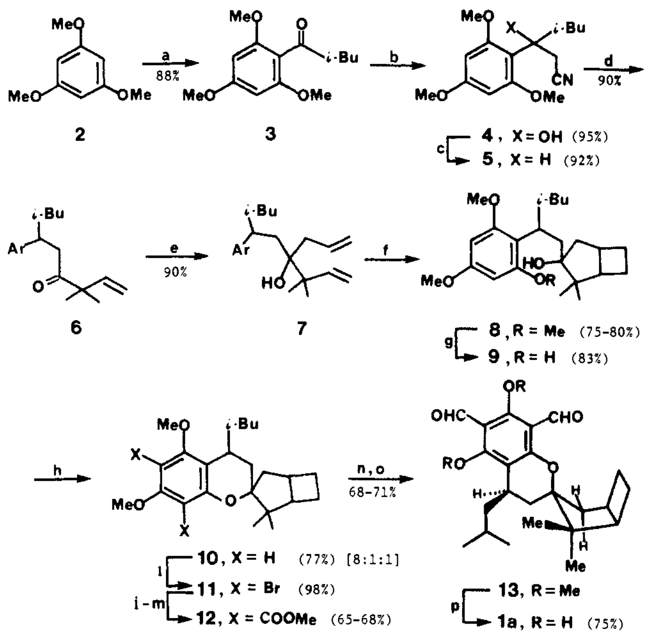
Scheme I^a



^{a}(a) $Me_2CHCH_2COCl/AlCl_3$; (b) $LiCH_2CN$; (c) Et_3SiH/CF_3COOH; (d) $Me_2C{=}CHCH_2MgCl$; (e) $CH_2{=}CHCH_2MgBr$; (f) CuOTf/$h\nu$; (g) EtSNa/DMF; (h) $BF_3{\cdot}OEt_2/CH_2Cl_2$; (i) Br_2/CH_2Cl_2; (j) n-BuLi/THF; (k) CO_2; (l) HCl; (m) CH_2N_2; (n) DIBAlH/PhMe; (o) PDC; (p) BCl_3.

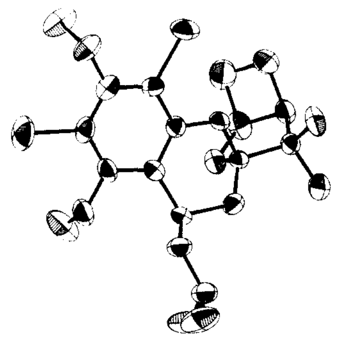
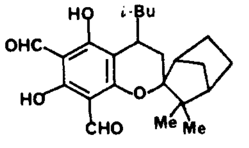


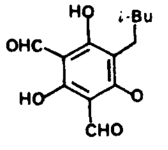
Figure 1. X-ray structure of **11**.[8]

sorptions between δ 2.37 and 2.74 which we assign to the methine hydrogens at positions 11 and 14. Demethylation of **13** with BCl_3 completed our total synthesis of **1a** (mp 129–130 °C).

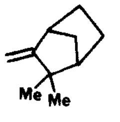
Evidently, the structures of robustadial A, and presumably robustadial B, are isomeric with those proposed previously.[2] Several facts lead us to postulate a bicyclo[2.2.1]heptane structure **15** for the robustadials. Thus, the aromatic acetogenin isopentyl



15



16



17

portion **16** of robustadials is identical with that found in the euglobals, a family of acetogenin terpenoids isolated from buds and leaves of *Eucalyptus globulus*.[9] Generally, the remaining terpenoid portion of the euglobals corresponds to known terpenes or sesquiterpenes. The remaining terpenoid portion of **15** corresponds to a known terpene, camphene (**17**). Furthermore, ^{1}H NMR resonances above δ 2.3 are reasonable for the bridgehead methine hydrogens of a bicyclo[2.2.1]heptyl moiety. Finally, the presumption of a cyclobutyl moiety in robustadials was supported by the appearance of a peak in the high-resolution mass spectrum at m/e 28 (C_2H_4).[2] Our postulated structure **15** for the robustdials is only tenable if the mass spectrum of camphene exhibits major fragments corresponding to those observed for the terpene portion of robustadials. Indeed, the mass spectrum of camphene not only shows a peak at m/e 28.046 (21%, C_2H_4) but also peaks at m/e 91 (30%), 107 (39%), and 136 (23%) corresponding to prominant peaks in the mass spectrum of robustadials.[2]

Acknowledgment. This work was supported by grants from the National Science Foundation (to R.G.S.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (to W.Y.). We thank Professors Xu, Snyder, and Nakanishi for copies of spectra of the robustadials.

Supplementary Material Available: Tables of data collection details, fractional atomic coordinates, and anisotropic thermal parameters for non-hydrogen atoms of **11**, as well as analytical and spectral data for all new compounds (9 pages). Ordering information is given on any current masthead page.

---

(9) Sawada, T.; Kozuka, M.; Komiya, T.; Amano, T.; Goto, M. *Chem. Pharm. Bull.* **1980**, *28*, 2546. Amano, T.; Komiya, T.; Hori, M.; Goto, M.; Kozuka, M.; Tokunosuke, S. *J. Chromatogr.* **1981**, *208*, 347. Kozuka, M.; Sawada, T.; Kasahara, F.; Mizuta, E.; Amano, T.; Komiya, T.; Goto, M. *Chem. Pharm. Bull.* **1982**, *30*, 1952. Kozuka, M.; Sawada, T.; Mizuta, E.; Kasahara, F.; Amano, T.; Komiya, T.; Goto, M. *Ibid.* **1982**, *30*, 1964.

Photofragment Infrared Fluorescence in the Photodissociation of Gas-Phase $Mn_2(CO)_{10}$

R. G. Bray,* P. F. Seidler, J. S. Gethner, and R. L. Woodin

Exxon Research and Engineering Co.
Corporate Research Science Laboratories
Annandale, New Jersey 08801

Received October 28, 1985

We report here the first application of frequency- and time-resolved infrared fluorescence[1] to investigate the structure and dynamics of organometallic intermediates. Photolysis at 351 nm of gas-phase $Mn_2(CO)_{10}$[2] produces vibrationally excited species which have been identified by characteristic emission near 2000 cm^{-1}. Bimolecular collisional energy transfer rates of one of these species have been measured for seven collider gases.

Samples of $Mn_2(CO)_{10}$ (7–60 mtorr) contained in a glass cell at 79–80 °C were irradiated with a XeF excimer laser (351 nm, 15-ns pulse width, 2-Hz repetition rate) using low laser fluences (<100 μJ cm^{-2} per pulse) to minimize multiphoton absorption processes.[3] An InSb detector monitored the transient infrared fluorescence over the 3950–1800-cm^{-1} region at right angles to the photolysis beam. The amplified detector output was then averaged over 100 pulses with a transient digitizer.

---

(1) See, for previous applications of this technique: Leone, S. R *Acc. Chem. Res.* **1983**, *16*, 88 and references cited therein.

(2) For revelant studies, see: (a) Wrighton, M. S.; Graff, J. L.; Luong, J. C.; Reichel, C. L.; Robbins, J. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H. Ed.; American Chemical Society: Washington, DC, 1981. (b) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (c) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (d) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (e) Dunkin, I. R.; Harter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248. (f) Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089. (g) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536. (h) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249. (i) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785. (j) Leopold, D. G.; Vaida, V. *J. Am. Chem. Soc.* **1984**, *106*, 3720. (k) Freedman, A.; Bersohn, R. *J. Am. Chem. Soc.* **1978**, *100*, 4116. (l) Weitz, E., private communication.

(3) (a) Karny, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33. (b) Leutwyler, S.; Even, U. *Chem. Phys. Lett.* **1981**, *84*, 188. (c) Rothberg, L. J.; Gerrity, D. P.; Vaida, V. *J. Chem. Phys.* **1981**, *74*, 2218. (d) Lichtin, D. A.; Bernstein, R. B.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 1830.

0002-7863/86/1508-1312$01.50/0

Table I. Phenomenological Second-Order Rate Constants[a] and Average Energy Transferred per Collision[b] for Vibrational Collisional Deactivation

	$Mn(CO)_5$		azulene			
	15 kcal mol^{-1} [c]		48 kcal mol^{-1} [c]		85 kcal mol^{-1} [c]	
collider gas	$10^{11}k$	$\langle \Delta E \rangle$	$10^{11}k$	$\langle \Delta E \rangle$	$10^{11}k$	$\langle \Delta E \rangle$
$Mn_2(CO)_{10}$	27.4 ± 1.0	325				
azulene			25.2 ± 1.0	1217	13.6 ± 0.3	1425
n-butane	9.26 ± 0.60	216	11.7 ± 1.2	707	9.41 ± 0.28	1234
NO	4.99 ± 0.27	110				
CH_4	4.92 ± 0.25	78	3.10 ± 0.13	173	3.70 ± 0.36	448
CO	3.75 ± 0.17	77	1.92 ± 0.09	151	2.20 ± 0.10	375
Ar	3.24 ± 0.13	80	1.29 ± 0.08	119	1.07 ± 0.03	215
He	1.69 ± 0.05	17	0.663 ± 0.074	37	0.69 ± 0.09	83

[a] From linear least-squares fits of data; units are cm^3 s^{-1}; uncertainties are $\pm 1\sigma$. [b] Reference 8b; units are cm^{-1}. [c] Average excess vibrational energy.[4b,8a]

The observed fluorescence was biexponential: the fast component decayed within 0.5–10 μs, while the weaker slow component decayed within 2–10 ms. We crudely characterized the fluorescence spectrum using additional infrared bandpass filters. Most of the fast fluorescence is restricted to the narrow range 2000–1970 cm^{-1}, while the slow component appears primarily in the region of 2500–1980 cm^{-1}, with about 60% of the emission occurring between 2040 and 1980 cm^{-1}. No emission from free CO was detected (2090–2210 cm^{-1}).

The infrared fluorescence could arise from the primary photoproducts of reactions 1 and 2 or subsequently formed chemi-

$$Mn_2(CO)_{10} \rightarrow Mn(CO)_5 + Mn(CO)_5 \qquad (1)$$

$$Mn_2(CO)_{10} \rightarrow Mn_2(CO)_9 + CO \qquad (2)$$

luminescent molecules, e.g., $Mn_2(CO)_{10}$. Since $Mn_2(CO)_9$ would be expected, on the basis of solution absorption spectra, to fluoresce over the relatively broad region of 2070–1980 cm^{-1},[2i] and gas-phase $Mn_2(CO)_{10}$ exhibits a strong infrared absorption at 2024 cm^{-1} and two weaker bands at 1992 and 2052 cm^{-1}, both $Mn_2(CO)_9$ and $Mn_2(CO)_{10}$ could make only a minor contribution to the fast component. The solution infrared absorption spectrum of $Mn(CO)_5$, however, shows a single broad peak at ca. 1990 cm^{-1}.[2i] We accordingly assign the fast fluorescence to $Mn(CO)_5$, which is consistent with the recently reported Mn–Mn bond dissociation energy of 32–41 kcal mol^{-1}.[4a] Mn–Mn bond cleavage results in $Mn(CO)_5$ fragments with sufficient excitation for infrared emission but insufficient excitation for further dissociation.[4b] Furthermore, Mn–CO bond scission either is a minor photodissociation process at 351 nm or produces fragments having little vibrational excitation relative to $Mn(CO)_5$.[5] The slow component spectrum, in contrast, is consistent with either $Mn_2(CO)_9$ or $Mn_2(CO)_{10}$, which are produced via secondary reactions.

The pseudo-first-order decay rates for the fast fluorescence are linearly dependent on the partial pressure of added buffer gas (see Figure 1),[6] indicating that the observed lifetime of vibrationally excited $Mn(CO)_5$ is determined by collisional deactivation. The zero-pressure intercepts agree with crude estimates of the radiative lifetime (ca. 1 ms) of $Mn(CO)_5$.[7] The slopes of the lines give the second-order rate constants for collisional deactivation of vibrationally excited $Mn(CO)_5$ and are listed in Table I together with comparable data published for highly vibrationally excited azulene.[8a] The average energies transferred per collision were calculated from the observed rate constants for $Mn(CO)_5$ deactivation.[8b] Several points should be noted: (1) The similarity between the decay rates measured here and the azulene data indicates that collisional deactivation of vibrationally excited $Mn(CO)_5$, and not a chemical transformation, is indeed the process that is responsible for the fluorescence quenching. (2) The deactivation rates for $Mn(CO)_5$ and azulene are remarkably close considering the disparity in structure, the mass of the constituent atoms, and the reactivity of these species. (3) Calculation of the average energy transferred per collision for different buffer gases with $Mn(CO)_5$[8b] gives values that are 1.5–3 times smaller than with azulene,[8a] which possesses considerably greater excess vibrational energy.[4] Although the collisional cross section and the energy dependence of the calculated fluorescence intensity for $Mn(CO)_5$ and azulene are roughly comparable, the approximations involved do not permit a definitive statement concerning the dependence of the average energy transferred per collision as a function of internal energy content.[8a,9]

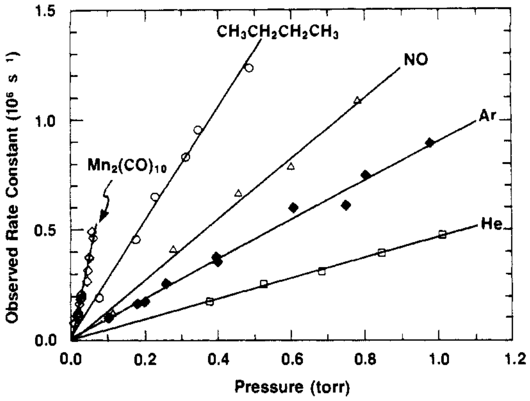


Figure 1. Observed rate constants for fast decay as a function of collider gas pressure: (◇) $Mn_2(CO)_{10}$; (○) $CH_3CH_2CH_2CH_3$; (△) NO; (◆) Ar; (□) He. Lines are least-squares fits of data.

The above results imply that thermal equilibration of primary photofragments is complete in much less than 1 ms. Consequently, the slow fluorescence must be due to the secondary production of an infrared chemiluminescent species, either $Mn_2(CO)_9$ or $Mn_2(CO)_{10}$, via exothermic reactions, such as radical recombination. We are continuing to investigate the chemical processes responsible for the slow decay and are extending this technique,

---

(4) (a) Martinho Simoes, J. A.; Schultz, M. C.; Beauchamp, J. L. *Organometallics* **1985**, *4*, 1238. (b) For Mn–Mn photodissociation, we estimate the average excess vibrational energy at 13–16 kcal mol^{-1} for each $Mn(CO)_5$, on the basis of a minimum Mn–Mn bond dissociation energy of 32–41 kcal mol^{-1} [4a] and the energy partitioning observed for photodissociation of $Re_2(CO)_{10}$.[2k] The average Mn–CO bond dissociation energy is ca. 21 kcal mol^{-1},[4c] using the above Mn–Mn bond energy. (c) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1161.

(5) (a) Assuming a typical metal–carbonyl first bond dissociation energy of 35–40 kcal mol^{-1},[5b] ca. 41–46 kcal mol^{-1} are available after Mn–CO photodissociation for disposal into the vibrational, translational, and, to a minor extent, the rotational degrees of freedom of the $Mn_2(CO)_9$ and CO photofragments. (b) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

(6) The contribution to the decay rates due to collisions with $Mn_2(CO)_{10}$ has been subtracted from those data for experiments involving added buffer gas.

(7) This estimate is based on the integrated absorption coefficient of solution phase $Mn_2(CO)_{10}$ carbonyl absorption bands.[2c]

(8) (a) Barker, J. R. *J. Phys. Chem.* **1984**, *88*, 11 and references therein. (b) The formalism and assumptions given in ref 8a were used for these calculations.

(9) Hippler, H.; Lindemann, L.; Troe, J. *J. Chem. Phys.* **1985**, *83*, 3906. Hippler, H.; Troe, J.; Wendelken, H. J. *J. Chem. Phys.* **1983**, *78*, 6709, 6718; *Chem. Phys. Lett.* **1981**, *84*, 257.

which complements transient infrared absorption,[21,10] to other organometallic systems.

Acknowledgment. We acknowledge J. A. Mancuso for his expert technical assistance during the course of this work. We thank Eric Weitz for communicating unpublished results from related experiments on $Mn_2(CO)_{10}$ and John R. Barker for discussions on energy transfer.

---

(10) (a) Ouderkirk, A. J.; Wermer, P.; Schultz, N. L.; Weitz, E. *J. Am. Chem. Soc.* **1983**, *105*, 3354. (b) Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1983**, *79*, 1089. (c) Seder, T. A.; Church, S. P.; Ouderkirk, A. J.; Weitz, E. *J. Am. Chem. Soc.* **1985**, *107*, 1432. (d) Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 2203.

Selenoaldehydes: Preparation and Dienophilic Reactivity

Grant A. Krafft*[1] and Peter T. Meinke

Department of Chemistry, Syracuse University
Syracuse, New York 13244-1200

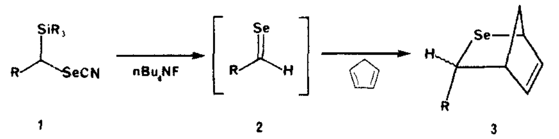
Received October 18, 1985

Selenoaldehydes have been elusive compounds by virtue of their high reactivity and difficulty of preparation.[2] Only a handful of literature reports discuss this rare class of compounds. The simplest of the selenoaldehydes, selenoformaldehyde, has been reported as a bridging ligand in binuclear osmium[3] and manganese[4] complexes and as a simple ligand in mononuclear rhodium complexes.[5] Recently, selenoformaldehyde in trace quantities has been detected in the gas phase by near-infrared and infrared spectroscopy, following flash pyrolysis of its trimer,[6] and by microwave[7] and photoelectron[8] spectroscopy of pyrolysis mixtures of dimethylselenide. No report, however, describing the specific preparation or characterization of selenoformaldehyde in condensed phases has appeared. Selenoacetaldehyde has been characterized in the gas phase by microwave spectroscopy following pyrolysis of its trimer,[9] but it and other simple alkyl or aryl selenoaldehydes have been reported only as trimers or polymers in condensed phases.[10] Selenoketene also has been observed in the gas phase by microwave spectroscopy following pyrolysis of 1,2,3-selenodiazole.[11] Two reports describe the isolation of several electron-rich selenoaldehydes,[12] though these derivatives are more accurately charactered as vinylogous selenoformamides. In this paper we report the preparation of simple alkyl and aryl selenoaldehydes, including selenoformaldehyde, and describe the intermolecular cycloadditions of these selenoaldehydes with cyclopentadiene.

Table I

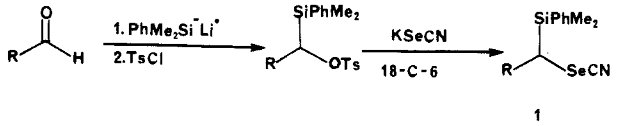
compound	R	endo:exo	% yield
3a	H		66
3b	Me	2.3:1	83
3c	Et	4.3:1	78
3d	Pr	3.4:1	76
3e	Ph	2.6:1	81
3f	$PhCH_2$	3.5:1	89
3g	*t*-Bu	9.0:1	39

Selenoaldehyde formation occurs efficiently and under mild conditions by the fluoride-induced elimination of cyanide from α-silyl selenocyanates **1**, as illustrated in eq 1. The selenoaldehydes **2** are generated slowly at 0 °C by syringe pump addition of Bu_4NF/THF to the α-silyl selenocyanates in the presence of 2 equiv of cyclopentadiene and readily undergo the Diels–Alder reaction to form the bicyclic adducts **3**.[13] Representative examples are provided in Table I.[14,15] The yields of bicyclic adducts are quite high (66–89%) except for the selenopivaldehyde analogue (39%), indicating efficient selenoaldehyde generation and cycloaddition. The slow generation and in situ trapping prevent accumulation of the reactive selenoaldehydes, suppressing trimerization or polymerization.



(1)

The α-silyl selenocyanate precursors are prepared quite readily by addition of the appropriate aldehyde to $PhMe_2SiLi$[16] in THF at −78 °C, trapping of the α-silyl alkoxide with *p*-toluenesulfonyl chloride, and displacement of the *p*-toluenesulfonate with KSeCN, as shown in eq 2. Yields for this sequence are high, ranging from 70% to 90%. It is possible to execute this sequence in one reaction vessel, though yields are generally higher when the α-silyl tosylates are isolated and purified. This sequence converts simple aldehydes to selenoaldehydes in three steps with one purification, and proceeds in overall yields of 62–80%. The α-silyl selenocyanates are stable molecules and can be purified readily by flash chromatography on silica gel.



(2)

The Diels–Alder reaction of substituted selenoaldehydes with cyclopentadiene gave mixtures of exo and endo stereoisomers, with the endo isomer predominating in all cases. The mixtures were inseparable by GC or HPLC except for **3e**. Exo and endo isomer ratios were determined by NMR integration.

These Diels–Alder reactions closely parallel the analogous reaction of thioaldehydes with cyclopentadiene, in which endo:exo ratios range from 3.5:1 to 7:1.[17] The structures of these Diels–

---

[1] Fellow of the American Cancer Society, 1983–1986.

[2] For reviews on selenocarbonyl compounds, see, for instance: (a) Hogg, D. R.; Landquist, J. K.; Ohno, A. *Org. Compds. Sulphur, Selenium, Tellurium* **1981**, *6*, 148–206. (b) Hogg, D. R.; Metzner, P.; Voss, J.; Walter, W. *Org. Compds. Sulphur, Selenium, Tellurium* **1979**, *5*, 118–186. (c) Metzner, P.; Hogg, D. R.; Walter, W.; Voss, J. *Org. Compds. Sulphur, Selenium, Tellurium* **1977**, *4*, 124–185. (d) Magnus, P. D. *Compr. Org. Chem.* **1979**, *3*, 520–521.

[3] Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53–C56.

[4] (a) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechschmitt, K.; Pfisterer, H.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 314–315. (b) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechschmitt, K.; Pfisterer, K.; Ziegler, M. L. *Angew. Chem., Suppl.* **1983**, 363–395.

[5] (a) Paul, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 316–317. (b) Paul, W.; Werner, H. *Angew. Chem., Suppl.* **1983**, 396–404.

[6] Judge, R. H.; Moule, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 5406–5407.

[7] Brown, R. D.; Godfrey, P. D.; McNaughton, D. *Chem. Phys. Lett.* **1985**, *118* (1), 29–30.

[8] Bock, H.; Aygen, S.; Rosmus, P.; Solouki, B.; Weissflog, E. *Chem. Ber.* **1984**, *117*, 187–202.

[9] Hutchinson, M.; Kroto, H. W. *J. Mol. Spectrosc.* **1978**, *70*, 347–356.

[10] (a) Bridger, H. J.; Pittman, R. W. *J. Chem. Soc.* **1950**, 1371–1375. (b) Jensen, K. A.; Bøje, L.; Henriksen, L. *Acta Chem. Scand.* **1972**, *26*, 1465–1470. (c) Lewis, D. T. *J. Chem. Soc.* **1940**, 831–832.

[11] Bak, B.; Nielsen, O. J.; Svanholt, H. *Chem. Phys. Lett.* **1978**, *55*, 36–39.

[12] (a) Reid, D. H.; Webster, R. G.; McKenzie, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2334–2339. (b) Ger. Pat. 910,199, 1954; *Chem. Abstr.* **1959**, *53*, 936*h*.

[13] A typical experimental procedure for selenoaldehyde cycloaddition is described as follows. Preparation of **3f**: To a vigorously stirred solution of 115 mg (0.334 mmol) of 1-(phenyldimethylsilyl)-2-phenylethyl selenocyanate and 44 mg (0.67 mmol) of cyclopentadiene in 8 mL of CH_2Cl_2 under N_2 at 0 °C was added an 8-mL solution (0.401 mmol) of *n*-Bu_4NF in THF over a 1-h period via syringe pump. The reaction mixture was subsequently warmed to room temperature, then diluted to 50 mL with pentane, filtered through activated, neutral aluminum oxide, and concentrated at reduced pressure. Flash chromatography on activated, neutral aluminum oxide (25:1:1, pentane/Et_2O/CH_2Cl_2) provided 74.0 mg (89.2%) of a 3.5:1 mixture of endo and exo cycloadducts **3f** as a colorless oil.

[14] All adducts and precursors gave satisfactory NMR, IR, and mass spectral data.

[15] Selenoformaldehyde was prepared from Me_3SiCH_2SeCN, obtained by potassium selenocyanate displacement of Me_3SiCH_2Cl in the presence of catalytic 18-crown-6 in refluxing THF.

[16] George, M. V.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 403–406.