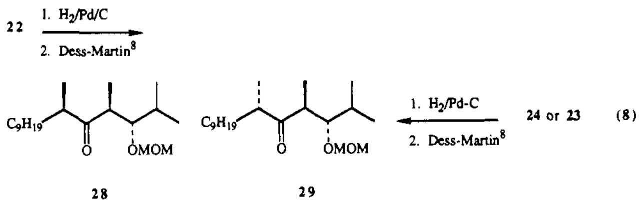


reaction (**24**). However, upon hydrogenation and oxidation both were converted to ketone **29**.

Likely transition states for the BF_3- and $MgBr_2$-promoted additions are depicted in Figure 1. In each case an anti C=O/C=C arrangement satisfactorily accounts for the observed diastereoselectivity assuming an anti disposition for the $SnBu_3$ moiety.[10] A Cram-Felkin mode of addition is preferred in the BF_3-mediated reaction whereas $MgBr_2$ induces chelation control.[6] Extensions of these findings and further scrutiny of the proposed transition state through the use of enantioenriched aldehydes and stannanes is in progress.

Typical Experimental Procedure. 2,4-Dimethyl-5-tridecyn-3-ol (9b). To a solution of 0.20 mL (1.68 mmol) of $BF_3 \cdot Et_2O$ in 8 mL of CH_2Cl_2 was added dropwise a mixture of 180 mg (0.40 mmol) of allenic stannane **4** and 0.10 mL (1.12 mmol) of isobutyraldehyde (**8b**) in 3 mL of CH_2Cl_2 at −78 °C. The mixture was stirred at −78 °C for 30 min, quenched with saturated $NaHCO_3$, and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether, 4:1) to yield 72 mg (80%) of alcohol **9b** as a single isomer: IR (film) ν 3442, 2929, 2856, 1467, 1378, 1133, 990 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 (m, J = 4.3 Hz, 1 H, HOCH), 2.56 (m, 1 H, propargylic CH), 2.13 (dt, J = 2.3, 7.1 Hz, 2 H, propargylic CH_2), 1.95 (m, 1 H, CH(CH_3)$_2$), 1.68 (d, J = 4.1 Hz, 1 H, OH), 1.46–1.26 (m, 10 H, $(CH_2)_5$), 1.13 (d, J = 6.9 Hz, 3 H, C≡CCHCH_3), 0.94 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 0.89 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 0.87 (t, J = 7.0 Hz, 3 H, CH_2CH_3); MS calcd for $C_{15}H_{28}O$ (M − CH(CH_3)$_2$) 181, found 181. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.20; H, 12.54.

Acknowledgment. Support from the National Institutes of Health (Research Grant 2 RO1 GM29475) and the National Science Foundation (Research Grant CHEM 8912745) is gratefully acknowledged.

Supplementary Material Available: Experimental procedures and ^{1}H NMR spectra for compounds **4**, **9a–c**, **14**, **20**, **22**, **24**, and **26–29** (23 pages). Ordering information is given on any current masthead page.

---

(10) The anti orientation was first suggested by Yamamoto.[5] Certain intramolecular additions have been shown to proceed through a *synclinal* arrangement. Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. Marshall, J. A.; Gung, W. Y. *Tetrahedron* **1989**, *45*, 1043.

Tris(trimethylsilyl)silane (TTMSS): Formation of Carbon-Centered Radicals from 1,3-Dithiolanes and 1,3-Dithianes[1]

Prabhat Arya,* Connie Samson,[2] Maurice Lesage, and David Griller[3]

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Received August 13, 1990

Summary: Tris(trimethylsilyl)silane (TTMSS), a nontoxic reagent, can be used to generate carbon-centered radicals from 1,3-dithiolanes and 1,3-dithianes.

The formation of carbon–carbon bonds through free-radical reactions is an important strategy in synthetic chemistry.[4] Tributyltin hydride, a free-radical mediator, has been the reagent of choice for the formation of radicals for many years because organotin radicals generate carbon-centered radicals from a variety of functional groups. However, the high toxicity of this reagent and the difficulty of removing it from the reaction products makes it less than optimal.

$$RX + Bu_3Sn^\bullet \rightarrow R^\bullet + Bu_3SnX$$

$$R^\bullet + Bu_3SnH \rightarrow RH + Bu_3Sn^\bullet$$

$$X = I, Br, Cl, SPh, SePh$$

Recently, we have shown that tris(trimethylsilyl)silane (TTMSS) can be used as a free-radical mediator due to its low Si-H bond energy.[5] Many trialkylsilicon hydrides are not suitable because of the high silicon–hydrogen bond strengths. TTMSS has a Si–H bond strength of 79 kcal mol^{-1}, which is very close to Sn–H bond strength 74 kcal mol^{-1} in Bu_3SnH. The weaker bond strength of tris(trimethylsilyl)silane is probably due to the bonding interaction between β-silicon d orbitals and the semioccupied p orbital on the central atom in the corresponding silyl radical.[6] The nontoxic TTMSS is ecologically superior to tributyltin hydride, and the ready purification of the products from the reaction mixtures makes it an attractive reagent.

$$RX + (Me_3Si)_3Si^\bullet \rightarrow R^\bullet + (Me_3Si)_3SiX$$

$$R^\bullet + (Me_3Si)_3SiH \rightarrow RH + (Me_3Si)_3Si^\bullet$$

$$X = I, Br, SePh$$

The role of Bu_3SnH for the desulfurization of dithiolanes and the corresponding cyclizations from thioxalanes have been studied by Gutierrez[7a] and Fallis.[7b] In this paper, we

---

(1) Issued as NRCC publication number 32311.

(2) NRC summer student, 1990.

(3) Present address: Peat Marwick Stevenson & Kellogg, Management Consultants, Ottawa, Canada.

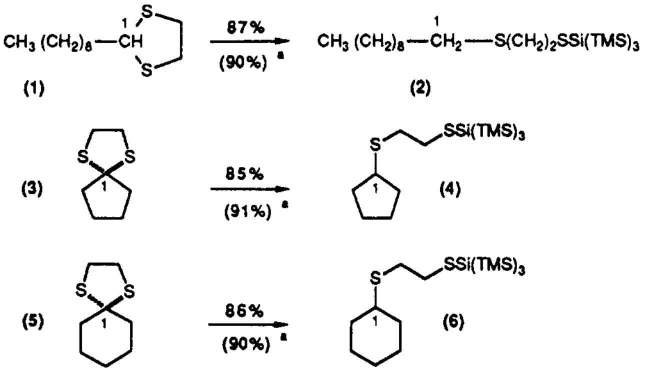
(4) (a) Hart, D. J. *Science* **1984**, *223*, 883. (b) Giese, B. In *Radicals in Organic Synthesis Formation of Carbon–Carbon Bonds*; Pergamon: New York, 1986. (c) Neuman, W. P. *Synthesis* **1987**, 665. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (e) Curren, D. P. *Synthesis* **1988**, 417 and 489.

(5) (a) Chatgilialoglu, C.; Griller D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3641. (b) Chatgiliagloglu, C.; Griller D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 364. (c) Lesage, M.; Chatgilialoglu, C.; Griller, D. *Tetrahedron Lett.* **1989**, *30*, 2733. (d) Giese, B.; Kopping, B.; Chatgilialoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681. (e) Alberti, A.; Chatgilialoglu, C. *Tetrahedron* **1990**, *46*, 3963. (f) Jurgen, K.; Giese, B. *Synlett* **1990**, 91.

(6) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.

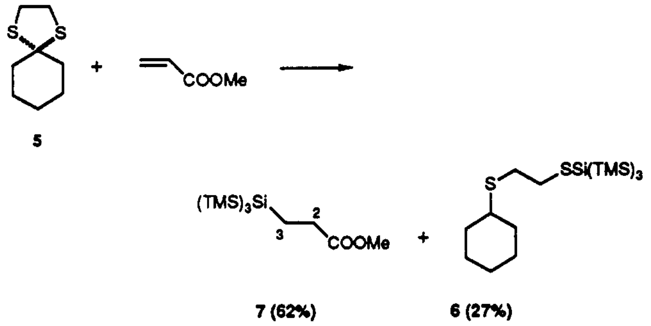
0022-3263/90/1955-6248$02.50/0 Published 1990 by the American Chemical Society

Scheme I[a]



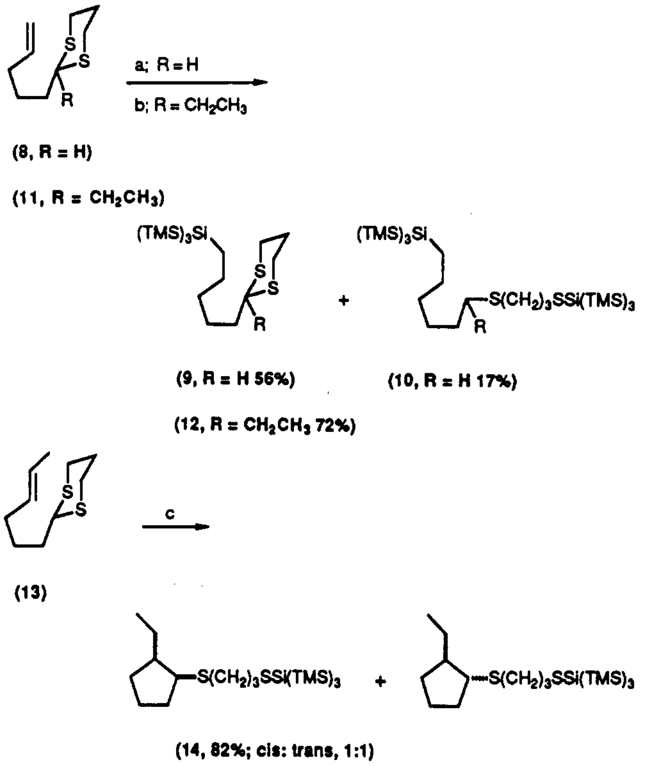
[a] Tris(trimethylsilyl)silane, AIBN, toluene, 80–85 °C, 2 h. GC yield in parentheses.

Scheme II[a]



[a] Tris(trimethylsilyl)silane, AIBN, toluene, 85 °C, 2.5 h.

Scheme III[a]



[a] (a) Tris(trimethylsilyl)silane, AIBN, toluene 70 °C, 3 h; (b) TTMSS, AIBN, toluene, 90 °C, 3.5 h; (c) TTMSS, AIBN, toluene 85 °C, 2.5 h.

report our preliminary results of the reactions of 1,3-dithiolane and 1,3-dithiane derivatives with tris(trimethylsilyl)silane.

The 1,3-dithiolane of decanal (1) on treatment with 1 equiv of TTMSS in toluene using AIBN as an initiator at 85 °C gives cleavage of one of the carbon–sulfur bonds. The product was purified over silica gel by flash column (EtOAc–hexane, 1:40) to give the corresponding thioether derivative **2**, identified from ^1H NMR, ^{13}C NMR and MS spectra (CIMS m/z 481, M + 2) in 87% yield.[8] The ^1H NMR showed a signal for two protons (at C-1) at δ 2.55 (t, J = 7.4 Hz), which appeared due to the ring opening of 1,3-dithiolane of decanal. Similarly, the 1,3-dithiolane of cyclopentanone (**3**) and that of cyclohexanone (**5**) undergo cleavage of one carbon–sulfur bond to give the thioether derivatives **4** (CIMS m/z 409, M + 1) and **6** (CIMS m/z 423, M + 1) in 85% and 86%, respectively. The products **4** and **6** were easily identified using ^1H NMR, ^{13}C NMR, and MS spectra. The cleavage of the remaining carbon–sulfur bond from dithiolanes was not observed even with the use of an excess of TTMSS. This is the first demonstration of carbon-centered radical formation via the cleavage of a carbon–sulfur bond using a silane as a radical mediator.

We, further studied the trapping of carbon-centered radicals generated from 1,3-dithiolanes with an electron-deficient olefin systems using TTMSS as a radical mediator. Thus, a mixture of the 1,3-dithiolane of cyclohexanone (**5**), methyl acrylate, TTMSS, and AIBN as initiator on warming in toluene (85 °C) gave an unexpected result. The major product resulted from the attack of the tris(trimethylsilyl) radical at the methyl acrylate.[9] The products were isolated using flash column (EtOAc–hexane; 1:30) to give **7** (62%) and **6** (27%). The ^{13}C NMR of **7** showed signals at δ 32.9 and 2.7 for C-2 and C-3 and had EIMS m/z 229, M − CH_3. This suggests that the trapping of tris(trimethylsilyl)silyl radical by an electron-deficient olefin is much faster than the ring opening of the 1,3-dithiolane derivative, when TTMSS is used as a radical mediator.

In addition to these simple processes, we further examined the chemoselectivity of TTMSS toward the carbon-sulfur bond of 1,3-dithianes in the presence of other functional groups. Thus, the reaction of 1,3-dithiane derivative **8** (0.0005 M) with TTMSS (0.0006 M) using AIBN as an initiator in toluene (8 mL) at 70 °C suprisingly did not give us any cyclized product(s).[10] Purification using flash column (EtOAc–hexane, 1:30) gave **9** (CIMS m/z 437, M + 1) and **10** (CIMS m/z 685, M + 1) in 56% and 17%. The product **9** (major) was formed by the preferential attack of the silyl radical to the less hindered side of the double bond to 1,3-dithiane ring system, whereas **10** (minor) was obtained from **9**, furthered by the attack of the silyl radical to 1,3-dithiane. The ^1H NMR of **9** showed a signal at δ 4.02 (t, J = 6.7 Hz, 1 H, C1-H) and ^{13}C NMR δ 47.6 (1,3-dithiane ring intact), 7.5 (C-6 next to silyl group), whereas **10** showed no peak near δ 4.0, instead a triplet at 2.56 (J = 7.0 Hz, 2 H) appeared due to the opening of 1,3-dithiane ring. Similarly, **11** under the reaction conditions with slightly higher temperature (90 °C) gave **12** (CIMS m/z 465, M + 1) in 72% as expected from

---

(7) (a) Gutierrez, C. G.; Stringham, R. A.; Nitasaka, T.; Glasscock, K. G. *J. Org. Chem.* **1980**, *45*, 3393. (b) Yadav, V. K.; Fallis, A. G. *Tetrahedron Lett.* **1988**, *29*, 897; **1989**, *30*, 3283.

(8) All the new compounds were characterized by ^1H NMR, ^{13}C NMR, MS, and elemental analyses.

(9) Silyl radicals are known to attack the carbon atom of C, C π-bonds and the oxygen atom of C, O π-bonds. Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; Plenum: New York, 1983; Vol. 30, p 113.

(10) With *n*-tributyltin hydride, similar types of compounds are known to give the mixture of cyclic products as reported in ref 7b.

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

Joel M. Hawkins,* Timothy A. Lewis, Stefan D. Loren, Axel Meyer, James R. Heath, Yoko Shibato, and Richard J. Saykally

Department of Chemistry, University of California, Berkeley, California 94720

Received November 9, 1990

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.

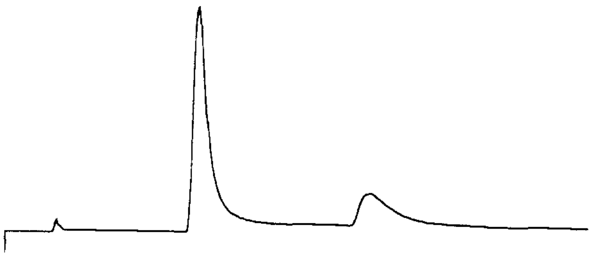
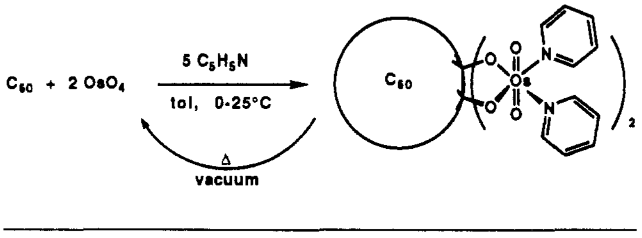


Figure 1. HPLC separation of C_{60} (12.2 min) and C_{70} (23.5 min) on a Pirkle column[7] (eluted with hexane at 5.0 mL/min, detected at 280 nm).

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



---

(1) (a) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. (c) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* In press.

(2) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713. (c) Kroto, H. *Pure Appl. Chem.* **1990**, *62*, 407.

(3) The conversion of C_{60} to $C_{60}H_{36}$ (structure undetermined) by Birch reduction is described in ref 1c.

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

(5) Pirkle, W. H.; Finn, J. M.; Hamper, B. C.; Schreiner, J.; Pribish, J. R. In *Asymmetric Reactions and Processes in Chemistry*; Eliel, E. L., Otsuka, S., Eds.; ACS Symposium Series 185; American Chemical Society: Washington, DC, 1982; pp 245-260.

(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.

0022-3263/90/1955-6250$02.50/0