quenching probably proceed via the mechanism ascribed for the reaction **2** → **3** → **7**.

References and Notes

(1) For a review see H. J. Shine, *MTP Int. Rev. Sci.*, **3**, 65 (1973).
(2) (a) V. N. Drozd, *J. Org. Chem. USSR (Engl. Transl.)*, **3**, 359, 531, 2026 (1968); (b) W. E. Truce and W. Brand, *J. Org. Chem.*, **35**, 1828 (1970); (c) W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, **18**, 99 (1970).
(3) D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 711 (1950).
(4) All new compounds gave satisfactory elementary analyses.
(5) T. Sato and K. Uno, *J. Chem. Soc., Chem. Commun.*, 579 (1972).
(6) The NMR spectra were recorded at 100 MHz. Proton chemical shifts are reported in parts per million downfield from $SiMe_4$. The decoupling experiments were carried out with the aid of a Hewlett-Packard 4204A oscillator.
(7) The absorptions at 6.67 and 7.08 ppm could clearly be observed in a tetradeuterated derivative of **3**. However, even in **3** the presence of the *o*-tolyl moiety did not hinder the assignment of the other bands. Deuterated **1** was prepared from 2,2′-dihydroxymethylbiphenyl and benzene-d_6 and rearranged to deuterated **3**.
(8) (a) T. H. Sidall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969); (b) R. Adams and J. Campbell, *J. Am. Chem. Soc.*, **72**, 153 (1950).
(9) (a) The NMR spectrum is complex due to hindered rotation.[8a] At 140 °C, a simple spectrum was obtained. (b) See also: M. Oki, *Angew. Chem.*, **15**, 87 (1976). (c) This behavior is analogous to **7**.
(10) S. C. Agrawal and B. L. Van Duuren, *J. Org. Chem.*, **40**, 2307 (1975).
(11) B. M. Trost and P. L. Kinson, *J. Am. Chem. Soc.*, **92**, 2591 (1970); **97**, 2438 (1975).

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The Preservation of Metal–Carbon Bonds and Metalloid–Carbon Bonds during Direct Fluorination: a Surprise Even to Fluorine Chemists

Sir:

Occasionally chemical experiments prove successful which surprise even the researchers initiating the work. Such is the case with the preservation of metal-carbon bonds during direct fluorination.

Before the fact, one could have written general logical mechanisms for elimination of methyl groups or cleavage of all metal-carbon bonds such that certain failure would be projected. These pathways still contribute to the overall reaction even under the reported conditions but are not catastrophic.

We have demonstrated preservation of mercury-carbon and silicon-carbon bonds during the process of direct fluorination by the fluorination of dimethylmercury to give bis(trifluoromethyl)mercury and of tetramethylsilane to give a series polyfluoro-tetramethylsilanes. The versatility of the method of direct fluorination has been previously demonstrated by the fluorination of structurally unusual hydrocarbons,[1] polymers,[2] and inorganic compounds[3] to mention just a few.

Dimethylmercury can be fluorinated to its perfluoro analogue, bis(trifluoromethyl)mercury, by low temperature fluorination. Yields of 6.5% (based on 1.53 g of $Hg(CH_3)_2$) can be obtained by fluorination at −78 to −90 °C. A fluorine concentration of 1.67%, obtained using a mixture of 1 cm^3/min fluorine to 60 cm^3/min helium, was used for 5 days in the cryogenic zone reactor.[1] The bis(trifluoromethyl)mercury was separated from fluorocarbons and unreacted dimethylmercury on a vacuum line. The reaction can be represented as follows.

$$\mathrm{Hg(CH_3)_2 + F_2/He \xrightarrow[5\ days]{-78\ ^\circ C} Hg(CF_3)_2 + HgF_2 + CF_4 + CF_3H + CF_2H_2 + CFH_3}$$

The physical properties and ^{19}F NMR agree with authentic samples prepared by alternative methods.[4] It has been found that $Hg(CF_3)_2$ does not react with 3% F_2 at −78 °C. It has also been found that $Hg(CF_3)_2$ does react slowly with 3% fluorine at 0 °C and appreciably at room temperature, forming HgF_2 and CF_4.

We have found it possible to preserve silicon-carbon bonds under low temperature direct fluorination and are able to isolate many polyfluorotetramethylsilanes produced by controlled low temperature fluorination of tetramethylsilane. Using 1.67% fluorine, obtained by combining flows of 1 cm^3/min fluorine and 60 cm^3/min helium, in a cryogenic zone reactor[1] in which 1.65 g of tetramethylsilane has been frozen at −110 °C, one can recover up to 75% of the fluorine substituted starting material containing all four silicon-carbon bonds intact. Varying degrees of fluorination are observed. Compounds of the type $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$, have been isolated and characterized (see Table I). Under the above conditions, we did not isolate any fluoromethylsilanes of the type $Si(CH_3)_3F$, $Si(CH_3)_2F_2$, and $Si(CH_3)F_3$. Several of the compounds are listed below along with their proton and fluorine NMR's. A considerable degree of fluorination results under the above conditions. In fact, only at −150 °C can one slow the fluorination process to allow the isolation of a single partially fluorinated species, $Si(CH_3)_3(CH_2F)$ (55% yield), as the sole product along with unreacted tetramethylsilane. The infrared, mass spectrum, and NMR of $Si(CH_3)_3(CH_2F)$ agree with that reported in the literature.[5]

Rapid metal-carbon bond vibrational and translational relaxation processes occurring at cryogenic surfaces may account for the isolation of these compounds. Obviously, the formation of three hydrogen fluoride molecules and three carbon fluorine bonds per methyl group is so exothermic that one could not explain the retention of metal-carbon bonds on energetic grounds. Work is now underway on the tungsten hexamethyl system and successful preliminary results have been achieved with a number of metal alkyl systems such as cadmium and tin.

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Table I[a]

	^1H[b]					^{19}F[c]				
	CH_3	CH_2F	J_{HF}	CHF_2	J_{HF}	CH_2F	J_{HF}	CHF_2	J_{HF}	J_{FF}
$Si(CH_3)(CH_2F)_2(CHF_2)$	−0.06	4.32	47.3	5.68	45.9	199.60	47.0	61.08	45.8	1.5
$Si(CH_2F)_2(CHF_2)_2$		4.66	46.6	5.91	45.4	202.87	46.4	59.88	45.4	2.0
$Si(CH_2F)_3(CHF_2)$		4.54	46.6	5.87	45.4	201.41	46.6	60.03	45.4	1.7
$Si(CH_2F)(CHF_2)_3$		4.68	46.2	5.82	45.0	204.39	46.6	59.57	45.0	2.4
$Si(CH_2F)_4$		4.24	47.0			200.13	46.9			

[a] All samples were run as neat liquids. Shifts are in parts per million. Coupling constants are in hertz. [b] + downfield from external Me_4Si. [c] + upfield from external TFA.

References and Notes

(1) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 513 (1975).
(2) A. J. Otsuka and R. J. Lagow, *J. Fluorine Chem.*, **4**, 371 (1974); R. J. Lagow and J. L. Margrave, *Polym. Lett.*, **12**, 177 (1974).
(3) N. J. Maraschin and R. J. Lagow, *J. Am. Chem. Soc.*, **94**, 8601 (1972).
(4) R. Eujen and R. J. Lagow, *Inorg. Chem.*, **14**, 3128 (1975).
(5) E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. A*, 2285 (1970).

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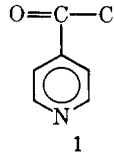
Anodic and Cathodic Reactions on a Chemically Modified Edge Surface of Graphite

Sir:

We have recently reported that carbon electrodes can be chemically modified to produce a chiral surface.[1] Thus, an electrode which had been heated in air was successively treated with thionyl chloride and (*S*)-phenylalanine methyl ester ((*S*)-PheM) producing a material labeled (*S*)-C_{el}PheM. This was used as a cathode in aqueous solution to produce chiral alcohols from prochiral ketones, indicating that (*S*)-C_{el}PheM was capable of inducing asymmetry. These experiments (with suitable controls) demonstrated the feasibility of achieving more selective electrochemical processes through chemical modification of electrode surfaces. A number of questions concerning the structure of C_{el}PheM and the mechanism of electrode reactions on such surfaces were raised by this initial study. For example, since carbon electrodes are primarily composed of graphitic microcrystallites, and since graphite has two kinds of crystal faces, edge and basal,[2] it was of interest to know if modification and, therefore, asymmetric synthesis was taking place on one or both of these surfaces. This was tested using highly ordered pyrolytic graphite, and the results are reported here. A wide variety of applications were also suggested by the initial study. We report here that amino acid modified carbon electrodes can be used at positive potentials. This allowed us to perform the first asymmetric anodic reaction.

Highly ordered pyrolytic graphite (HOPG)[3] has not to our knowledge been used for preparative electrochemistry. It is interesting to us because it has a structure closely similar to a single crystal of graphite. Therefore, each piece has well-defined edge surfaces and basal surfaces, and these can be used independently.[4] A perfect basal surface is simply one layer of carbon atoms in the graphitic array. The edge surface is composed of the layer ends and is generally covered with surface oxides. Thus, it is expected that the chiral modifier will be attached at the edge surface via the surface oxides.[1]

Two pieces (0.5 (edge height) × 2 × 3 cm) of HOPG were treated with $SOCl_2$ and (*S*)-PheM as usual.[1] The modified electrodes (HOPG–PheM) were then masked. On one piece, the edge surface was covered with silicon rubber so that electrochemistry could only occur on the basal surface. This electrode was used in 50% ethanol, 50% aqueous buffer acetate at −1.1 V vs. SCE for the reduction of 4-acetylpyridine (**1**)[1] and gave optically inactive **2** (yield >90%). The basal surface of the second piece was coated with silicon rubber. Reduction using the edge surface gave (−)-**2** (yield >90%) with enantiomeric excess of 2%. This result indicates that the asymmetric chemistry is taking place on edge surfaces, not basal, when a carbon rod is used.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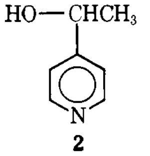
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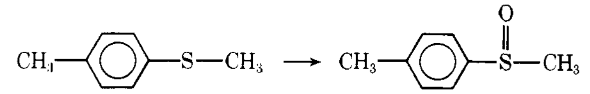
Table I. Photoelectron Spectroscopy Results[a]

Sample	Band intensity (Counts/s)				
	C(1s)	N(1s)	Cl(2s)	S(2p)	O(s)
HOPG + $SOCl_2$	49K	Nil	600	Nil	3.5K
HOPG + $SOCl_2$ + PheM	54K	660	300	Nil	12.5K
HOPG + PheM	50K	Nil	Nil	Nil	5.0K

[a] Results from the edge surface of HOPG.

This conclusion has been reinforced by x-ray photoelectron spectroscopy (XPS or ESCA). Four samples of HOPG were analyzed[5] for N, S, Cl, and C. The first was an unmodified piece and little N, S, or Cl was found in either surface. The second was HOPG which had been treated with $SOCl_2$ and then washed with acetone. It showed a markedly increased Cl signal but no S signal (Table I). The third sample was treated successively with $SOCl_2$ and the PheM and washed as usual. It showed a strong nitrogen signal from the edge surface. The basal surface did show nitrogen, but only about 20% of that from the edge.[6] A sample of HOPG which had been soaked in phenylalanine methyl ester solution and then thoroughly washed with water and acetone gave no nitrogen signal on the edge.

Finally, we wish to report that the anodic, asymmetric synthesis of sulfoxides[6] is possible on C_{el}PheM and that a similar differentiation of edge and basal chemistry is seen on modified HOPG. The reactant was *p*-tolyl methyl sulfide. As described in the accompanying communication the corresponding sulfoxide can be produced anodically in high chemical yield. On graphite in 2% aqueous acetonitrile at 1.1 V vs. Ag|0.1 M $AgNO_3$ in CH_3CN, it is formed in >90% current and material yield.



Using (*S*)-C_{el}PheM under these same conditions the product sulfoxide (chemical and electrical yield >90%) is optically active (enantiomeric excess 2.5% of (−)). Optical purity was assured by an unchanged rotation after gas chromatographic purification. Oxidation on the basal surface of HOPG modified as above with (*S*)-phenylalanine methyl ester gave optically inactive sulfoxide. Oxidation on the edge surface of (*S*)-HOPG–PheM gave optically active product (enantiomeric excess 0.5% of (−)).[8]

Thus, the results in total demonstrate that HOPG is useful for preparative electrochemistry, that HOPG–PheM is modified on the edge surface, not basal, and the modification is useful at positive potentials. These data seem transferable to results on ordinary carbon and indicate that the activity of modified carbon electrodes results at least in part from electrochemistry on the edge surfaces of microcrystallites of graphite and not from modified basal surfaces.

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References and Notes

(1) B. F. Watkins, J. R. Behling, E. Kariv, and L. L. Miller, *J. Am. Chem. Soc.*, **97**, 3549 (1975).
(2) J. S. Mattson and H. B. Mark, "Activated Carbon", Marcel Dekker, New York, N.Y., 1971.
(3) Supplied by Dr. A. Moore, Union Carbide Corporation, Parma, Ohio.
(4) I. Mocros and E. Yeager, *Electrochim. Acta*, **15**, 953 (1970).