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the above reaction. Interestingly, the reaction of 13 (1.0 equiv) with TTMS (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 C₆₀ (Buckminsterfullerene): Chromatography and Osmylation

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Received November 9, 1990

Summary: Treatment of C₆₀ with osmium tetroxide and pyridine gives the osmate ester (2:1 adduct) establishing that oxygen functionality can be added to C₆₀ without disrupting the carbon framework.

The efficient macroscopic preparation of C₆₀ by the contact-arc vaporization of graphite rods¹ has recently brought this enchanting molecule from the realm of molecular beam experiments² into that of synthetic organic chemistry. We are interested in selectively adding functional groups to C₆₀ in a way that leaves the carbon skeleton intact and allows for further transformation.³ We report here the chromatographic separation of C₆₀ and C₇₀ on a Pirkle column and the osmylation of C₆₀.

We have found that the crude benzene-soluble material from the carbon-arc apparatus¹ is a complex mixture. Flash chromatography⁴ by dry loading onto silica gel and elution with hexanes gives a 40% recovery of material that is almost exclusively C₆₀ and C₇₀. C₆₀ and C₇₀ 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 C₆₀ and C₇₀ 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

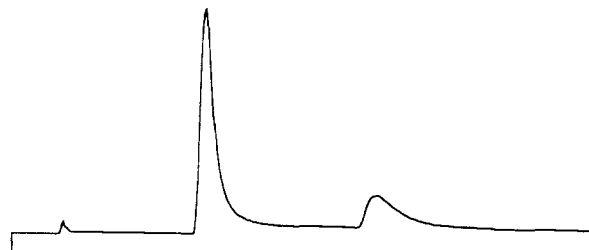
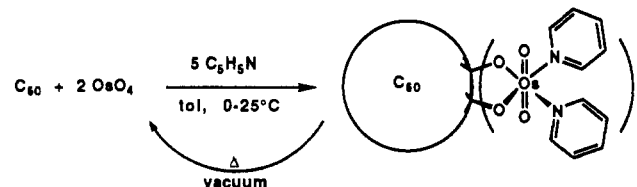


Figure 1. HPLC separation of C₆₀ (12.2 min) and C₇₀ (23.5 min) on a Pirkle column⁷ (eluted with hexane at 5.0 mL/min, detected at 280 nm).

purified C₆₀ and C₇₀ are shown in Figures 2 and 3. The small mass 720 peak in the C₇₀ spectrum is probably due to fragmentation;⁹ no C₆₀ was visible by HPLC or ¹³C NMR,¹⁰ the former being quite sensitive.¹¹ The ¹³C NMR spectrum of purified C₇₀ confirms¹² that one of the C₇₀ peaks is not under the C₆₀ peak as suspected on the basis of the examination of C₆₀/C₇₀ mixtures.¹³ The pronounced separation of C₆₀ and C₇₀ on the Pirkle column suggests that electron donor-acceptor complexes of these aromatic carbon clusters can be prepared, and we are pursuing this possibility.

We chose the powerful but selective oxidant osmium tetroxide for the functionalization of C₆₀. The pyridine-accelerated osmylation of polycyclic aromatic hydrocarbons is well known.¹⁴ Treatment of a homogeneous toluene solution of a ca. 4:1 C₆₀/C₇₀ mixture and 2 equiv of osmium tetroxide 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 C₆₀ and C₇₀ had reacted according to TLC. Filtration and washing with toluene



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(3) The conversion of C₆₀ to C₆₀H₃₆ (structure undetermined) by Birch reduction is described in ref 1c.

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(6) Taylor et al. just reported the separation of C₆₀ and C₇₀ 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) C₇₀ ¹³C NMR (C₆D₆): δ 150.7, 148.1, 147.4, 145.4, 130.9.

(11) The relative molar absorptivities of C₇₀ and C₆₀, $\epsilon(C_{70})/\epsilon(C_{60})$, is 1.2 at 280 nm.

(12) Taylor et al. just reported a similar but 0.6 ppm upfield shifted spectrum of C₇₀ 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.

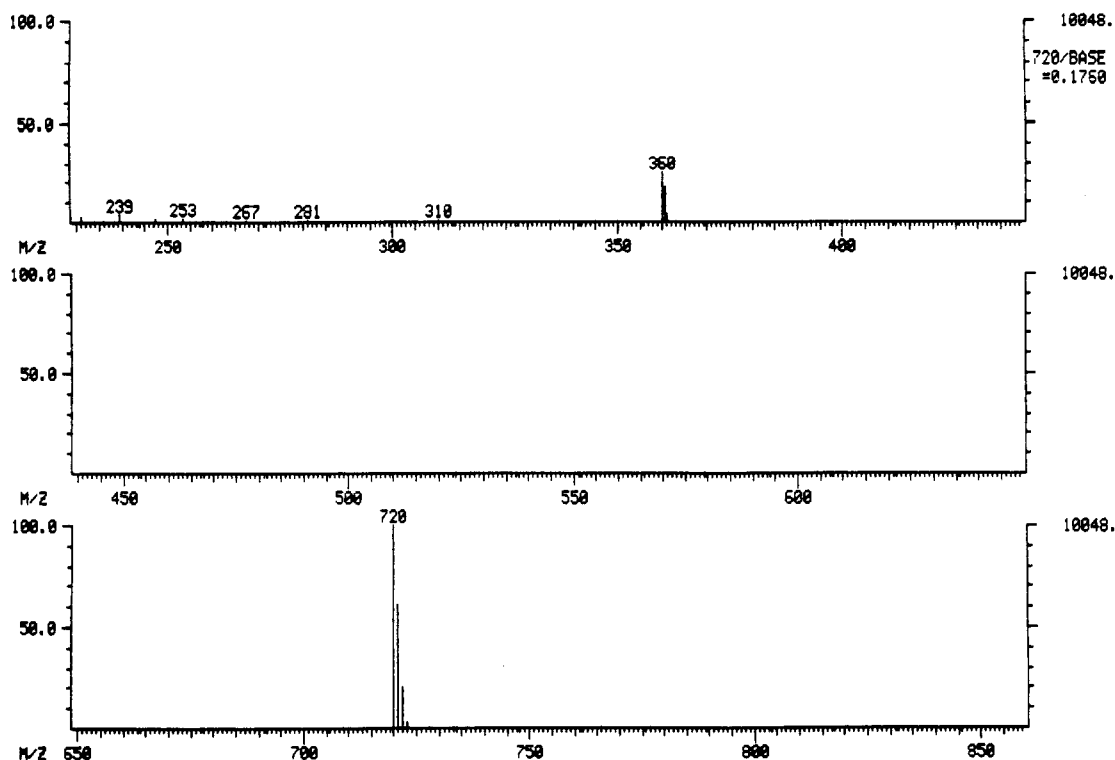


Figure 2. Electron impact mass spectrum of chromatographed C_{60} .

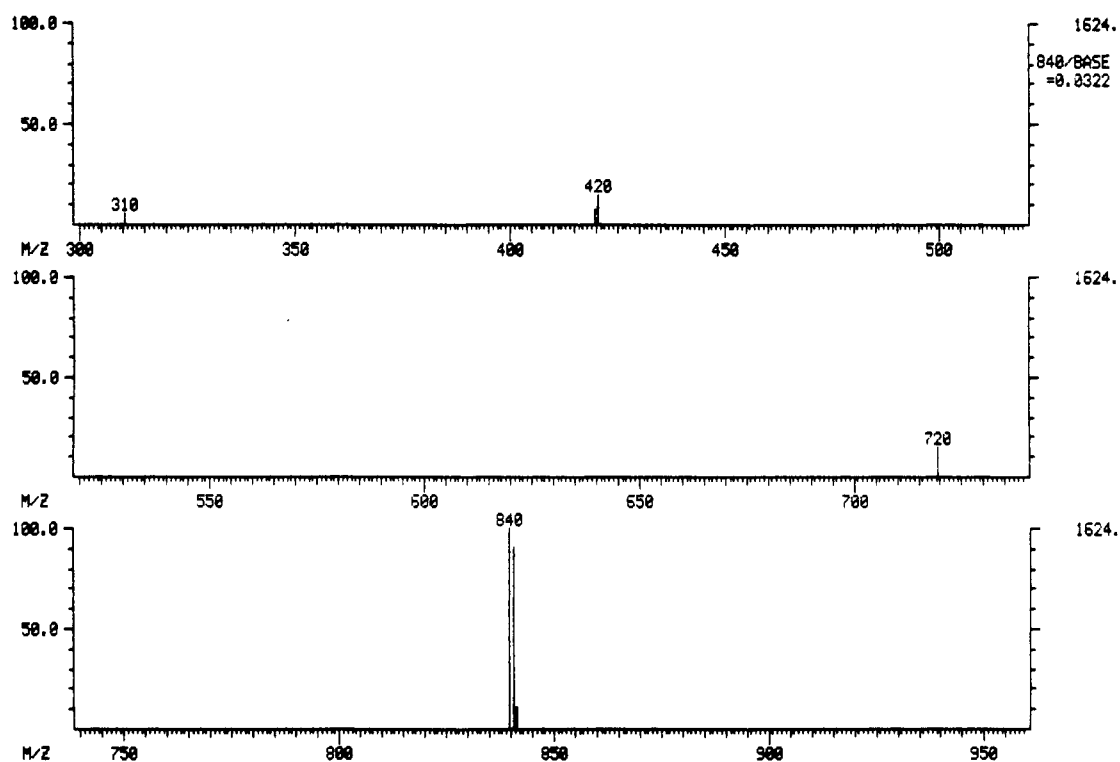


Figure 3. Electron impact mass spectrum of chromatographed C_{70} .

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 tetroxide 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} ($\nu_{as}(\text{OsO}_2)$).¹⁴⁻¹⁶ Pyridine

resonances were visible in the ^1H NMR ($\text{DMSO}-d_6$); 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-

(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 $\text{C}_{80}\text{H}_{20}\text{N}_4\text{O}_8\text{Os}_2$: 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

(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.

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.

Acknowledgment. J.M.H. is grateful to the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (New Faculty Grant), the Shell Oil Company Foundation (Shell Faculty Fellowship), Xerox Corporation, Monsanto Company, and the Merck Sharp & Dohme Research Laboratories for financial support. J.R.H. thanks the NASA SETI foundation and R.J.S. thanks the National Science Foundation for support. We thank Joseph Lyssikatos for assistance with the ^{13}C NMR spectrum of C_{70} .

Articles

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

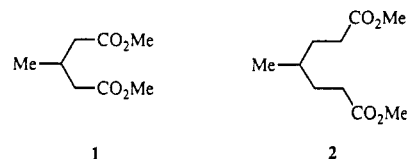
D. L. Hughes,* J. J. Bergan, J. S. Amato, M. Bhupathy, J. L. Leazer, J. M. McNamara, D. R. Sidler, P. J. Reider, and E. J. J. Grabowski

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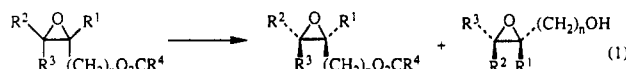
Received June 20, 1990

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 LTD₄ 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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