142439-04-1; **10b**, 142439-05-2; **10c**, 26209-66-5; **10d**, 15865-21-1; **10e**, 142439-06-3; **10f**, 21053-50-9; **10h**, 142439-08-5; **10i**, 89241-25-8; **11**, 142438-95-7; **12**, 142439-09-6; **13**, 142439-10-9; **16**, 779-52-2; **16**-^{13}C, 142439-16-5; **17**, 142439-17-6; **18**·HCl, 886-06-6; **18**, 73-63-2; **19**, 142438-96-8; **20a**, 142438-97-9; **20b**, 17721-98-1; **20c**, 142438-98-0; **21a**, 142439-12-1; **21b**, 142439-13-2; **21c**, 142439-14-3; **22**, 17721-98-1; **23**, 142439-15-4; **31** (R = C(CH$_3$)$_3$), 142439-11-0; Ru$_3$(CO)$_{12}$, 15243-33-1; 2-phenylpyrrolidine, 1006-64-0; 2-benzylpyrrolidine, 35840-91-6; pyrrolidine, 123-75-1; 2-(methoxymethyl)pyrrolidine, 135523-48-7; bromoacetic acid, 105-36-2; *tert*-butyl bromoacetate, 5292-43-3; octahydroindole, 4375-14-8; piperidine, 110-89-4; 1-bromo-3,3-dimethyl-2-butanone, 5469-26-1; 2-bromo-1-phenyl-1-ethanone, 70-11-1; 1-bromo-2-octanone, 26818-08-6; 2-bromo-1-(2-naphthyl)-1-ethanone, 613-54-7; decahydroisoquinoline, 6329-61-9; 2,2,6,6-tetraethylpiperidine, 768-66-1; 2,6-dimethylpiperidine, 504-03-0; 2-hexyloxirane, 2984-50-1; 2-phenyloxirane, 96-09-3; cobalt chloride, 34240-80-7.

Supplementary Material Available: Description of experimental procedures, listing of crystal data, bond lengths and angles, torsion angles, and atomic parameters, and ORTEP plots for **13** (10 pages); listing of observed and calculated structure factors for **13** (11 pages). Ordering information is given on any current masthead page.

A Room Temperature Synthesis of Perstanna[1.1.1]propellanes and the Structure/Property Relationships Revealed by a Comparison of Two Derivatives

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Contribution No. 8635 from the Division of Chemistry and Chemical Engineering and the Beckman Institute Molecular Materials Resource Center, California Institute of Technology, Pasadena, California 91125. *Received May 15, 1992*

Abstract: Chemical reduction of hexakis(2,6-diethylphenyl)cyclotristannane (**2**) with 2.3 equiv of lithium metal in THF provides hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**1**) (31% yield) and octakis(2,6-diethylphenyl)tetracyclo-[4.1.0.0^{1,5}.0^{2,6}]heptastannane (**4**) (~1% yield). With 1.2 equiv of lithium metal, the same procedure provides 1,2,2,3,3,4,4-heptakis(2,6-diethylphenyl)cyclotetrastannane (**3**) (85% yield) and tris(2,6-diethylphenyl)stannane (**5**) (103% yield). A proposed mechanism to account for the formation of **3** proceeds through the intermediacy of the monovalent tin species, [R$_2$Sn]$^-$ (R = 2,6-diethylphenyl) (**9**) and 1-lithio-1,2,2,3,3,4,4-heptakis(2,6-diethylphenyl)cyclotetrastannane (**14**). Evidence for the existence of **9** is provided by an ESR spectrum of a mixture of **2**, 0.5% potassium amalgam (1 equiv), and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt) (1 equiv) in THF which displays a single strong resonance centered at $g = 2.024$ [a($^{119/117}$Sn) = 152 G]. Compound **14** has been synthesized separately by deprotonation of **3** with lithium diisopropylamide in THF, and it has been isolated as an orange microcrystalline material (43% yield). Reaction of **14** with an excess of lithium metal produces **1** in a 30% yield which supports the observation that this compound appears to be the key intermediate in the transformation of **2** to **1** and **4**. Single crystals of **4**, obtained from a toluene/acetonitrile solvent mixture at −40 °C, are, at 20 °C, monoclinic, space group $C2/c$–C^6_{2h} with a = 27.968 (7) Å, b = 16.000 (4) Å, c = 38.510 (11) Å, β = 103.17 (2)°, V = 16780 (8) Å^3, and Z = 8 {d_{calcd} = 1.501 g cm^{-3}; μ_a(Mo Kα) = 2.09 mm^{-1}}. The molecular structure of **4**, as obtained from crystallographic analysis (R_1 = 0.047 for 6189 independent reflections), reveals that the [1.1.1]propellane core of this compound is contracted relative to **1** with a mean Sn$_{\mathrm{bh}}$–Sn$_{\mathrm{br}}$ bond length value of 2.845 (18) Å and a Sn$_{\mathrm{bh}}$–Sn$_{\mathrm{bh}}$ distance of 3.348 (1) Å. On the basis of a correlation between the reduction of this latter value with an hypsochromic shift and increased intensity of an electronic transition, assumed to originate from the HOMO of perstanna[1.1.1]propellanes, in going from **1** to **4**, a significant bonding interaction between the two inverted tetrahedral tin atoms in this class of compounds is proposed. Cyclic voltammetry of **4** in THF shows two quasireversible one-electron reduction waves at $E_{1/2}$ = −1.35 and −1.90 V (V vs NHE) which correspond to the [**4**]/[**4**]$^-$ and the [**4**]$^-$/[**4**]$^{2-}$ redox couples, respectively. Finally, chemical reduction of **4** can be achieved with 0.1% potassium amalgam in THF in the presence of crypt to generate, in situ, the complex [**4**]$^-$[K,crypt]$^+$, and the isotopic ESR spectrum (25 °C) of this species displays a single resonance centered at g = 1.95. Simulation of this spectrum can be accomplished by assuming hyperfine interactions with three sets of equivalent tin nuclei with the following parameters: a($^{119/117}$Sn) = 22 G (2 Sn atoms); a($^{119/117}$Sn) = 50 G (2 Sn atoms); a($^{119/117}$Sn) = 65 G (3 Sn atoms); line width = 6.5 G.

Introduction

In 1989, we reported the isolation and characterization of the first, and to date, only, example of a heavy-atom group 14 [1.1.1]propellane, the pentastannane derivative, Sn$_5$R$_6$ (R = 2,6-diethylphenyl) (**1**), and have since explored the properties and chemical reactivity of this exceedingly stable molecule.[1] However, the low yield (ca. 15%) and the experimental difficulties encountered with the preparation of **1** through the thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (**2**) at 200 °C has severely limited its availability. Herein, we now report that **1** can be conveniently prepared through an alternative, low-temperature, higher-yielding procedure which also provides access to (1) the first example of a substitutionally-unsaturated cyclopolystannane, heptakis(2,6-diethylphenyl)cyclotetrastannane (**3**), and (2) the new perstanna[1.1.1]propellane derivative, octakis(2,6-diethylphenyl)tetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptastannane (**4**). A comparison of the properties and molecular structure of this latter compound with those of **1** provides the first direct experimental evidence for a significant bonding interaction between the two bridgehead tin atoms in perstanna[1.1.1]propellanes.

Results and Discussion

Chemical Reduction of 2. In the course of studies directed toward the production of monovalent tin species, we made the

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(1) (a) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454. (b) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839. (c) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 5070.

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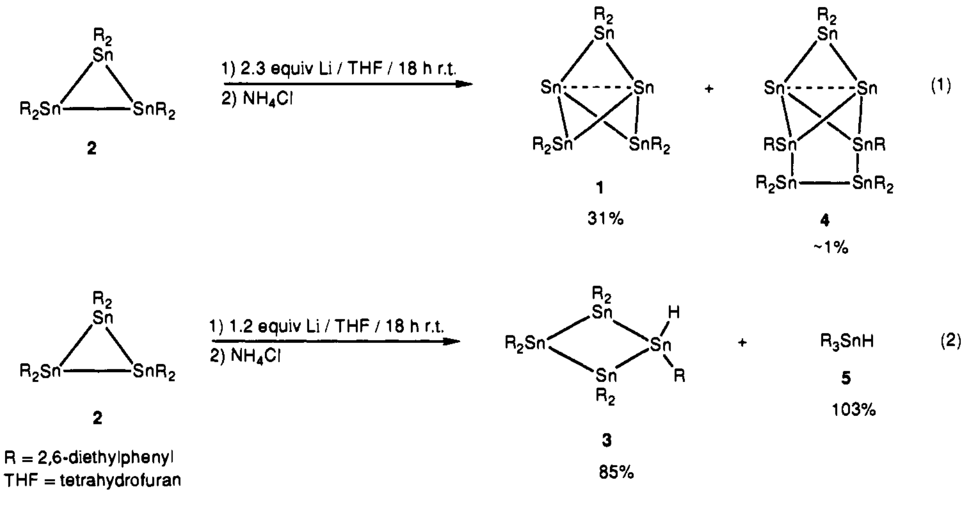
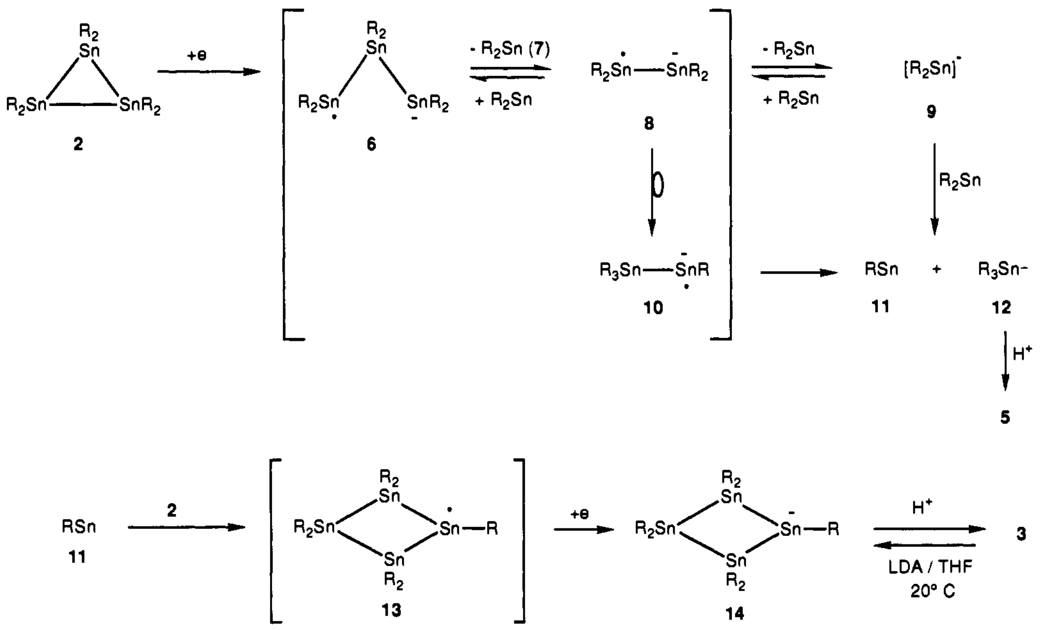
Scheme I



R = 2,6-diethylphenyl
THF = tetrahydrofuran

Scheme II



R = 2,6-diethylphenyl
LDA = lithium diisopropylamide
THF = tetrahydrofuran

remarkable discovery that addition of an excess of lithium metal (6 equiv) to a partial suspension of **2** in tetrahydrofuran (THF) (1 g/10 mL) provides, after stirring at room temperature for 18 h, removal of the unreacted lithium (3.7 equiv), quenching with ammonium chloride, and column chromatography, the two perstanna[1.1.1]propellanes: blue-violet **1** (31% yield) and burgandy **4** (~1% yield) (reaction 1, Scheme I). Inspection of the course of this reaction by thin layer chromatography revealed that **2** is completely consumed within 2 h, at which time two new compounds, identified as **3** and tris(2,6-diethylphenyl)stannane (**5**), and a trace of **1** appear as the sole products. As the reaction proceeds, **3** is then consumed with a concomitant increase in the amounts of **1** and **5**, and after several hours, **4** appears. In keeping with these observations, compound **3** could be selectively obtained in high yield (85%) by either quenching the reaction after the initial disappearance of **2** or limiting the amount of lithium metal employed to 1.2 equiv (completely consumed after 18 h) (reaction 2, Scheme I).

Concerning a possible mechanism for the formation of the ring-expanded products **1**, **3**, and **4** from the chemical reduction of the cyclotristannane **2**, the nature and yields of the products obtained in the first stage of this process ($t \leq 2$ h) appear to be consistent with the mechanism shown in Scheme II. Thus, upon one-electron reduction, it is likely that **2** undergoes depolymerization, similar to that proposed for photolytic degradation of cyclopolystannanes,[2] through first a Sn–Sn bond cleavage followed by successive loss of 2 equiv of the divalent stannylene, R_2Sn (**7**), to ultimately provide the anionic mononuclear monovalent tin species, $[R_2Sn]^-$ (**9**).

Support for the existence of a compound such as **9** was obtained from an ESR spectrum taken, at room temperature, of the deep-red reaction mixture produced from **2**, 0.5% potassium amalgam (1 equiv), and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt) (1 equiv) in THF. As shown in Figure 1, this spectrum exhibits a single strong resonance centered at $g = 2.024$ which is superimposed upon the triplet arising from hyperfine interactions within isotopomers of this species that possess either one or a number of equivalent ^{117}Sn and ^{119}Sn nuclei (nuclear spin, $I = {}^1/_2$).[3] That this spectrum can most likely be

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(2) Neumann, W. P.; Schwarz, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 812.

(3) Wertz, J. E.; Bolton, J. R. *Electron-Spin Resonance. Elementary Theory and Practical Applications*; Chapman and Hall: New York, 1986.

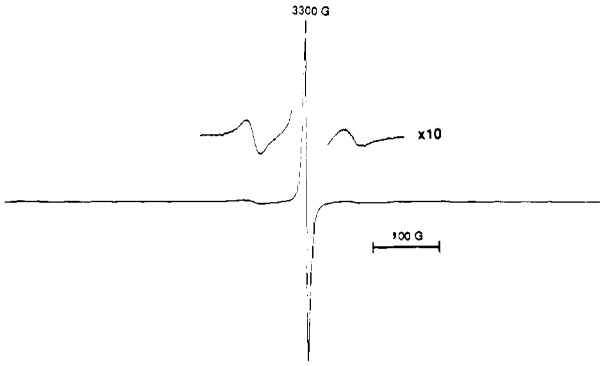

Figure 1. ESR spectrum, taken at 25 °C, of the deep-red mixture produced upon the chemical reduction of **2** with 0.5% potassium amalgam in THF containing 1 equiv of crypt.

attributed to **9** is determined on the basis of the following. First, from simulations which take into account the natural abundance of the two isotopes (7.61% for ^{117}Sn and 8.58% for ^{119}Sn),[4] the relative intensity of the triplet to the central singlet signal, which arises from isotopomers having tin nuclei with $I = 0$, can only be produced by a *mononuclear* tin species rather than any di- or polystannane radicals, such as **6** and **8**, and thus, these latter compounds probably have only transient lifetimes at best. Second, the relatively small absolute magnitude of the hyperfine coupling constant observed for the radical species in Figure 1, $a(^{119/117}\mathrm{Sn}) = 152$ G, suggests that its unpaired electron is confined to an orbital with significant p character, as expected for **9** on the basis of molecular orbital arguments.[5] In contrast, trivalent organostannyl radicals of the type $R_3Sn^\bullet$, which are pyramidal rather than planar in structure, have much larger ^{119}Sn hyperfine coupling constants [e.g. $a(^{119}\mathrm{Sn}) = 1550$ G for R = phenyl, $a(^{119}\mathrm{Sn}) = 1776$ G for R = bis(trimethylsilyl)methyl] due to confinement of the unpaired electron to an orbital that is rich is s character.[6] Finally, the distinctive increased line broadening of the triplet (line width = 15 G) relative to the singlet (line width = 5 G) can be interpreted as arising from an *anionic* species that is undergoing rapid interconversion between different ion-pair structural forms, each of which possess a different $a(^{117/119}\mathrm{Sn})$ value,[7] and this observation in addition to the first two are consistent with **9** being the identity of the radical species in question.

With regard to the role played by the anion **9** in forming **3** and **5**, as shown in Scheme II, it is possible that this monovalent compound serves as a source of the highly-reactive, transient, neutral Sn(I) species, RSn (**11**), through ligand exchange with the stannylene **7**, and that this process is driven forward by formation of the stable anionic species, R_3Sn^- (**12**). Whether this ligand exchange reaction proceeds through the reduced distannene **8** via a process analogous to a distannene/stannylstannylene rearrangement[8] as shown in Scheme II (i.e. **8** to **10**) or through a reversible equilibrium of **9** with **11** and the anion R^-[9] is still a question open to speculation. However, once formed, it is conceivable that **11** inserts into a Sn–Sn bond of **2** to form the ring-expanded product **13** which, on the basis of the ESR data above, must be rapidly reduced under the reaction conditions to provide the cyclotetrastannane anion **14** (Scheme II). Compound **14** has also been synthesized by the deprotonation of **3** with lithium diisopropylamide (LDA) in THF, and it was found that not only is this anion robust in solution but also it could be isolated as a stable orange microcrystalline material as well. More importantly, however, reaction of **14** with an excess of lithium metal in THF once again provides, after 18 h, a 30% yield of **1**, and this observation is consistent with the conclusion that **14** is indeed the key intermediate in the conversion of **2** to **1** and **4**. Further mechanistic investigations are still in progress, and specifically, elucidation of the pathway for the conversion of **14** to **1** and **4**,[11] however, at this stage, it can be concluded that the chemical reduction of **2** represents a superior method for the production

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**[a,b]

Bond Lengths					
Sn_1–Sn_3	3.348 (1)	Sn_1–Sn_5	2.820 (1)	Sn_4–Sn_7	2.842 (1)
Sn_1–Sn_2	2.859 (1)	Sn_2–Sn_3	2.861 (1)	Sn_5–Sn_6	2.842 (1)
Sn_1–Sn_4	2.861 (1)	Sn_3–Sn_4	2.821 (1)	Sn_6–Sn_7	2.902 (1)
		Sn_3–Sn_5	2.848 (1)		

Bond Angles			
$Sn_2Sn_1Sn_3$	54.2 (1)	$Sn_2Sn_1Sn_5$	91.4 (1)
$Sn_3Sn_1Sn_4$	53.3 (1)	$Sn_4Sn_1Sn_5$	82.7 (1)
$Sn_3Sn_1Sn_5$	54.2 (1)	$Sn_2Sn_3Sn_4$	92.8 (1)
$Sn_1Sn_3Sn_2$	54.2 (1)	$Sn_2Sn_3Sn_5$	90.8 (1)
$Sn_1Sn_3Sn_4$	54.5 (1)	$Sn_4Sn_3Sn_5$	82.9 (1)
$Sn_1Sn_3Sn_5$	53.4 (1)	$Sn_5Sn_6Sn_7$	97.5 (1)
$Sn_1Sn_2Sn_3$	71.6 (1)	$Sn_4Sn_7Sn_6$	98.4 (1)
$Sn_1Sn_4Sn_3$	72.2 (1)	$Sn_1Sn_4Sn_7$	112.9 (1)
$Sn_1Sn_5Sn_3$	72.4 (1)	$Sn_3Sn_4Sn_7$	107.7 (1)
$Sn_2Sn_1Sn_4$	92.0 (1)	$Sn_1Sn_5Sn_6$	107.1 (1)
		$Sn_3Sn_5Sn_6$	114.5 (1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2.

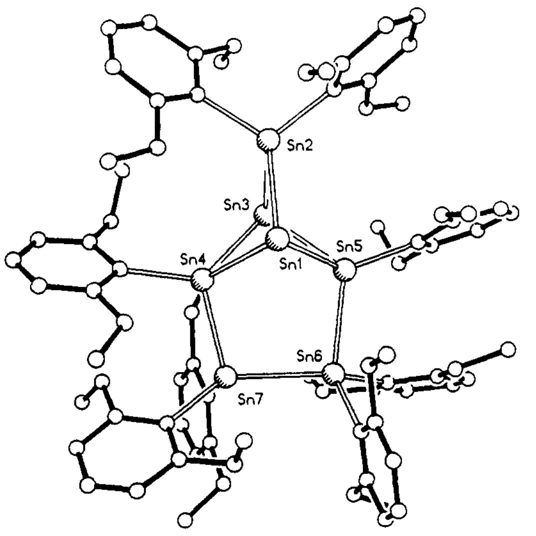

Figure 2. Molecular structure of **4** with all non-hydrogen atoms represented by spheres of varying sizes. Hydrogen atoms have been omitted for purposes of clarity.

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(4) The contribution of hyperfine interactions within isotopomers possessing ^{115}Sn nuclei ($I = {}^1/_2$, natural abundance = 0.35%) can be ignored for most practical purposes.

(5) For theoretical and experimental studies of the analogous H_2C^- molecule, see: Knight, L. B., Jr.; Winiski, M.; Miller, P.; Arrington, C. A.; Feller, D. *J. Chem. Phys.* **1989**, *91*, 4468 and references cited therein.

(6) (a) Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* 1976, 2369. (b) Lehnig, M.; Buschhaus, H.-U.; Neumann, W. P.; Apoussidis, Th. *Bull. Soc. Chim. Belg.* **1980**, *89*, 907. (c) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*: Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: New York, 1982; Vol. 2, p 595.

(7) (a) Hirota, N. *J. Phys. Chem.* **1967**, *71*, 127. (b) Symons, M. C. R. *J. Phys. Chem.* **1967**, *71*, 172.

(8) We have previously proposed that the same species RSn (**11**), which oligomerizes to form the perstanna[*n*]prismanes, $[RSn]_{2n}$ (n = 4 and 5), and the radical $R_3Sn^\bullet$, which dimerizes to form the distannane, R_3Sn–SnR_3, are produced during the thermolysis of **2** via the bimolecular disproportionation of stannylene **7**.[10] A likely mechanism for this disproportionation involves formation of the dimer distannene, R_2Sn–SnR_2, which then rearranges to the stannylstannylene, R_3Sn–SnR, prior to Sn–Sn bond scission. Recently, experimental evidence for an analogous facile digermene/germylgermylene rearrangement in solution has been obtained, see: Baines, K. M.; Cooke, J. A. *Proceedings of the XXV Silicon Symposium*; Los Angeles, 1992, Abstract No. 5.

(9) The formation of R_3Sn^- from the reaction of R^- with R_2Sn is well-precedented, see: (a) Gilman, H.; Rosenberg, S. D. *J. Am. Chem. Soc.* **1952**, *74*, 531; **1953**, *75*, 2507. (b) Blake, D.; Coates, G. E.; Tate, J. M. *J. Chem. Soc.* **1961**, 618. (c) Gilman, H.; Marrs, O. L.; Sim, S.-Y. *J. Org. Chem.* **1962**, *27*, 4232.

(10) (a) Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9*, 2865. (b) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 1856.

(11) Additional mechanistic suggestions made by a reviewer are gratefully acknowledged.

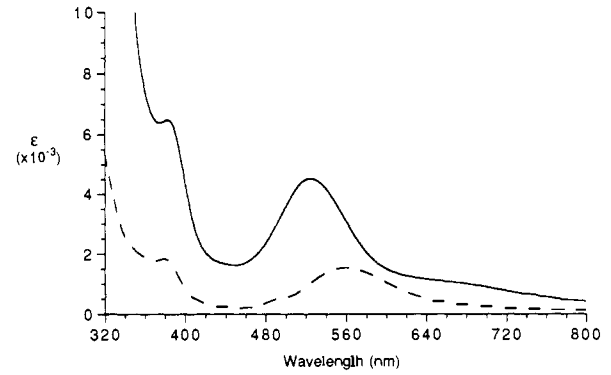

Figure 3. A comparison of the electronic spectra for **1** (dashed line) and **4** (solid line).

of **1**, and accordingly, this intriguing molecule should become more readily available for study.[12] In addition, given the known reactivity of the Sn–H and Sn–Li functional groups,[13] compounds **3** and **14** should prove to be valuable precursors to a variety of new heteroleptically-substituted cyclotetrastannanes.

Molecular Structure and Properties of 4. Compound **4**, being only the second heavy atom group 14 [1.1.1]propellane to be isolated to date, is of interest with regard to the additional information it might provide concerning the nature of bonding in these formally nonclassical molecules. As Figure 2 and Table I reveal, the [1.1.1]propellane core of **4** is contracted relative to **1** [mean $\mathrm{Sn_{br}}$–$\mathrm{Sn_{bh}}$ (br = bridging, bh = bridgehead) bond length value of 2.845 (18) Å in **4** vs 2.858 (11) Å in **1**], and this results in the two bridgehead tin atoms being drawn closer together in the former compound [$\mathrm{Sn_{bh}}$–$\mathrm{Sn_{bh}}$ distance of 3.348 (1) Å in **4** vs 3.367 (1) Å in **1**].[1a] Although these solid-state differences appear small, they are significant, especially since it has been shown that some physical properties of polystannanes, such as the magnitude of one-bond tin–tin coupling constants, are highly sensitive to small changes in Sn–Sn bond length.[14] Furthermore, as we have previously suggested, due to shallow potential energy minima and the nonbonded steric interactions which occur between bulky substituents in synthetic derivatives, the geometric parameters of polycyclic polystannanes are easily shifted away from their equilibrium values even in stereochemically rigid frameworks.[1c] Hence, it is likely that the structural differences between **1** and **4** may become augmented in solution due to a decrease in nonbonded interactions about the [1.1.1]propellane core in the latter relative to the former.

Some important questions which come to mind from this structural comparison of **1** and **4** is whether other differences in the physical properties of the two perstanna[1.1.1]propellanes can be correlated with the reduction in the bridgehead–bridgehead distance found for **4** and whether this correlation can then provide additional information concerning the magnitude of any bonding interaction which might exist between the two inverted tin atoms in these structures. Recent theoretical studies of the parent pentastanna[1.1.1]propellane system **1a** (R = H in **1**) suggest that this bonding interaction is either extremely small or nonexistent,[15] and to date, there has been no experimental evidence to suggest otherwise.[1b] However, from the comparison of the electronic spectra of **1** and **4** shown in Figure 3, it can be seen that the lowest energy transition for **1** at λ_{max} 558 nm (ϵ_{max} 1540), tentatively assigned as originating from the highest occupied molecular orbital, which is also the main MO of interest in terms of the bonding interaction in question,[15a] appears to respond to a reduction in the $\mathrm{Sn_{bh}}$–$\mathrm{Sn_{bh}}$ distance by undergoing an hypsochromic shift and an increase in intensity [cf. λ_{max} 528 nm (ϵ_{max} 4541) for **4**]. Qualitatively, this behavior is similar to the Sn–Sn bond length dependence of the $\sigma \rightarrow \sigma^*$ transition found for distannanes, $\mathrm{R_3Sn{-}SnR_3}$,[16] and hence, it suggests that there is indeed a significant bonding interaction between the two bridgehead tin atoms in perstanna[1.1.1]propellanes and that the MO corresponding to this interaction is stabilized upon reduction of the distance between these two centers. In this regard, it is important to point out that Gordon and co-workers[15a] have recently shown that a bond critical point, representing a bond path between the two $\mathrm{Sn_{bh}}$ atoms,[17] appears in the interbridgehead region of pentastanna[1.1.1]propellane (**1a**) upon compression of the $\mathrm{Sn_{bh}}$–$\mathrm{Sn_{bh}}$ distance from its equilibrium value. Since the level of theory used in these theoretical studies presently tends to overestimate the Sn–Sn bond lengths of strained polycyclic polystannanes (e.g. $\mathrm{Sn_{bh}}$–$\mathrm{Sn_{bh}}$ = 3.463 Å, $\mathrm{Sn_{br}}$–$\mathrm{Sn_{bh}}$ = 2.876 Å for **1a**),[15a,18] the data presented here may help to bring about a refinement in this theory, and hence a closer correlation between theory and experiment for other heavy atom molecular systems as well.

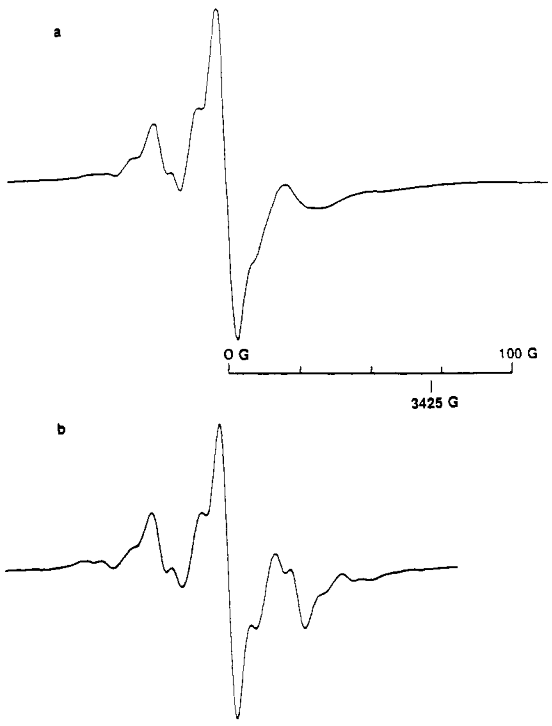

Figure 4. (a) ESR spectrum, taken at 25 °C, of $[\mathbf{4}]^-[\mathrm{K,crpyt}]^+$ in THF. (b) Simulation of spectrum in (a) with the parameters provided in the text.

As a final note, compound **4** displays other properties that are very similar to those of **1** and this suggests that the characteristics of these two compounds are likely to be representative of perstanna[1.1.1]propellanes in general. Thus, cyclic voltammetry of **4** in THF revealed that this compound undergoes two quasi-reversible one-electron reduction waves at $E_{1/2} = -1.35$ and -1.90 V (V vs NHE) which correspond to the $[\mathbf{4}]/[\mathbf{4}]^-$ and the $[\mathbf{4}]^-/[\mathbf{4}]^{2-}$ redox couples, respectively (cf. $E_{1/2} = -1.41$ and -1.93 V for **1**[1b]). In addition, chemical reduction of **4** could also be achieved with 0.1% potassium amalgam in THF in the presence of crypt to generate, in situ, the complex $[\mathbf{4}]^-[\mathrm{K,\ crypt}]^+$. As Figure 4 shows, an isotropic ESR spectrum, taken at 25 °C, of this species displays

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[12] It is now known that **4** is also produced in the thermolysis of **2** and this represents a more secure method for producing this particular compound since its yield is somewhat variable by the methodology presented here.

[13] Neumann, W. P. *The Organic Chemistry of Tin*; John Wiley & Sons: New York, 1970.

[14] Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255.

[15] (a) Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247. (b) Nagase, S. *Polyhedron* **1991**, *10*, 1299.

[16] For R = Ph: Sn–Sn = 2.770 (4) Å [Preut, H.; Haupt, H.-J.; Huber, F. *Z. Anorg. Allg. Chem.* **1973**, *396*, 81], λ_{max} 246 nm (ϵ_{max} 32059). For R = 2,6-diethylphenyl: Sn–Sn = 3.052 (1) Å,[1a] λ_{max} 287 nm (ϵ_{max} 20382).

[17] For a discussion of bond critical points and bond paths as they relate to moleuclar structure, see: (a) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *9*, 18. (b) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

[18] Also compare the theoretical and experimental Sn–Sn bond lengths, 2.887 Å and 2.854_{av} Å, respectively, determined for perstanna[4]prismane (octastannacubane) and a synthetic derivative (Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329 and ref 10a).

a single resonance centered at $g = 1.95$ which can be satisfactorily simulated assuming that hyperfine interactions with three sets of equivalent tin atoms occur with the following values: $a(^{119/117}\mathrm{Sn}) = 22$ G (2 Sn atoms); $a(^{119/117}\mathrm{Sn}) = 50$ G (2 Sn atoms); $a(^{119/117}\mathrm{Sn}) = 65$ G (3 Sn atoms); line width = 6.5 G. This simulation also indicates that the Sn–Sn bonded framework of **4** retains structural integrity upon reduction which is also in keeping with the observations made for **1**.

Experimental Section

Manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Silica gel (400 mesh) for column chromatography was pretreated by heating (250 °C) under vacuum (10^{-3} mmHg) for 3 days. Lithium metal (99%) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt) were used as obtained from Aldrich. Lithium diisopropylamide was prepared from diisopropylamine and butyllithium in diethyl ether and isolated in the glovebox as a white solid by removal of the solvent, addition of hexane, and filtration. Hexakis(2,6-diethylphenyl)cyclotristannane (**2**) was prepared as previously described.[19]

Elemental analyses were performed by Oneida Research Services, Inc. and crystallographic analysis by Crystalytics Co. Silica gel TLC plates were visualized with either a short-wave UV lamp housed within a glovebox or by staining the plate, outside the glove box, with a 20% solution of phosphomolybdic acid in absolute ethanol (Aldrich), followed by heating the plate on a hot plate. By this latter method, organotin compounds appear as blue spots. ^{1}H and ^{119}Sn spectra were recorded at 500 and 186 MHz, respectively, on a Bruker AM spectrometer using benzene-d_6 or toluene-d_8 as the solvent and tetramethyltin as the reference for ^{119}Sn NMR. NMR spectra were simualted on a Macintosh IIci computer with use of the NMR II software of Calleo Co. Infrared absorption spectra were recorded on a Perkin-Elmer spectrometer using Nujol mulls, and absorption spectra were recorded on a Shimadzu UV–vis spectrometer using hexane as the solvent. ESR spectra were recorded with an IBM ESP 300 spectrometer operating at X-Band frequencies and isotropic ESR spectra were simulated on a MacIntosh IIci computer with use of the ESR II software of Calleo Co. without compensation for anisotropic line widths. Electrochemical measurements were made according to the procedures previously reported.[1b]

Preparation of Hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (1) and Octakis(2,6-diethylphenyl)tetracyclo[4.1.0^{1,5}.0^{2,6}]heptastannane (4). To a partial suspension of 1 g (0.87 mmol) of **2** in 10 mL of THF was added 30 mg (5.22 mmol) of freshly cut pieces of lithium metal, and the mixture was stirred at room temperature. After 5 min, a deep orange-red color developed, and after 2 h, TLC (10:1 hexane/Et_2O) showed no trace of **2**. Stirring was continued for a total of 18 h, and then the excess lithium metal was removed by pipetting the THF solution to a new flask (18 mg of lithium metal recovered). To this solution was added 350 mg (6.54 mmol) of solid ammonium chloride, and the mixture was stirred at room temperature for an hour, whereupon the solid material was removed by filtration and the filtrate then concentrated in vacuo to give a dark reddish-purple residue. This was taken up in a minimum volume of a 7:1 hexane/toluene solvent mixture and the resulting solution applied to a preequilibrated silica gel chromatography column (5 cm × 7 cm). Elution with the same solvent mixture under ambient pressure provided fractions from which, in order of their elution, 110 mg of **1** (31% yield), 64 mg of **3**, and 4 mg of **4** (~1%) were obtained. Compound **4** proved to be identical to a burgandy compound isolated from the thermolysis of **2**, and collection of material from multiple runs of both procedures provided enough sample for the complete characterization of **4**. Spectroscopic analysis of **4**: ^{1}H NMR (toluene-d_8) see supplementary material. UV–vis; see Figure 3. Anal. Calcd for $C_{80}H_{104}Sn_7 \cdot C_7H_8$ (toluene): C, 52.55; H, 5.68. Found: C, 52.41; H, 6.31.

Crystallographic Analysis of Compound 4.[20] Single crystals of this dark purple microcrystalline compound could be obtained by dissolving it into a minimum volume of toluene and then adding enough acetonitrile until the solution became slightly turbid at which time the solution was cooled to −40 °C. Crystallographic data are summarized in Table II. Single crystals of 4 are, at 20 °C, monoclinic, space group $C2/c$–C^6_{2h} (No. 15) with $a = 27.968$ (7) Å, $b = 16.000$ (4) Å, $c = 38.510$ (11) Å, $\beta = 103.17$ (2)°, $V = 16780$ (8) Å^3, and $Z = 8$ {$d_{\mathrm{calcd}} = 1.501$ g cm^{-3}; μ_a(Mo Kα) = 2.09 mm^{-1}}. A total of 11549 independent absorption-corrected reflections having 2θ(Mo Kα) <45.8° (the equivalent of 0.6 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.85° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved using "direct methods" techniques with the Siemens SHELXTL-PLUS software package as modified at Crystalytics Co. The resulting structural parameters were refined to convergence {R_1(unweighted, based on F) = 0.047 for 6189 independent absorption-corrected reflections having 2θ(Mo Kα) < 45.8° and $I > 3\sigma(I)$} using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms (except the disordered solvent atoms which were isotropically refined) and isotropic thermal parameters for all hydrogen atoms. The sixteen methyl groups were refined as rigid rotors with sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 or sp^3 hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotopic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. There appear to be two regions in the lattice which are occupied by disordered toluene and/or acetonitrile solvent molecules of crystallization. The first of these is near the C_2 axis at $(0,y,^1/_4)$ and is occupied by half-normal occupancy carbon atoms C_{1s}–C_{5s}; the second is near the inversion center at $(^1/_4,^3/_4,0)$ and is occupied by half-normal occupancy carbon atoms C_{6s}–C_{9s}.

Table II. Crystal, Data Collection, and Refinement Parameters for 4

formula	$C_{80}H_{104}Sn_7$
system	monoclinic
cryst size, mm	0.28 × 0.45 × 0.55
a, Å	27.968 (7)
b, Å	16.000 (4)
c, Å	38.510 (11)
β, deg	103.17 (2)
V, Å^3	16780 (8)
D(calcd), g cm^{-3}	1.501
space group	$C2/c$–C^6_{2h} (No. 15)
Z	8
temp, °C	20
radiation	Mo Kα (graphite monochromated)
scan technique	ω
μ, mm^{-1}	2.09
$2\theta_{\max}$, deg	45.8
no. of data	11549
no. of data in refinement	6189
R	0.047
criteria	$I > 3\sigma(I)$

Preparation of 1,2,2,3,3,4,4-Heptakis(2,6-diethylphenyl)cyclotetrastannane (3). To a partial suspension of 1 g (0.87 mmol) of **2** in 10 mL of THF was added 7 mg (1.17 mmol) of freshly cut pieces of lithium metal, and the mixture was stirred at room temperature. After 5 min, a deep orange-red color developed, and after 18 h, the lithium metal appeared to be completely consumed. At this time, 350 mg (6.54 mmol) of solid ammonium chloride was added and the mixture stirred at room temperature for an additional hour, whereupon the solid material was removed by filtration. The filtrate was then concentrated in vacuo to give an orange-red residue which was then taken up in a minimum volume of a 7:1 hexane/toluene solvent mixture and the resulting solution applied to a preequilibrated silica gel chromatography column (5 cm × 7 cm). Elution with the same solvent mixture under ambient pressure provided fractions from which, in order of elution, 303 mg of **5** (103% yield) and 620 mg of **3** (85% yield) were obtained. Spectroscopic data for **3**: ^{1}H NMR (toluene-d_8) δ (ppm) 0.4–1.4 (br, 42 H), 2.5–3.1 (br, 28 H), 6.6–7.2 (m, 21 H), 7.63 (s, 1 H, $^1J[^{119}\mathrm{Sn}^{-1}\mathrm{H}] = 1322$ Hz, $^2J[^{119}\mathrm{Sn}-^1\mathrm{H}] = 69$ Hz, $^3J[^{119}\mathrm{Sn}^{-1}\mathrm{H}] = 221$ Hz) (see supplementary material). ^{119}Sn {^{1}H} NMR (toluene-d_8) δ 23.8 (Sn_2, $^1J[^{119}\mathrm{Sn}_2-^{119}\mathrm{Sn}_3] = 938$ Hz, ^2J-$[^{119}\mathrm{Sn}_2-^{117}\mathrm{Sn}_2] = 1110$ Hz), −54.8 (Sn_3, $^1J[^{119}\mathrm{Sn}_2-^{119}\mathrm{Sn}_3] = 938$ Hz) (Note: the resonance for Sn_1 could not be located presumably due to a negative NOE buildup during acquisition (broad band decoupling)). Inverse gated decoupling was not effective even with a relaxation delay time of 10 s.[21] UV–vis (hexane) $\lambda_{\max}$ 278 nm ($\epsilon_{\max}$ 62 400); IR (Nujol) $\nu_{\mathrm{Sn-H}}$ 1803 cm^{-1}. Anal. Calcd for $C_{70}H_{92}Sn_4$: C, 59.70; H, 6.58. Found: C, 60.06: H, 6.80.

Chemical Reduction of 2 with 0.5% Potassium Amalgam. In a glovebox, 60 mg (0.052 mmol) of **2**, 30 mg (0.052 mmol) of crypt, and 400 mg (0.052 mmol K) of 0.52% potassium amalgam were placed together in a quartz ESR tube (5 mm) equipped with a 14/20 ground glass joint. The tube was attached to a high-vacuum line and then ca. 2 mL of degassed THF (dried over potassium mirror) was vacuum transferred to

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(20) Detailed information is supplied in the supplementary material.

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the tube, whereupon the mixture turned deep-red. The tube was torch sealed under vacuum and an ESR spectrum of the mixture was taken at room temperature. This spectrum is shown in Figure 1.

Preparation of 1,2,2,3,3,4,4-Heptakis(2,6-diethylphenyl)-1-lithocyclotetrastannane (14). To a solution of 500 mg (0.36 mmol) of **3** in 5 mL of THF was added a solution of 42 mg (0.40 mmol) of LDA in 1 mL of THF at room temperature whereupon the solution turned orange-red. After the mixture was stirred at room temperature for 30 min, the solvent was removed in vacuo and the residue was taken up in a minimum volume of toluene. The resulting solution was then cooled to −40 °C, and after 18 h, 250 mg of the THF adduct of **14** (ca. 3:1 by ^{1}H NMR) was collected as an orange microcrystalline material (43% yield). ^{1}H NMR (toluene-d_8), see supplementary material. Anal. Calcd for $C_{70}H_{91}LiSn_4 \cdot C_4H_8O$: C, 59.80; H, 6.71. Found: C, 59.56; H, 6.84.

Preparation of $[4]^-[K,crypt]^+$. In a glovebox, 10 mg (0.005 mmol) of **4**, 3 mg (0.005 mmol) of crypt, and 500 mg of 0.1% potassium amalgam were placed together in a quartz ESR tube equipped with a 14/20 ground glass joint. The tube was attached to a high-vacuum line and then ca. 2 mL of THF (dried over potassium mirror) was vacuum transferred to the tube. The tube was torch sealed under vacuum and an ESR spectrum obtained. This spectrum, which is consistent with that expected for $[4]^-[K,crypt]^+$, is shown in Figure 4 along with a best simulation which uses the following parameters: $g = 1.95$, $a(^{119/117}Sn) = 22$ G (2 Sn atoms); $a(^{119/117}Sn) = 50$ G (2 Sn atoms); $a(^{119/117}Sn) = 65$ G (3 Sn atoms); line width = 6.5 G.

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Supplementary Material Available: ^{1}H NMR spectra of compounds **3**, **4**, and **14** and listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors for the crystallographic analysis of **4** (33 pages). Ordering information is given on any current masthead page.

Photochemical and Photophysical Studies of Bicyclo[4.3.0]non-1(6)-en-2-one

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Contribution from the Department of Chemistry, Faculty of Arts and Sciences, New York University, New York, New York 10003, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. *Received June 17, 1991. Revised Manuscript Received May 18, 1992*

Abstract: The properties of the lowest excited triplet state of bicyclo[4.3.0]non-1(6)-en-2-one (BNEN) have been investigated by nanosecond transient absorption spectroscopy, photoacoustic calorimetry, measurements of $^1O_2$ quantum yields, and photochemical studies in solution. Both the lifetime (1.4 μs) and the energy (74–76 kcal mol^{-1}) of the BNEN triplet reflect its exceptional conformational rigidity, which prohibits relaxation along the $^3(\pi,\pi^*)$ potential energy surface by twisting around the C=C bond. Fumaro- and maleonitrile quench the BNEN triplet at a diffusion-controlled rate by triplet energy transfer. This process leads to cis–trans isomerization of the alkenes. The BNEN triplet displays extensive self-quenching with $k_{sq} = 2.6 \times 10^7$ M^{-1} s^{-1}. This process involves intermolecular H-abstraction, but formation of dimeric triplet 1,4-biradicals cannot be excluded. The product of the former is a radical (**3**) with a lifetime of 4.1 μs. Its transient absorption spectrum (λ_{max} 299 nm) is hypsochromically shifted with respect to that of the BNEN triplet (λ_{max} 311 nm). The solvent effects on the photophysical properties suggest that the T_1 state of BNEN is a (π,π^*) state in acetonitrile and an (n,π^*) state in benzene. The BNEN triplet undergoes neither [2 + 2] cycloaddition reactions with itself, cyclopentene, fumaronitrile, or maleonitrile nor the lumiketone rearrangement, but readily abstracts H-atoms from itself, cyclopentene, and 2-propanol.

Introduction

The photoreactions and excited-state properties of cyclic enones continue to be of interest.[1] Recent studies indicate that the lifetimes, energies, and reactivity of enone triplets are determined by their ability to twist around the double bond.[2]

Conformationally flexible substituted cyclohexenones efficiently undergo [2 + 2] cycloaddition reactions as well as the lumiketone rearrangement. Recently, we reported[3] that in the photoreactions of 3-methylcyclohexenone with maleo- and fumaronitrile the formation of [2 + 2] cycloadducts occurs with complete loss of stereochemistry concomitant with isomerization of the starting alkene. This unequivocally demonstrates the intermediacy of a common set of rotationally equilibrated triplet 1,4-biradicals. The rate constants for quenching of 3-methylcyclohexenone by fumaro- and maleonitrile, combined with the quantum yields for formation of [2 + 2] cycloadducts and for cis–trans isomerization of the alkenes, suggest that energy transfer from the 3-methylcyclohexenone triplet to fumaro- and maleonitrile is not occurring, despite the favorable energetics of this process.[3] In contrast, the lumiketone rearrangement of structurally related 4,4-disubstituted cyclohexenones appears to involve a high degree of concertedness and is known to occur stereospecifically in a number of cases.[4]

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