 1:3 mixture of *syn*- and *anti*-7-phenyl-7-methoxynorbornene[4] was stirred at room temperature with excess sodium–potassium alloy in 1,2-dimethoxyethane in an evacuated reactor,[5] gas evolution was observed and a deep green[6a] solution formed over a period of 30 min. The gas was collected and mass spectrometric analysis identified it as ethylene contaminated with solvent, 1,2-dimethoxyethane. The yield of ethylene was estimated to be 60% from mass spectrometric analysis. An NMR sample of the filtered solution in DME-d_{10} showed a clean spectrum of the phenylcyclopentadienide ion, II (Figure 1), as the only other species present. A ^{13}C NMR spectrum[6b] confirmed this conclusion. It is noteworthy that neither of the starting materials nor any other products were detected within the 5% limits set by sensitivity criteria. The structure of ion II was deduced from the characteristic phenyl anion absorptions and the AA′BB′ pattern of a monosubstituted cyclopentadiene in the proton spectrum. Proton decoupling confirmed the coupling interactions. When the anion solution was poured into ethanol, the color immediately discharged, but the transparent mixture darkened and turned black within 5 min. No low molecular weight product was obtained from a subsequent ether extract. This observation is consistent with the known chemistry of phenylcyclopentadienes.[7]



In an analogous pair of reactions, *syn*- and *anti*-9-phenyl,9-methoxybenzonorbornene were separately cleaved at −40 °C by Cs/K/Na alloy.[8] In 2 h at 0 °C gas evolution was complete yielding a clean solution of the 2-phenylindenide anion as the sole product. The proton spectrum showed a singlet 6.20 (H1), an AA′BB′ pattern 6.30, 7.00 (H4, H5, respectively), and the characteristic phenyl anion pattern at 6.78 (Hp), 7.15 (Hm overlapping H5), and 7.62 (Ho). Methanol quench yielded 2-phenylindene.

These observations now provide a rational explanation for several literature reports. Treatment of norbornadiene with amyl sodium gave a quantitative yield of the cyclopentadienyl anion and acetylene in 5 h.[11] When 7-*tert*-butoxynorbornadiene was cleaved with sodium/potassium alloy, only a 20%