and G7-A8 mismatch steps, while much smaller twist values of 16-30° were found for all other base pair steps.

Secondly, two phosphorus resonances shifted downfield from ca. -4 to -2 ppm in the one-dimensional ^{31}P spectrum. From a ^{31}P-^{1}H correlation experiment,[6,14] these markedly downfield-shifted ^{31}P peaks were assigned to 4P/8P (i.e., 3GpA4 and 7GpA8) via the already assigned H3'/H4' protons, see Figure 1.

Thirdly, to search more widely for alternate structures, a Monte Carlo conformational search[15-17] incorporating the refined NOE distance constraints was performed on the dinucleotide steps 3G-4A and 5G-6C using a modified program for nucleic acid molecules (Chuprina). Twist, roll, and slide and x-, y-, and z-displacements were used as variables, the sugar conformation was varied throughout the S domain, and the χ angles were restricted to the broad anti range to reduce the search time. Twelve million different dinucleotide conformations were generated starting from a B-form model. Those conformations that did not fit the experimental NOE distance constraints were rejected, and only the remaining ~300 that fit all of the experimental data were used for statistical analysis. For the ~300 acceptable 3G-4A conformers, the ϵ angles were *all* in the -120° to -80° range and all ζ angles were ca. +170° (i.e., no t,g^- conformers), while the corresponding angles in the ~300 allowed G-C steps were +160° ± 30° and -120° ± 60°, respectively (i.e., all t,g^-).

Our observation of a 2 ppm ^{31}P downfield shift and a 77° twist at the 3GpA4 step agrees with previously proposed shift/twist correlations.[3,18,19] Furthermore, our refined values of ca. +105° for ζ and ca. -150° for α in the B_{II} phosphate are in qualitative agreement with Gorenstein's proposal[18] that $\zeta(t) - \alpha(t)$ phosphates should resonate downfield of $\zeta(g^-) - \alpha(g^-)$ conformations. However, the correlations between ^{31}P chemical shift and $J_{H3'-P}$ proposed by Gorenstein and co-workers[14,20] are not borne out by our results. These authors[14,20] predicted that a predominantly B_{II} conformation should have a phosphorus chemical shift of -3.0 ppm and a $J_{H3'-P}$ value of 10 Hz. The chemical shift of the 4P and 8P B_{II} phosphates (ϵ = -50°) is -2.0 ppm (about twice the predicted downfield shift), and they have $J_{H3'-P}$ values of less than 5 Hz rather than the predicted 10 Hz, suggesting that the assumptions underlying the predictions need to be reexamined. While ζ and α appear to be correlated to the ^{31}P chemical shift, ϵ and $J_{H3'-P}$ do not.

In a recently published paper, Li et al.[11] reported the construction of an energy-minimized model of an ATGAGC/GCGAAT hexamer containing adjacent G:A mismatch base pairs that satisfied their partial NMR distance data. In constructing this model, all torsional angles were kept as close as possible to standard B-form DNA values (i.e., B_I phosphates were imposed). In contrast, the structure generated from our full data set of refined NMR distances (with no prior backbone assumptions), together with the anomalous chemical shift of the phosphodiester linking the adjacent GA pairs, strongly suggests that this step involves a B_{II} backbone conformation and that a B_I conformation at this step is incompatible with a complete set of experimental distance data. Finally, we note that 3P and 7P, preceding the B_{II} phosphates at the mismatch site, are shifted upfield to ca. -4.7 ppm from the ca. -4 ppm shift of the normal B_I phosphates.

Acknowledgment. This work was supported by NIH Grant GM32681.

Registry No. Guanine, 73-40-5; adenine, 73-24-5; d(ATGAGCGAATA), 116338-86-4.

(14) Nikonowicz, E. P.; Gorenstein, D. G. *Biochemistry* **1990**, *29*, 8845-8858.
(15) Zhurkin, V. B.; Lysov, Y. P.; Ivanov, V. I. *Biopolymers* **1978**, *17*, 377-412.
(16) Go, N.; Scheraga, H. A. *Macromolecules* **1970**, *3*, 178-187.
(17) Miller, K. J. *Biopolymers* **1979**, *18*, 959-980.
(18) Gorenstein, D. G. In *Phosphorus-31 NMR: Principles and Applications*; Gorenstein, D. G., Ed.; Academic Press: New York, 1984.
(19) Ott, J.; Eckstein, F. *Biochemistry* **1985**, *24*, 253-258.
(20) Roongta, V. A.; Jones, C. R.; Gorenstein, D. G. *Biochemistry* **1990**, *29*, 5245-5258.

Expedient Assembly of Carbocyclic, Heterocyclic, and Polycyclic Compounds by Me_3Sn Radical Mediated Carbocyclizations of Dienes and Trienes: A Novel Oxidative Cleavage of the C-Sn Bond

Stephen Hanessian* and Roger Léger

Department of Chemistry, Université de Montréal Montréal, Québec, Canada H3C 3J7

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The formation of carbocyclic and heterocyclic compounds from terminal dienes by free-radical processes has received considerable attention in recent years.[1-5] However, except for a single example involving a transannular reaction,[6] and excluding vinylic radicals,[7] the use of trialkylstannyl radicals for the carbocyclization of dienes has remained largely unexplored. This is probably due to early reports of mono- or bis-addition without cyclization[6,8] or due to the view that the stannyl alkyl radical adduct would revert to alkene rather than cyclize, especially in dilute solution.[9] The paucity of methods to efficiently cleave an unactivated C-Sn bond[10,11] has undoubtedly been an added deterrent in considering the obvious potential of this approach to ring formation. We now report that trimethylstannyl radicals[12] add to the unsubstituted terminal olefinic carbon atom of a variety of activated and

(1) For recent excellent reviews, see: (a) C-Radikale. In *Methoden der Organischen Chemie*; Regitz, M., Giese, B., Eds.; Houben-Weyl: Stuttgart, Germany, 1989; Vol. E19A. (b) Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron* **1990**, *46*, 1385. (c) Curran, D. P. *Synthesis* **1988**, *417*, 489. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (e) Giese, B. *Radicals in Organic Synthesis-Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (f) Hart, D. J. *Science* **1984**, *223*, 883.
(2) For a review on halocarbon-centered radicals, see: Bellus, D. *Pure Appl. Chem.* **1985**, *57*, 1827. See also: Fields, D. L., Jr.; Shechter, H. *J. Org. Chem.* **1986**, *51*, 3369. Brace, N. O. *J. Am. Chem. Soc.* **1964**, *86*, 523.
(3) For aryl sulfonyl radicals, see: Chuang, C.-P. *Synlett* **1990**, 527. (b) Chuang, C.-P.; Ngoi, T. H. J. *Tetrahedron Lett.* **1989**, *30*, 6369. (c) De Riggi, I.; Surzur, J.-M.; Bertrand, M. P. *Tetrahedron* **1988**, *44*, 7119. (d) Serra, A. C.; da Silva Corrêa, C. M. M. *J. Chem. Res.* **1989**, 85. (e) Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1985**, 897.
(4) For silyl radicals, see: Kulicke, K. J.; Giese, B. *Synlett* **1990**, 91. Kraus, G. A.; Liras, S. *Tetrahedron Lett.* **1990**, *31*, 5265.
(5) For some examples of radical cyclizations from dienes, see: (a) Enholm, E. J.; Kinter, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7784. (b) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268. (c) Yang, Z.-Y.; Burton, D. J. *J. Org. Chem.* **1991**, *56*, 5125. (d) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561. (e) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911. (f) Newcomb, M.; Courtney, A. R. *J. Org. Chem.* **1980**, *45*, 1707. (g) Ashby, E. C.; DePriest, R. *J. Am. Chem. Soc.* **1982**, *104*, 6144. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (h) Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250 and references cited therein.
(6) Fish, R. H.; Kuivila, H. G.; Tyminski, I. R. *J. Am. Chem. Soc.* **1967**, *89*, 5861.
(7) (a) Yoo, S.-E.; Yi, K. Y.; Lee, S.-H.; Jeong, N. *Synlett* **1990**, 575. (b) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2829. (c) Broka, C. A.; Reichert, D. E. C. *Tetrahedron Lett.* **1987**, *28*, 1503. (d) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (e) Ardisson, J.; Férézou, J. P.; Julia, M.; Pancrazi, A. *Tetrahedron Lett.* **1987**, *28*, 2001. (f) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.
(8) Iyoda, J.; Shiihara, I. *J. Org. Chem.* **1970**, *35*, 4267. Kuivila, H. G. *J. Organomet. Chem.* **1964**, 47. Neumann, W. P.; Niermann, H.; Sommer, R. *Justus Liebigs Ann. Chem.* **1962**, *659*, 27. van der Kerk, G. J. M.; Noltes, J. C. *J. Appl. Chem.* **1959**, 106.
(9) Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616, see also ref 1c, p 430; ref 7b.
(10) For a review, see: Abraham, M. H.; Grellier, P. L. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; J. Wiley & Sons: New York, 1985; Vol. 2, p 25. For a second review, see: Barker, P. J.; Winter, J. N. p 151.
(11) For simple primary alkylstannanes, see: (a) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593. (b) Lochynski, S.; Boduszek, B.; Shine, H. J. *J. Org. Chem.* **1991**, *56*, 914. (c) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Chem. Pharm. Bull.* **1984**, *32*, 887. For secondary alkylstannanes, see: (d) Herndon, J. W.; Wu, C.; Harp, J. J.; Kreutzer, K. A. *Synlett* **1991**, 1. (e) Herndon, J. W.; Wu, C. *Tetrahedron Lett.* **1989**, *30*, 6461. (f) Rieche, A.; Bertz, T. *Angew. Chem.* **1958**, *70*, 507. (g) Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606. See also: Sosnovsky, G.; Brown, J. H. *Chem. Rev.* **1966**, *66*, 529. Alleston, D. L.; Davies, A. G. *J. Chem. Soc.* **1958**, 1550. For other reactions, see: Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1482. MacDonald, T. L.; Mahalingam, S.; O'Dell, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 6767. Piers, E.; Roberge, J. Y. *Tetrahedron Lett.* **1991**, *32*, 5219.
(12) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 303.

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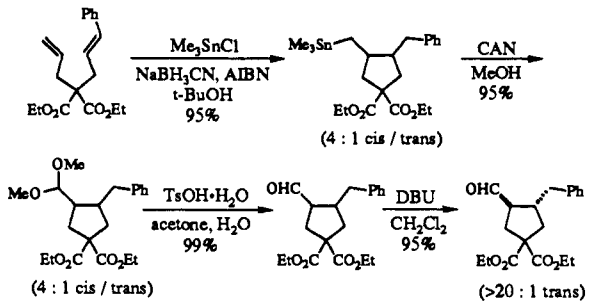
Scheme I



unactivated dienes and trienes to produce excellent yields of monocyclic, bicyclic, and polycyclic compounds containing a vicinally substituted (trimethylstannyl)methyl group and an appropriate branch. We also show that the C–Sn bond in a number of these products can be oxidatively cleaved to the corresponding aldehydes (isolated as their dimethyl acetals) using ceric ammonium nitrate in methanol. Scheme I illustrates an example of a typical sequence.

Table I lists examples of trimethyltin hydride-mediated carbocyclization reactions of a variety of dienes and trienes and their products of oxidative destannylation following the protocol shown in Scheme I.[13] The facile formation of 3,4-disubstituted tetrahydrofurans and pyrrolidines from readily available dienes[14,15] with a predominance of the cis isomers[16] and the compatibility of various protective groups in this unique oxidative destannylation[17] are noteworthy features (entries b, c, and g). Entries d, e, and f illustrate the remarkably facile carbocyclizations of selected allyl ethers to produce 1,6-dioxatriquinanes and 1,6-dioxahydrindacenes, respectively. The feasibility of this novel carbocyclization with aliphatic dienes to produce carbocyclic and carbobicyclic compounds from activated and nonactivated dienes is shown in entries g–j. Cyclization proceeded smoothly with the enantiomerically pure diene tribenzoate shown in entry g to give a preponderance of the isomer with a syn orientation of the carbon substituents. Related carbocycles have been produced from acyclic carbohydrate olefins via ω-halo and other radical sources.[5d,18] An example of the formation of a vicinally substituted cyclohexane model can be seen in the last entry in Table I.

The direct isolation of aldehydes (or their dimethyl acetals) with little if any change in the original stereochemistry of the vicinal substituents in the cyclic product is a noteworthy feature in this unprecedented oxidative destannylation reaction. The mechanism probably involves electron transfer from CAN (reduction potential 1.44 V)[19] to produce a (trimethylstannyl)methyl radical cation,[11a,b] which can reversibly disproportionate to an alkyl radical and Me_3Sn^+. Attack by a second molecule of CAN could produce a cerium(IV)-coordinated nitrate ester intermediate, which can fragment to give initially the aldehyde and then the dimethyl acetal in situ. Occasionally, nitrate esters may be formed via a ligand transfer reaction,[20] thus competing with the main oxidation, as in the case of secondary and relatively hindered alkyl radicals (entries d and e).[21] It is of interest that the aldehyde

Table I. Addition–Cyclization of Trimethyltin Radical with Dienes and Trienes and Oxidative Destannylation with Ceric Ammonium Nitrate (CAN)

Entry	Substrate	Yield[a], Ratio[b]	Yield[a], Ratio[b]
a.	X = O, R = Ph	84%, (2 : 1)	60%, (2 : 1)
b.	X = NTs, R = H	98%, (2 : 1)	64%, (2 : 1)
c.	X = NCbz, R = H	85%, (2 : 1)	58%, (2 : 1)
d.		86%, (2 : 1)	23%, (2 : 1) + 29%, (2 : 1)
e.		42%[c,d]	24%[c] + 29%[c]
f.		85%, (2 : 1)	54%, (2 : 1)
g.		52%[c,e]	80%
h.		92%, (2 : 1)	76%, (2 : 1)
i.		54%, (6 : 1)	96%, (4 : 1 endo / exo)
j.		97%, (1 : 1)	87%, (1 : 1)

[a] Isolated product by flash chromatography. [b] Determined by NMR or HPLC (cis and endo products are always major). [c] Separable by chromatography. [d] Tricyclic compound, 41% (2:1 exo/endo). [e] Other isomers 27%.

(13) In a typical procedure, the diene or triene (6.8 mmol) is treated with trimethyltin chloride (14 mmol), sodium cyanoborohydride (14 mmol), and AIBN (cat.)[12] in refluxing *tert*-butyl alcohol (0.02 M). After heating for 3–6 h, the reaction mixture is quenched with 5% ammonium hydroxide and then processed in the usual way. The products are isolated by flash column chromatography (see the supplementary material). A referee has suggested the possible toxicity of some of the more volatile products.

(14) See, for example: Naim, A.; Mills, G.; Shevlin, P. B. *Abstracts of Papers*, 201st National Meeting of the American Chemical Society, Atlanta, GA, Spring, 1991; American Chemical Society: Washington, DC, 1991; ORG 311; ref 5c.

(15) Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *J. Org. Chem.* **1985**, *50*, 5620. Hawthorne, D.-G.; Johns, S. R.; Willing, R. I. *Aust. J. Chem.* **1976**, *29*, 315; see also refs 3c, 5c.

(16) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. Beckwith, A. L. J.; Blair, I.; Philipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613. Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959. See also: Giese, B. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 553; ref 1c, p 420.

(17) In a typical reaction, 1.2 mmol of trialkylstannyl derivative in 24 mL of MeOH is treated with ceric ammonium nitrate (12 mmol) at 25 °C, and the solution is allowed to stir for 12 h. The reaction mixture is poured in ether, the solution washed three times with water, dried, and processed as usual to give the dimethyl acetal derivative. Oxidation using the Herndon[11e] and Ochiai[11g] methods led to modest yields of the corresponding alcohols (24–36%) in some cases.

(18) RajanBabu, T. V.; Fukunaga, T. *J. Am. Chem. Soc.* **1989**, *111*, 296. RajanBabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759. Bartlett, P. A.; McLaren, K. L.; Ting, P. C. *J. Am. Chem. Soc.* **1988**, *110*, 1633. Wilcox, C. S.; Thomasco, L. M. *J. Org. Chem.* **1985**, *50*, 546.

(19) Galli, C. *J. Org. Chem.* **1991**, *56*, 3238.

(20) See, for example: Trahanovsky, W. S.; Flash, P. J.; Smith, L. M. *J. Am. Chem. Soc.* **1969**, *91*, 5068. Ho, T.-L. *Synthesis* **1973**, 347.

(21) Oxidation of 3-(trimethylstannyl)-1-(benzyloxy)cyclohexane (CAN, 10 equiv, MeOH) gave the ketone (21%) and the nitrate (60%).

is predominantly formed when the reaction is carried out in aqueous methanol (1:1) or when the reaction is conducted at a low temperature and for a short duration.[22] Further studies on the scope and the mechanism of these reactions will be reported in due course.

Acknowledgment. We thank NSERCC and FCAR for generous financial assistance and fellowships to R.L. We also thank Sacha Ninkovic for his skillful assistance in optimizing entry j (Table I).

Supplementary Material Available: Experimental procedures, physical constants, and spectroscopic data (9 pages). Ordering information is given on any current masthead page.

(22) Oxidative destannylation in the presence of a 2,4,6-trimethoxybenzyl or 3,4-(methylenedioxy)benzyl group leads to the aldehyde directly (CAN 2 equiv, MeOH, slow addition, 2 h, 0 °C, 58 and 68%, respectively), a sequence which was used in the total synthesis of lignans: Hanessian, S.; Léger, R. *Synlett*, in press.

Hypervalent Selenurane with the Chalcogenium Cation (Se^+, S^+) from 1,11-(Methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*]-[1,5]diselenocin and Its Sulfur Derivative: Interconvertible Redox Structures by Multicenter Chalcogenide Participation

Hisashi Fujihara,* Hisatomo Mima, Tomoki Erata,† and Naomichi Furukawa*

Department of Chemistry and Institute of Applied Physics, University of Tsukuba Tsukuba, Ibaraki 305, Japan

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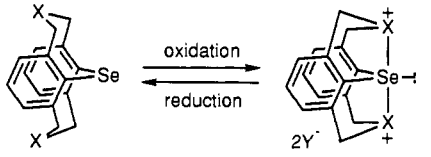
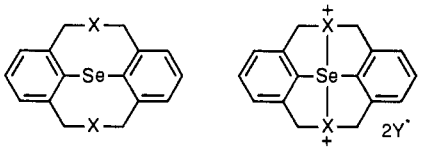
Although it was recently shown that the transannular interaction between two heteroatoms (Se–Se, Se–N) of selenium heterocycles can produce the diselenide dication and the hypervalent σ-ammonioselenuranes, such behavior by fourth-row elements and multichalcogenides has received less attention.[1,2] We have now found that transannular bond formation occurs between the three chalcogen atoms (Se, S) of the new cyclic chalcogenides 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocin (**1**) and 1,11-(methanothiomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenathiocin (**3**) in the oxidation of **1** and **3** with concentrated H_2SO_4 or 2 equiv of $NOPF_6$. This multicenter chalcogenide participation provides a new type of hypervalent σ-selenurane with two apical selenonio or sulfonio ligands. Its selenurane dication undergoes a reversible two-electron reduction, which is an unprecedented reaction mode for selenuranes. Thus, two-electron redox reactions of **1** or **3** are accompanied by conformational changes of the chair and boat forms. Generally, selenuranes bear two electronegative groups such as oxygen atoms or halogen atoms at the apical positions, though the preparation and properties of selenuranes[3] are little known as compared with those of hypervalent organosulfur compounds.[4]

Scheme I



1, **3** (*chair*) **2**, **4** (*boat*)



1 X = Se
3 X = S
2 X = Se, Y = HSO_4
2a X = Se, Y = PF_6
4 X = S, Y = HSO_4
4a X = S, Y = PF_6

With regard to the conformational properties of tris-selenide **1**,[5] the chair and the boat forms can exist.[6] The conformers can be assigned by the ^1H NMR spectral data for the benzylic protons of the eight-membered ring.[6] The ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as an AB quartet peak at δ 3.88 and 5.33 (J = 12.8 Hz), which is assigned to the twin chair form (Scheme I). The ^1H NMR spectra of **1** do not change over the temperature range from −50 (in $CDCl_3$) to +180 °C [in $(CD_3)_2SO$], indicating that **1** is conformationally rigid. The proton-coupled ^{77}Se NMR spectrum of **1** in $CHCl_3$ shows the two peaks at δ 208.6 (s, SeAr) and at δ 365.7 (t, $^2J_{Se-H}$ = 31 Hz, $SeCH_2Ar$).[7,8]

When tris-selenide **1** was dissolved in concentrated D_2SO_4 (98%) at room temperature,[9] the conformation of **1** in $CDCl_3$ was changed completely to the twin boat form **2** in D_2SO_4, as shown by ^1H NMR spectroscopy, i.e., the benzylic methylene protons appear at δ 4.07 and 4.59 (AB q, J = 16.0 Hz) (Scheme I). This D_2SO_4 solution of **2** was stable for several weeks, and no deuterium exchange was observed at all. More significant spectroscopic evidence for the formation of **2** was obtained in the ^{77}Se NMR spectrum. The proton-noise-decoupled ^{77}Se NMR spectrum of the H_2SO_4 solution of **2** exhibits two resonances at δ 543.8 ($SeCH_2Ar$)[10] and at δ 816.6 (SeAr) (ratio 2:1), indicating remarkable

† Institute of Applied Physics.

(1) (a) Fujihara, H.; Akaishi, R.; Erata, T.; Furukawa, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1789–1790. (b) Iwasaki, F.; Morimoto, M.; Yasui, M.; Akaishi, R.; Fujihara, H.; Furukawa, N. *Acta Crystallogr.* **1991**, *C47*, 1463–1466. (c) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *J. Am. Chem. Soc.* **1991**, *113*, 6337–6338.

(2) Fujihara, H.; Chiu, J.-J.; Furukawa, N. *J. Am. Chem. Soc.* **1988**, *110*, 1280–1284.

(3) (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, Chapters 3 and 14. The term selenurane (selenane) has been used for tetracoordinate selenium(IV) compounds. (b) *Selenium Reagents and Intermediates in Organic Synthesis*; Paulmier, C., Ed.; Pergamon Press: New York, 1986.

(4) For a review, see: Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In *Organic Sulfur Chemistry, Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 8.

(5) NMR data. **1** ($CDCl_3$): ^1H δ 3.88, 5.33 (AB q, J = 12.8 Hz, 8 H), 6.97–7.01 (m, 4 H), 7.07–7.13 (m, 2 H); ^{13}C δ 32.9, 127.1, 130.3, 133.7, 149.3. **2** (D_2SO_4): ^1H δ 4.07, 4.59 (AB q, J = 16.0 Hz, 8 H), 7.04 (d, J = 7.6 Hz, 4 H), 7.33 (t, J = 7.6 Hz, 2 H); ^{13}C δ 41.3, 131.9, 134.8, 138.6, 142.3. **2a** (CD_3CN): ^1H δ 4.56, 5.06 (AB q, J = 15.8 Hz, 8 H), 7.53 (d, J = 7.6 Hz, 4 H), 7.79 (t, J = 7.6 Hz, 2 H); ^{13}C δ 39.7, 132.2, 135.3, 141.6. The ^{31}P NMR spectrum for **2a** shows a ^{31}P peak at δ −144.9 (sept, J_{PF} = 707 Hz, relative to H_3PO_4) in the region of ionic PF_6^-. **3** ($CDCl_3$): ^1H δ 3.79, 5.27 (AB q, J = 14.4 Hz, 8 H), 6.97–7.03 (m, 4 H), 7.08–7.15 (m, 2 H); ^{13}C δ 42.3, 127.8, 130.3, 134.5, 148.0. **4** (D_2SO_4): ^1H δ 4.05, 4.61 (AB q, J = 17.3 Hz, 8 H), 7.13 (d, J = 7.6 Hz, 4 H), 7.34 (t, J = 7.6 Hz, 2 H); ^{13}C δ 44.9, 130.1, 133.7, 139.1, 141.0; ^{77}Se δ 917.8 (s). **4a** (CD_3CN): ^1H δ 4.60, 5.10 (AB q, J = 16.2 Hz, 8 H), 7.59 (d, J = 7.6 Hz, 4 H), 7.78 (t, J = 7.6 Hz, 2 H); ^{13}C δ 43.4, 131.0, 135.7, 140.5; ^{31}P δ −144.9 (sept, J_{PF} = 707 Hz).

(6) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913–925. (b) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630–1634.

(7) All ^{77}Se chemical shifts (^{77}Se: spin $^1/_2$, natural abundance 7.6%) are relative to Me_2Se.

(8) The proton-decoupled ^{77}Se NMR (76.3 MHz) spectrum of **1** in $CHCl_3$ shows that the Se peak of $SeCH_2Ar$ appears as a singlet at δ 365.7. The value of $^2J(^{77}Se, H_A$ or $H_B)$ is most likely related to the Se–C–H dihedral angle; the details will be reported elsewhere.

(9) Concentrated H_2SO_4 acts either as an oxidant or as a strong acid: Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *12*, 155.

(10) The ^{77}Se peak of $SeCH_2Ar$ for **2** appears as a triplet peak ($^2J_{Se-H}$ = 28 Hz) a δ 543.8 in the proton-coupled ^{77}Se NMR spectrum.

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