the above reaction. Interestingly, the reaction of **13** (1.0 equiv) with TTMSS (1.2 equiv) in toluene, using AIBN as initiator gave the cyclic product **14** as nonseparable mixture of 1:1 cis and trans isomers.

Further explorations of tris(trimethylsilyl)silane in free-radical reactions are in progress.

Acknowledgment. We thank the Mass Spectroscopy Lab, University of Ottawa, for recording CI mass spectra; Anne Webb, Elemental Analysis Lab (NRC, Ottawa) for elemental analysis; and Dan Wayner for stimulating discussions.

Supplementary Material Available: General procedures and experimental results for new compounds (5 pages). Ordering information is given on any current masthead page.

Organic Chemistry of C_{60} (Buckminsterfullerene): Chromatography and Osmylation

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Summary: Treatment of C_{60} with osmium tetroxide and pyridine gives the osmate ester (2:1 adduct) establishing that oxygen functionality can be added to C_{60} without disrupting the carbon framework.

The efficient macroscopic preparation of C_{60} by the contact-arc vaporization of graphite rods[1] has recently brought this enchanting molecule from the realm of molecular beam experiments[2] into that of synthetic organic chemistry. We are interested in selectively adding functional groups to C_{60} in a way that leaves the carbon skeleton intact and allows for further transformation.[3] We report here the chromatographic separation of C_{60} and C_{70} on a Pirkle column and the osmylation of C_{60}.

We have found that the crude benzene-soluble material from the carbon-arc apparatus[1] is a complex mixture. Flash chromatography[4] by dry loading onto silica gel and elution with hexanes gives a 40% recovery of material that is almost exclusively C_{60} and C_{70}. C_{60} and C_{70} are quite mobile on silica gel and separate only slightly on the flash column. HPLC on silica gel gives partial but incomplete separation. We reasoned that a stationary support containing π-acids might increase the retention and promote the discrimination of these π-basic aromatic clusters. Pirkle's phenylglycine-based HPLC column was designed for the separation of enantiomers by interactions that include the attraction between π-basic aromatic groups on substrates and π-acidic dinitrobenzamide groups on the stationary support.[5] We have found that this column can separate C_{60} and C_{70} by a wide margin, $\alpha = 2.25$ (Figure 1).[6] On the commercially available semipreparative column,[7] ca. 0.5 mg of material can be separated per injection; large preparative columns are known.[8] Mass spectra of purified C_{60} and C_{70} are shown in Figures 2 and 3. The small mass 720 peak in the C_{70} spectrum is probably due to fragmentation;[9] no C_{60} was visible by HPLC or ^{13}C NMR,[10] the former being quite sensitive.[11] The ^{13}C NMR spectrum of purified C_{70} confirms[12] that one of the C_{70} peaks is not under the C_{60} peak as suspected on the basis of the examination of C_{60}/C_{70} mixtures.[13] The pronounced separation of C_{60} and C_{70} on the Pirkle column suggests that electron donor–acceptor complexes of these aromatic carbon clusters can be prepared, and we are pursuing this possibility.

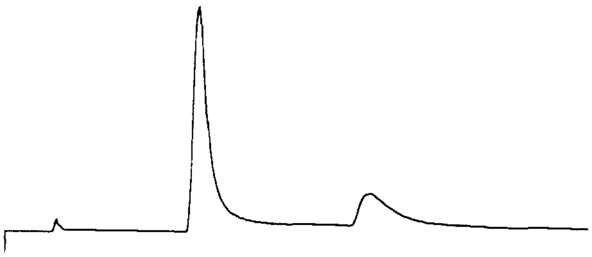
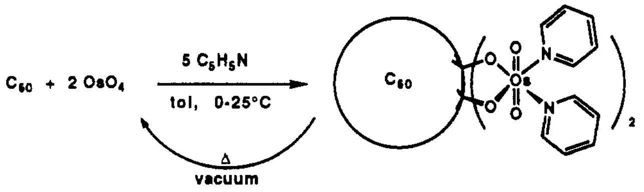


Figure 1. HPLC separation of C_{60} (12.2 min) and C_{70} (23.5 min) on a Pirkle column[7] (eluted with hexane at 5.0 mL/min, detected at 280 nm).

We chose the powerful but selective oxidant osmium tetraoxide for the functionalization of C_{60}. The pyridine-accelerated osmylation of polycyclic aromatic hydrocarbons is well known.[14] Treatment of a homogeneous toluene solution of a ca. 4:1 C_{60}/C_{70} mixture and 2 equiv of osmium tetraoxide at 0 °C with 5 equiv of pyridine gave a brown precipitate within 1 min. After 12 h at room temperature, the majority of the C_{60} and C_{70} had reacted according to TLC. Filtration and washing with toluene



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[4] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

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[6] Taylor et al. just reported the separation of C_{60} and C_{70} on alumina.[1b]

[7] Pirkle type 1-A ionically bound phenylglycine column, 25 cm × 10 mm i.d., Regis Chemical Company, Morton Grove, IL.

[8] Pirkle, W. H.; Finn, J. M. *J. Org. Chem.* **1982**, *47*, 4037.

[9] O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.

[10] C_{70} ^{13}C NMR (C_6D_6): δ 150.7, 148.1, 147.4, 145.4, 130.9.

[11] The relative molar absorptivities of C_{70} and C_{60}, $\epsilon(C_{70})/\epsilon(C_{60})$, is 1.2 at 280 mn.

[12] Taylor et al. just reported a similar but 0.6 ppm upfield shifted spectrum of C_{70} run in the presence of $Cr(acac)_3$.[1b]

[13] Meijer, G.; Bethune, D. S.; Wilson, R. J.; Johnson, R. D. Submitted for publication.

[14] (a) Schroder, M. *Chem. Rev.* **1980**, *80*, 187. (b) Wallis, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 8207.

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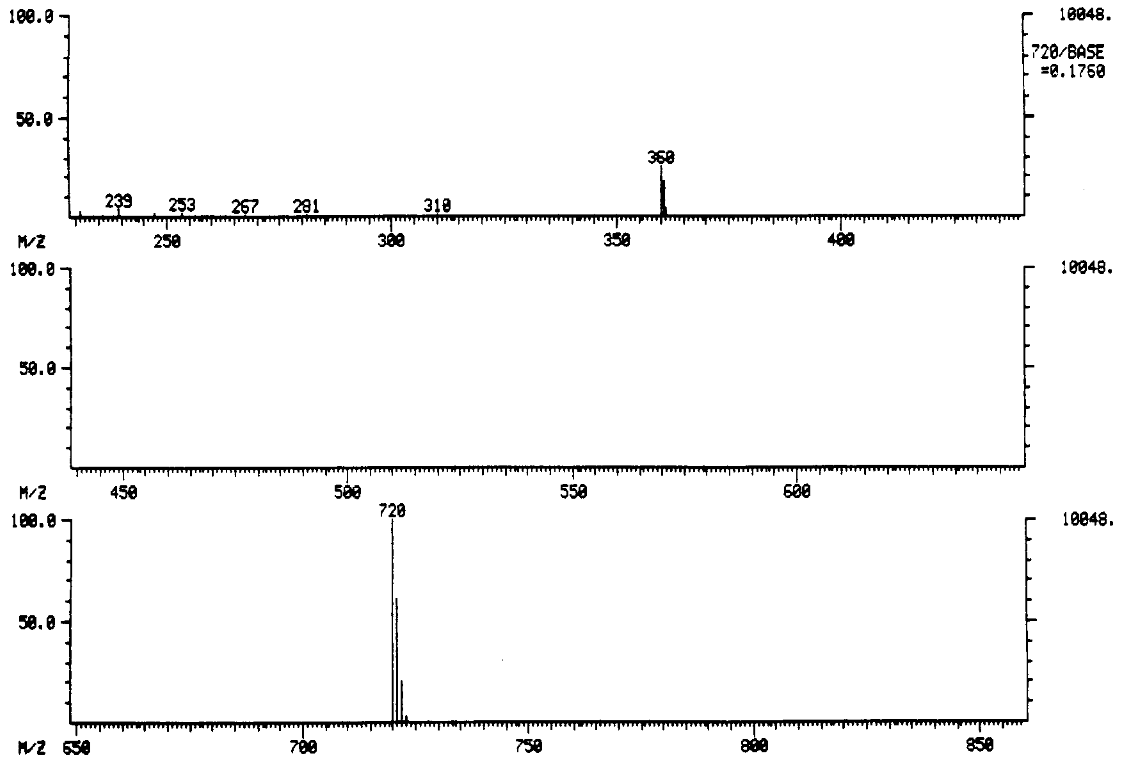

Figure 2. Electron impact mass spectrum of chromatographed C_{60}.

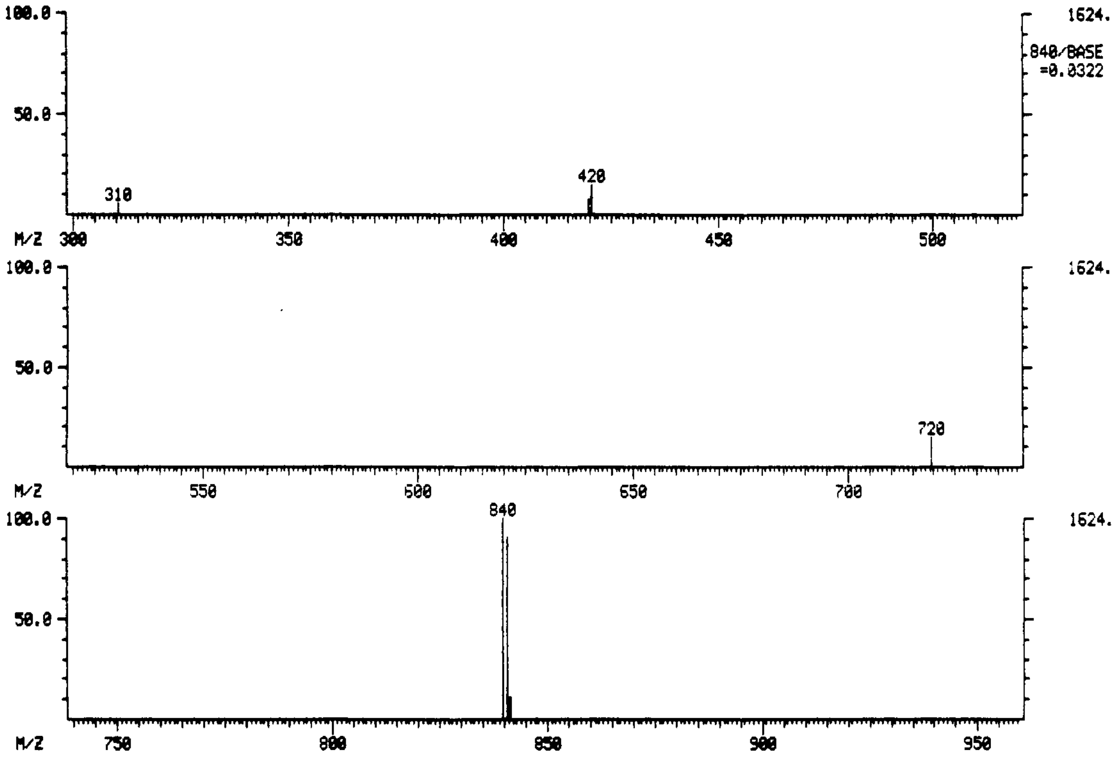

Figure 3. Electron impact mass spectrum of chromatographed C_{70}.

gave an 81% yield of osmate ester corresponding to the addition of two osmium(VI) units per carbon cluster. Use of 1 equiv of osmium tetraoxide and 2.5 equiv of pyridine gave the same material in 41% yield with respect to C_{60}.

The presence of the diolatodioxobis(amine)osmium(VI) ester moiety in the product was established by the characteristic IR band at 836 cm^{-1} ($\nu^{as}(OsO_2)$).[14-16] Pyridine resonances were visible in the ^{1}H NMR (DMSO-d_6); low solubility precluded ^{13}C NMR. The 2:1 stoichiometry is consistent with the elemental analysis.[17] The presence of the intact C_{60} skeleton was established by thermal re-

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(15) IR (KBr): 1607, 1482, 1450, 1215, 1069, 972, 954, 876, 836 (s), 763, 692, 627, 618, 526 cm^{-1}.

(16) Collin, R. J.; Jones, J.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* 1974, 1094.

(17) Elemental analysis of dried precipitate. Calcd for $C_{80}H_{20}N_4O_8Os_2$: C, 62.17; H, 1.30; N, 3.63; Os, 24.61. Found: C, 61.11; H, 1.42; N, 3.67; Os, 24.49.

version to C_{60} under vacuum.[18] This was first observed in the electron impact mass chromatogram. Heating the sample in the mass spectrometer probe under vacuum at ca. 290 °C and recording EI spectra at 0.45-min intervals gave spectra of OsO_4 and pyridine (maximum at 1.8 min) followed by the spectrum of C_{60} (maximum at 5.85 min). Prolonged heating is required to detect the C_{60} due to its low volatility; this was also observed for the spectrum of the pure cluster. A preparative version of this experiment whereby the osmate ester was heated under vacuum for 2 min (heat gun, 0.05 mmHg) gave a 47% combined yield of C_{60} and C_{70} (enriched in C_{60} relative to the starting material) as determined by HPLC with respect to a naphthalene standard. The osmate ester was free of unreacted C_{60} according to IR and TLC, so the C_{60} must have been reformed upon heating.

These experiments establish that heteroatom functionality can be added to C_{60} without disrupting the carbon framework. We are currently exploring the regiochemistry of the osmylation and converting the glycolates to other organic functional groups in order to manipulate the C_{60} framework.

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[18] $ReOCl(OCH_2CH_2O)(phen)$ similarly gives ethylene and $ReO_3Cl(phen)$ when heated under vacuum: Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981.

Articles

Lipase-Catalyzed Asymmetric Hydrolysis of Esters Having Remote Chiral/Prochiral Centers

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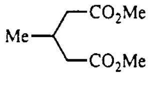
Enzymatic hydrolysis of prochiral and racemic dithioacetal esters having up to five bonds between the prochiral/chiral center and the ester carbonyl group proceeds with selectivities up to 98% enantiomeric excess when commercially available lipases are used. For lipase from *Pseudomonas* sp., chemical yields and ee's were better with the substrate having four bonds between the prochiral center and ester carbonyl than with the three-bond or five-bond analogues, demonstrating that selectivity does not necessarily diminish as the distance between the chiral center and the reaction site increases. These findings are the cornerstone of efficient chemoenzymatic syntheses of both enantiomers of a potent LTD_4 antagonist.

Use of hydrolytic enzymes to resolve racemic carboxylic esters and amides, or to stereospecifically hydrolyze prochiral or meso diesters, has become a powerful tool in organic synthesis.[1] However, in most cases, the compounds undergoing the enzymatic reaction have the prochiral or chiral center only one or two bonds away from the reacting carbonyl group, and often the ester groups are held in rigid, cyclic frameworks. Only a few examples have been reported in which the chiral/prochiral center is three or more bonds from the reacting carbonyl center. With pig liver esterase, Tamm and co-workers found that increasing the length between the prochiral center and the ester group from two bonds in **1** to three bonds in **2** resulted in a lowering of the enantiomeric excess (ee) from 90% to 10% in the resulting half ester product.[2] Better success was achieved by Whitesides in the porcine pancreatic lipase hydrolysis of chiral epoxy esters (eq 1).[3] In these cases, the ee's of the recovered esters were 60–90% with $n = 1$ and 70–80% with $n = 2$, while the recovered alcohols had ee's in the range of 30–80%.[3]



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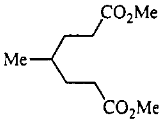

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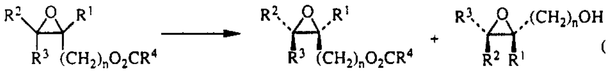

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