Free-Radical Homolytic Substitution at Selenium: An Efficient Method for the Preparation of Selenophenes[1]

Jennifer E. Lyons,[2] Carl H. Schiesser,*[2,3] and Katarina Sutej[2]

School of Biological and Chemical Sciences, Deakin University, Geelong, Victoria, Australia 3217, and School of Chemistry, University of Melbourne, Parkville, Victoria, Australia 3052

Received May 3, 1993•

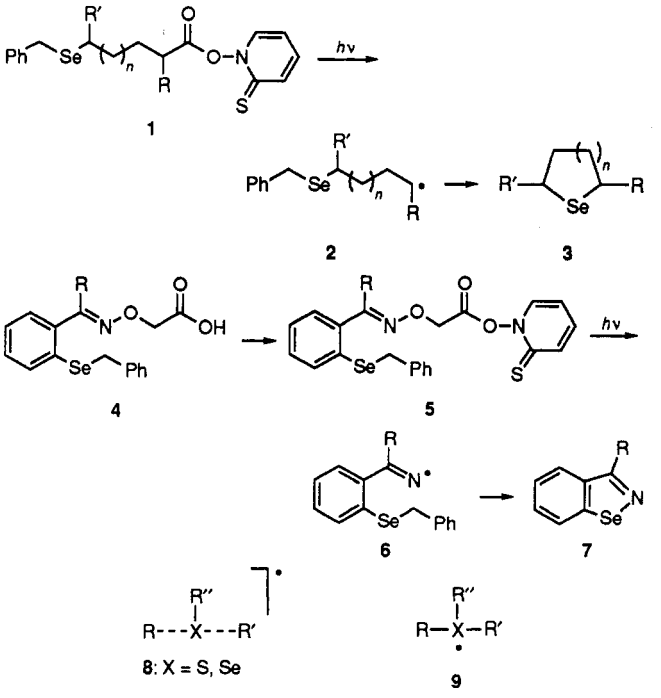
Substituted and unsubstituted 1-(benzylseleno)-4-iodobut-3-en-2-ols **12** and 2-(benzylseleno)-1-(2-iodophenyl)ethanols **18** react smoothly with tris(trimethylsilyl)silane in benzene at 80 °C (AIBN initiator) to afford selenophenes **16** and benzoselenophenes **21** in excellent yield. These reactions presumably involve intramolecular homolytic substitution by aryl and vinyl radicals **14** and **20** at the selenium atom with the expulsion of benzyl radical followed by facile dehydration to afford the aromatic selenophene ring system in each case. Competitive rate studies on the ring closure of the 2-[2-(benzylseleno)ethyl]phenyl radical **25** in the presence of tri-*n*-butyltin hydride to give 2,3-dihydrobenzo[*b*]selenophene (**27**) and 1-(benzylseleno)-2-phenylethane (**28**) provide a rate constant for ring closure (k_c) of approximately 3×10^7 s^{-1} at 80 °C. The determination of more accurate data is hampered by what we attribute to be the involvement of a slow, but competive nonradical process.

Introduction

Recent times have witnessed an enormous expansion in the use of free-radical methods in organic synthesis. This has come about due mainly to our increased understanding of free-radical processes[4] and the ready availability of new precursors and reagents designed specifically for radical-based syntheses.[5] We now have at our disposal high yielding free-radical methods which give rise to unprecedented levels of regio- and diastereocontrol in synthesis.[6,7]

During this time, most attention has focused on the formation of carbon–carbon bonds through the use of inter- and intramolecular addition reactions[8] with much less emphasis on the formation of bonds to heteroatoms. A notable exception has been the use of intramolecular homolytic substitution chemistry at the sulfur atom in alkyl sulfides and sulfoxides for the formation of carbon–sulfur bonds.[9-14]

Work in our laboratories has been directed toward the design, implementation, and understanding of homolytic substitution chemistry at heteroatoms other than sulfur. To that end, we recently reported[15,16] that alkyl radicals **2** derived from the corresponding thiohydroxamic esters[17] **1** undergo rapid and efficient intramolecular homolytic substitution at selenium atom to afford substituted and unsubstituted saturated selenium-containing heterocycles **3** in good yield. In addition, we have demonstrated[18] for the first time, that thiohydroxamic esters **5** derived from the *O*-carboxymethyl oxime derivatives[19] **4** of ketones and aldehydes decompose smoothly, upon irradiation, to afford the 1,2-benzoselenazoles **7** in a reaction which presumably involves intramolecular homolytic substitution by iminyl radical **6** at selenium atom.



There is still uncertainty concerning the mechanism of homolytic substitution reactions at sulfur and selenium. It is generally agreed[20] that that these reactions proceed

• Abstract published in *Advance ACS Abstracts*, September 1, 1993.

(1) Part of this work has been published in preliminary form: Schiesser, C. H.; Sutej, K. *Tetrahedron Lett.* **1992**, *33*, 5137.

(2) Deakin University.

(3) University of Melbourne. Direct correspondence to this address.

(4) Tedder, J. M.; Walton, J. C. *Acc. Chem. Res.*, **1976**, *9*, 183. Tedder, J. M.; Walton, J. C. *Tetrahedron* **1980**, *36*, 701. Ruechardt, C. *Topics Curr. Chem.* **1980**, *88*, 1. Wilt, J. W. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 333. Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. Beckwith, A. L. J.; Ingold, K. U. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, 161. Surzur, J.-M. in *Reactive Intermediates*; Abramovitch, A. A., Ed.; Plenum Press: New York, 1981; Vol. 2, Chapter 3. Julia, M. *Pure Appl. Chem.* **1974**, *40*, 553. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(5) Barton, D. H. R. *Tetrahedron* **1992**, *48*, 2529; and refs cited therein.

(6) Giese, B. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 969.

(7) Curran, D. P.; Shen, W.; Zhang, J.; Heffner, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 6738. Porter, N. A.; Swann, E.; Nally, J.; McPhail, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 6740. Giese, B.; Zehnder, M.; Rosh, M.; Zeitz, H.-G. *J. Am. Chem. Soc.* **1990**, *112*, 6741. Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296.

(8) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986; and refs cited therein.

(9) Kampmeier, J. A.; Evans, T. R. *J. Am. Chem. Soc.* **1966**, *88*, 4097.

(10) Benati, L.; Montevecchi, P. C.; Tundo, A.; Zanardi, G. *J. Chem. Soc. Perkin Trans. 1* **1974**, 1272.

(11) John, D. I.; Tyrrell, N. D.; Thomas, E. J. *J. Chem. Soc. Chem. Commun.* **1981**, 901.

(12) Beckwith, A. L. J.; Boate, D. R. *J. Chem. Soc. Chem. Commun.* **1986**, 189.

(13) Beckwith, A. L. J.; Boate, D. R. *J. Org. Chem.* **1988**, *53*, 4339.

0022-3263/93/1958-5632$04.00/0

via either a T-shaped transition structure 8 or radical intermediate, like 9 in which the attacking and leaving groups adopt a colinear arrangement. Experimental rate studies cast doubt on the existence of a hypervalent (9-S-3) intermediate in intramolecular homolytic substitution reactions by alkyl radical at the sulfur atom in alkyl sulfides.[21] Some ESR studies[22] and radical rearrangement reactions[23] imply the involvement of (9-S-3) sulfuranyl radical intermediates when radical stabilizing groups are present on sulfur, while the strict inversion of configuration observed when chiral sulfoxides are employed[24] provides strong evidence for the involvement of a single transition state (8) or transient intermediate, like 9, in these reactions. Very recently, *ab initio* calculations have provided further evidence for these observations. Calculations predict the existence of transient intermediates (9) in homolytic substitution reactions at sulfoxides,[25] while similar calculations for sulfides and selenides support the notion that single transition states (8) are involved.[25-27]

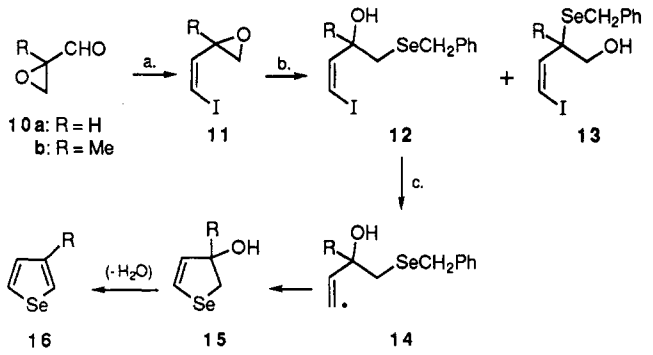
At the commencement of this work, we were aware of only three reports in which homolytic substitution by carbon-centered radicals at selenium had been carried out in a deliberate attempt to form carbon–selenium bonds. Perkins and Turner[28] and Newcomb and co-workers[29] used diphenyldiselenide to trap alkyl radicals while Byers and his colleagues[30] demonstrated that alkyl phenylselenides become involved in atom transfer reactions.

In an attempt to expand the synthetic utility of homolytic substitution chemistry, we have examined the intramolecular attack of vinyl and aryl radicals 14 and 20 at the selenium atom in alkyl selenides with the aim of preparing selenophenes. We now report that vinyl and aryl iodides 12 and 18 react with tris(trimethylsilyl)silane (TTMSS) to afford selenophenes 16 and benzoselenophenes 21 in excellent yield.

Results and Discussion

The precursors 12 to the vinyl radicals 14 were prepared according to Scheme I. Thus, glycidaldehyde and α-methylglycidaldehyde, prepared by treatment of acrolein and methacrolein with alkaline hydrogen peroxide,[31] were converted into the iodides 11 by the action of (iodomethylene)triphenylphosphorane as described by Stork and Zhao.[32] Interestingly, 11a was formed as a 12:1 mixture of *Z*/*E* isomers as determined by ^{1}H NMR spectroscopy, while 11b appeared to be isomerically pure (*Z*).

Scheme I[a]



[a] (a) Ph_3PCHI; (b) $(PhCH_2)_2Se/NaBH_4/EtOH$; (c) $(Me_3Si)_3SiH$/benzene/AIBN.

Unfortunately, treatment of the unsubstituted epoxide 11a with sodium benzylselenoate[16] yielded the required precursor 12a[33] in only 10% yield with the unwanted isomer 13a as the major product of reaction (50%). Presumably, the secondary site in the epoxide portion of 11a is activated over the primary position with respect to nucleophilic attack by the benzylselenide ion because it is also allylic. When the allylic position is blocked, as it is in 11b, exclusive formation of 12b[33] is observed (53%).

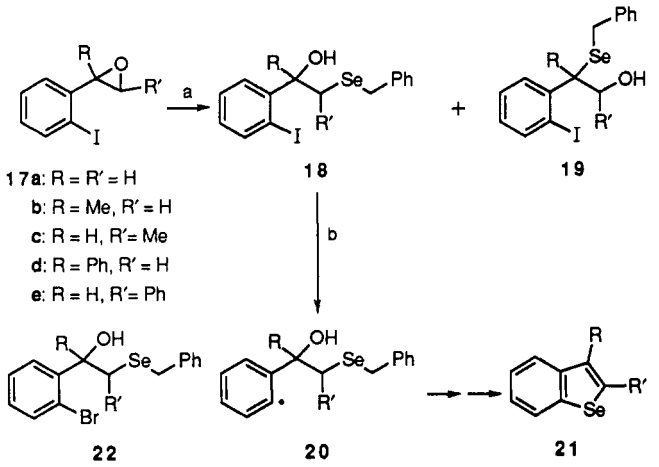
To our delight, when the precursors 12 were treated with tris(trimethylsilyl)silane (TTMSS) in benzene (0.05 M) at 80 °C (azobis(isobutyronitrile) (AIBN) initiator), quantitative conversion to selenophene (16a) and 3-methylselenophene (16b) was observed by ^{77}Se NMR spectroscopy (δ 610, 599 ppm, respectively[34]) and GS-MS of the crude reaction mixture. Presumably, the vinyl radical 14, once generated, undergoes intramolecular homolytic substition at the selenium atom with expulsion of benzyl radical to afford the alcohol 15 which subsequently undergoes facile dehydration to form the aromatic selenophene ring. To the best of our knowledge, this represents the highest yielding procedure for the formation of the selenophene ring system.

Because of their volatility and the scale of the reaction performed, we did not attempt to isolate 16a or 16b from the crude reaction mixture; instead we turned our attention to the preparation of the less volatile benzoselenophene ring system. Accordingly, precursors 18 to the aryl radicals 20 were prepared as depicted in Scheme II.

(Iodophenyl)oxiranes 17 were generally prepared by procedures described by Corey and Chaykovsky,[35] and

(14) Tada, M.; Uetake, T.; Matsumoto, M. *J. Chem. Soc. Chem. Commun.* **1990**, 1408.
(15) Schiesser, C. H.; Sutej, K. *J. Chem. Soc. Chem. Commun.* **1992**, 57.
(16) Benjamin, L. J.; Schiesser, C. H.; Sutej, K. *Tetrahedron* **1993**, *49*, 2557.
(17) Barton, D. H. R.; Motherwell, W. B.; Crich, D. *Tetrahedron* **1985**, *41*, 3901.
(18) Fong, M. C.; Schiesser, C. H. *Tetrahedron Lett.* **1993**, *34*, 4347.
(19) Boivin, J.; Fouquet, E.; Zard, S. Z. *Tetrahedron Lett.* **1991**, *32*, 4299.
(20) Volatron, F.; Demolliens; A., Lefar, J.-M.; Eisenstein, O. *Chem. Phys. Lett.* **1986**, 419. Volatron, F. *J. Mol. Struct. (THEOCHEM)* **1989**, *186*, 167.
(21) Ferris, K. F.; Roberts, D. H.; Franz, J. A. *J. Org. Chem.* **1987**, *52*, 2256.
(22) Perkin, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. Baban, J. A.; Roberts, B. P. *J. Chem. Soc. Perkin Trans. 2* **1978**, 678. Gara, W. B.; Roberts, B. P. *J. Chem. Soc. Perkin Trans. 2* **1979**, 1444. Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc. Perkin Trans. 2*, **1980**, 1497.
(23) Fong, M. C.; Schiesser, C. H. *Aust. J. Chem.* **1992**, *45*, 475.
(24) Beckwith, A. L. J.; Boate, D. R. *J. Chem. Soc. Chem. Commun.* **1986**, 189.
(25) Lyons, J. E.; Schiesser, C. H. *J. Chem. Soc. Perkin Trans. 2* **1992**, 1655.
(26) Ferris, K. F.; Franz, J. A. *J. Org. Chem.* **1992**, *57*, 777.
(27) Lyons, J. E.; Schiesser, C. H. *J. Organomet. Chem.* **1992**, *437*, 165.
(28) Perkins, M. J.; Turner, E. S. *J. Chem. Soc. Chem. Commun.* **1981**, 139.
(29) Newcomb, N.; Marquardt, D. J.; Kumar, M. V. *Tetrahedron* **1990**, *46*, 2345.
(30) Byers, J. H.; Gleason, T. G.; Knight, K. S. *J. Chem. Soc. Chem. Commun.* **1991**, 354.
(31) Payne, G. B. *J. Am. Chem. Soc.* **1959**, *81*, 4901.
(32) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 2173. See also: Bestmann, H. J.; Rippel, H. C.; Dostalek, R. *Tetrahedron Lett.* **1989**, *30*, 5261.
(33) Care must be taken to avoid prolonged exposure of organic selenides to bright light; decomposition with precipitation of elemental selenium is often observed.
(34) Luthra, N. P.; Odom, J. D. *The Chemistry of Organic Selenium and Tellurium Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, Chapter 6.
(35) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

Scheme II[a]



[a] (a) $(PhCH_2)_2Se/NaBH_4/EtOH$; (b) $(Me_3Si)_3SiH$/benzene/AIBN.

Table I. Isolated Percentage Yields of the Free-Radical Precursors 18 and Benzo[*b*]selenophenes 21 in This Study

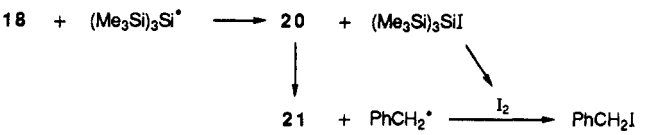
	% yield		
starting material	18	19	21
17a	52	24	80
17b	64	–	82
17c	–	85	–
17d	85	–	86
17e	33	47	93

Durst and co-workers.[36] Upon treatment with sodium benzylselenoate in the usual way, **17** was converted to the isomeric mixture of alcohols **18** and **19**,[33] the ratio of which depended upon the substituents R and R' and which were separated by flash chromatography. Product yields are displayed in Table I and clearly indicate that the required isomer **18** is isolated as the sole product when the benzylic site of attack is blocked by a substituent (R ≠ H). Unfortunately, when **17c** was reacted in this fashion, the sole product **19c** was that of incorrect regiochemistry. We attribute this to the activation of the benzylic position toward nucleophilic attack over the alternative, secondary, site of attack.

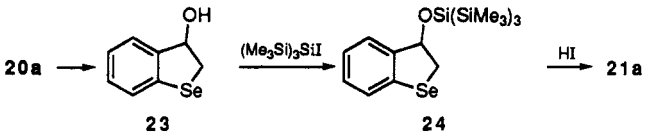
When the precursors **18** were treated with TTMSS in the usual way, near-quantitative conversion to the benzoselenophenes **21** was observed by ^{77}Se NMR spectroscopy in each case. The required products **21** were isolated in excellent yield (Table I) after flash chromatography. Presumably, as was suggested for **14**, radicals **20** undergo intramolecular homolytic substitution at the selenium atom followed by facile dehydration to afford the benzoselenophenes **21**.

Surprisingly, in certain instances the benzoselenophenes appeared to elute with trace amounts of benzyl iodide upon flash chromatography. ^1H NMR spectroscopy and GS-MS of the crude reaction mixture in each case confirmed that indeed benzyl iodide was produced in yields of 1–5% during the course of the reaction. We found it convenient to remove the benzyl iodide by reaction with triethylamine prior to chromatography in those instances where it appeared to coelute with the required product. When treated in this fashion, the benzoselenophenes could be isolated free of contamination and were consistent with previous reports.[34,37–39]

Scheme III



Scheme IV



The small quantities of benzyl iodide formed during the course of these reactions are unlikely to directly arise from the radical chain mechanism involving homolytic substitution at selenium. Rather, we believe that tris(trimethylsilyl)silyl iodide, a byproduct of the radical chain mechanism is unstable under the reaction conditions and partly decomposes to give small amounts of molecular iodine which are subsequently trapped by the chain-carrying benzyl radicals, as depicted in Scheme III. Other trialkylsilyl iodides are known to decompose to produce iodine upon standing.[40]

When the preparation of the parent system **21a** was attempted using tri-*n*-butyltin hydride instead of the silane (TTMSS), 2,3-dihydro-3-hydroxybenzo[*b*]selenophene (**23**) was the only product of radical ring closure isolated (83%). Clearly the silane or its products must catalyze the elimination process (**23** to **21**) in a way in which the tin-derived products cannot. We speculate that the elimination of **23** in the former process is a result of the reaction of tris(trimethylsilyl)silyl iodide and the alcohol **23**. The silylated product **24**, once formed, then undergoes acid-catalyzed elimination to give the product **21**, as depicted in Scheme IV. We would not expect tri-*n*-butyltin hydride to become involved in a similar process.

Interestingly, when the analagous bromide **22** was treated with TTMSS in the manner described, none of the expected product **21a** was observed by ^{77}Se NMR spectroscopy; instead 2,3-dihydro-3-hydroxybenzo[*b*]selenophene (**23**) was produced in minor amounts (δ 268 ppm). Unlike reactions involving iodides **18**, the major, and only other selenium-containing product in the reaction of **22** with TTMSS appeared in the NMR spectrum at δ –265 ppm and is consistent[41] with a product in which the silicon-centered radicals have attacked the selenium atom in preference to bromine. This, in turn, emphasizes the need for the more reactive iodo precursor in radical chain processes which involve intramolecular homolytic substitution at selenium.

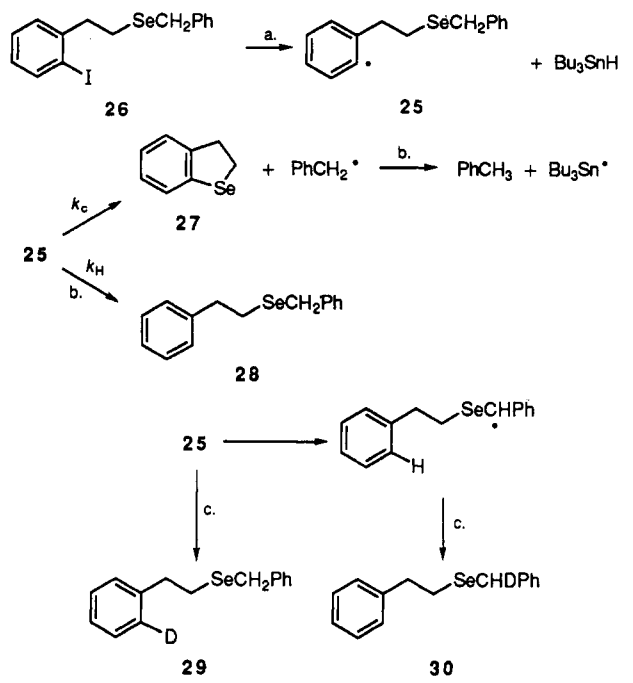
Kinetic Studies

In order to obtain a better understanding of homolytic substitution processes at selenium, we chose to examine the ring closure of the 2-[2-(benzylseleno)ethyl]phenyl radical **25** in the presence of tri-*n*-butyltin hydride (Scheme

(36) Akguen, E.; Glinski, M. B.; Dhawan, K. L.; Durst, T. *J. Org. Chem.* **1981**, *46*, 2730.

(37) Umezawa, S. *Bull. Chem. Soc. Jpn* **1939**, *14*, 363.
(38) Christiaens, L.; Renson, M. *Bull. Soc. Chim. Belg.* **1968**, *77*, 153.
(39) Christiaens, L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 235.
(40) Gunter, M. Private communication.
(41) McFarlane, H. C. E.; McFarlane, W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapt. 15.

Scheme V[a]



[a] (a) $Bu_3Sn^•$; (b) Bu_3SnH; (c) Bu_3SnD.

V). Treatment of the precursor **26**,[33] which was prepared by the reaction of 2-(2-iodophenyl)ethanol[42] with 4-toluenesulfonyl chloride followed by sodium benzylselenoate in ethanol, with TTMSS under the standard conditions afforded 2,3-dihydrobenzo[*b*]selenophene[43] (**27**) which was isolated in 63% yield.

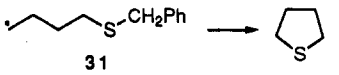
When the radical ring closure was repeated using tri-*n*-butyltin hydride (1.0 equiv, 0.02 M) at 80 °C for 3 h, both cyclized (**27**) and uncyclized material, namely 1-(benzylseleno)-2-phenylethane (**28**), were observed in a ratio of 3.3:1 by ^{1}H NMR spectroscopy in near-quantitative overall yield as assessed by integration against an internal standard (ethoxybenzene). Products were identified by comparison with the chemical shifts of diagnostic protons in authentic samples. In particular, **28** displays a singlet at δ 3.76 ppm corresponding to the two equivalent benzylic protons, while **27** displays a multiplet at δ 3.38 ppm corresponding to the four nonaromatic protons.

Application of the appropriate integrated rate expression[21,44,45] (eq 1 which integrates to eq 2), where $[27]_f$,

$$d[27]/d[28] = k_c/(k_H[Bu_3SnH]) \quad (1)$$

$$[27]_f = k_c \ln (([Bu_3SnH]_o + k_c/k_H)/([Bu_3SnH]_f + k_c/k_H))/k_H \quad (2)$$

$[Bu_3SnH]_o$, and $[Bu_3SnH]_f$ denote the final concentration of **27** and the inital and final concentrations of tri-*n*-butyltin hydride, respectively, and published values for the rate constant for the delivery of hydrogen from tri-*n*-butyltin hydride to aryl radical[46] to these data lead to an approximate value of 3×10^7 s^{-1} for the rate constant for ring closure (k_c) of **25** at 80 °C. This is to be compared with values of 1.4×10^6 s^{-1} at 80 °C for the ring closure of the 5-hexenyl radical[47] and 3.7×10^4 s^{-1} at 80 °C for the intramolecular homolytic substition at sulfur atom in the 4-(benzylthio)butyl radical[21] **31** indicating that intramolecular homolytic substition at the selenium atom is indeed a facile process.



31

Unfortunately, application of eq 1 yielded values of k_c which were found to be dependent on the inital reaction concentration,[48] suggesting that the radical process may be complicated by equilibria or competing side reactions. In addition, calculated values of k_c at various temperatures did not fit the Arrhenius expression, as we might have expected.

In order to assess whether or not intramolecular hydrogen abstraction from the benzylic position by the radical center in **25** is competitive with homolytic substitution, as had been observed in the case of the ring closure of the 4-(benzylthio)butyl radical[21] **31**, the iodide **26** was reacted with tri-*n*-butyltin deuteride (0.03 M) under the usual conditions and the crude reaction mixture subjected to ^{2}H NMR spectroscopy. Had intramolecular hydrogen abstraction in **25** been competitive, product **30** would have been observed in the ^{2}H NMR spectrum (δ ca. 3.8 ppm). Instead, the ^{2}H NMR spectrum revealed a signal at δ 7.2 ppm with no signal at δ 3.8 ppm, suggesting that this rearrangement is not competitive with ring closure. This is not surprising in light of the fact that the rate constant for the similar hydrogen transfer in the 4-(benzylthio)butyl radical **31** has been determined to be[21] 2.2×10^3 s^{-1} (25 °C), whereas our data suggest that ring closure of **25** is some 3 orders of magnitude more rapid than this.

The possibility of competitive nonradical side reactions was next examined. The iodide **26** was dissolved in benzene (0.02 M) and heated at 80 °C for 24 h without noticeable degredation, indicating that **26** is thermally stable under the reaction conditions. When **26** was treated with tri-*n*-butyltin hydride in benzene (0.02 M) at 80 °C for 24 h in the absence of radical initiator, both cyclized (**27**) and uncyclized (**28**) materials were observed by ^{1}H NMR spectroscopy in the usual manner, suggesting that the radical process is self-initiating. When the experiment was repeated in the presence of radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (3%), ^{119}Sn NMR spectroscopy of the crude reaction mixture revealed two signals at δ 79 and −88 corresponding to tri-*n*-butyltin iodide and unreacted tri-*n*-butyltin hydride, respectively,[49] while ^{1}H NMR spectroscopy revealed the presence of approximately 20% of cyclized material **27** (δ 3.38 ppm). These results confirm that formation of product **27** is retarded by the presence of the inhibitor. When the amount of inhibitor was increased to 34%, ^{1}H NMR spectroscopy still revealed small amounts (ca. 15%) of cyclized material after heating at 80 °C for 24 h.

These results suggest to us that while the dominant process operating in the ring closure of **26** under the

(42) Bennett, G. M.; Hafez, M. M. *J. Chem. Soc.* **1941**, 652.
(43) Renson, M. *Chem.Scr.* **1975**, *8A*, 29.
(44) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc. Chem. Commun.* **1974**, 472.
(45) Abeywickrema, A. N.; Beckwith, A. L. J.; Gerba, S. *J. Org. Chem.* **1987**, *52*, 4072.
(46) Johnson, L. J.; Lusztyk, J.; Wagner, D. D. M.; Abeywickrema, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.
(47) Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem* **1983**, *36*, 545.
(48) Calculated values of k_c at 80 °C ranged from 2.9×10^7 s^{-1} (0.02 M) to 4.0×10^7 s^{-1} (0.03 M).
(49) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

described (radical) conditions most probably involves intramolecular homolytic substitution at the selenium atom; it would appear that nonradical processes are also partly responsible for the formation of cyclized material.

We are currently further investigating these more subtle details of the homolytic substitution process at selenium.

Experimental Section

2-Iodoacetophenone and 2-iodobenzophenone were prepared according to published procedures.[51,52] Tris(trimethylsilyl)silane (TTMSS) was purchased from Aldrich and used without further purification. All melting points and boiling points are uncorrected. Melting points were determined using a Reichart hot stage apparatus. ^{1}H NMR were obtained on a JEOL JNM-GX270 spectrometer (in $CDCl_3$) operating at 270 MHz or on a JEOL PMX-60Si spectrometer (in CCl_4) operating at 60 MHz. ^{2}H, ^{13}C, ^{77}Se, and ^{119}Sn data were collected on a JEOL JNM-GX270 spectrometer. Chemical shifts relative to TMS (for ^{1}H and ^{13}C), externally referenced dimethylselenide (for ^{77}Se) or tetramethyltin (for ^{119}Sn) are reported in ppm (δ) downfield, along with assignments in parentheses. Abbreviations used are the following: s (singlet), d (doublet), t (triplet), m (multiplet), J (coupling constant). Mass spectra and GC-MS were recorded on a Hewlett Packard 5890 Series II spectrometer operating at 70 eV. Selected fragment ions are reported as their mass/charge ratio (m/z) followed by their relative intensities compared (in parentheses) to the base fragment. Elemental analyses were carried out by the Australian National University Microanalytical Service or Chemical and Micro Analytical Services Pty. Ltd. High-resolution mass spectra (HRMS) were recorded on a Kratos M25RF spectrometer at Flinders University.

(2-Iodoethenyl)oxirane (11a). 1.0 M Sodium bis(trimethylsilyl)amide in THF (17.4 mL, 17.4 mmol) was slowly added, with stirring, to a suspension of (iodomethyl)triphenylphosphonium iodide (9.2 g, 17.4 mmol) in THF (40 mL). After 1 min, the solution was cooled to −60 °C and hexamethylphosphoric triamide (HMPA) (5.2 mL) added, followed by cooling to −78 °C. Glycidaldehyde[31] (1.0 g, 13.9 mmol) was added and the solution stirred for a further 30 min, during which time the mixture warmed to room temperature. Hexane (350 mL) and ether (300 mL) were added, the resultant solution was washed with saturated ammonium chloride and water, and dried ($MgSO_4$) and the solvent was removed *in vacuo*. The residue was distilled to give the title oxirane as a colorless oil which crystallized on standing as a mixture of isomers (Z/E = 12:1) (800 mg, 32%): bp ~ 120 °C/30 mm (Kügelrohr); ^{1}H NMR ($CDCl_3$) δ 2.69 (dd, J = 2.6, 5.2 Hz, 1H; *E*-isomer), 2.75 (dd, J = 2.6, 5.2 Hz, 1H; *Z*-isomer), 2.96 (dd, J = 4.0, 9.5 Hz, 1H; *E*-isomer), 3.03 (dd, J = 4.2, 5.1 Hz, 1H; *Z*-isomer), 3.36 (ddd, J = 2.6, 7.4, 9.5 Hz, 1H; *E*-isomer), 3.64 (ddd, J = 2.6, 4.2, 7.7 Hz, 1H; *Z*-isomer), 5.97 (dd, J = 7.7, 8.1 Hz, 1H; *Z*-isomer), 6.27 (dd, J = 7.4, 14.7 Hz, 1H; *E*-isomer), 6.54 (d, J = 8.1 Hz, 1H; *Z*-isomer), 6.61 (d, J = 14.7 Hz, 1H; *E*-isomer); ^{13}C NMR δ 47.7, 54.4, 85.0, 96.1, 138.4; mass spectrum m/z (rel inten) 196 (28), 179 (39), 153 (100). Anal. Calcd for C_4H_5IO: C, 24.5; H, 2.6%. Found: C, 24.6; H, 2.5%. Substantial decomposition occurred during distillation.

(*Z*)-1-(2-Iodoethenyl)-1-methyloxirane (11b). The title compound was prepared in analogous fashion to that described for **11a**, using α-methylglycidaldehyde[31] (1.0 g, 11.6 mmol), (iodomethyl)triphenylphosphonium iodide (7.7 g, 14.5 mmol), 1.0 M sodium bis(trimethylsilyl)amide in THF (14.5 mL, 14.5 mmol), HMPA (4.4 mL), and THF (35 mL) and isolated as an isomerically pure colorless oil (1.2 g, 50%); bp ~ 80 °C/33 mm (Kügelrohr); ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 3H), 2.79 (d, J = 5.2 Hz, 1H), 2.81 (d, J = 5.2 Hz, 1H), 6.35 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 8.1 Hz, 1H); mass spectrum (CI) m/z (rel inten) 321 (2), 211 (100), 193 (30), 181 (46). Anal. Calcd for C_5H_7IO: C, 28.6; H, 3.4%. Found: C, 28.5; H, 3.4%. Substantial decomposition occurred during distillation.

1-(2-Iodophenyl)-1-methyloxirane (17b). Sodium hydride (290 mg, 12 mmol) was stirred in dry dimethyl sulfoxide (DMSO) (8 mL) at 70°C until the evolution of hydrogen had ceased (ca 90 min). THF (15 mL) was added and the solution cooled to −10 °C. Trimethylsulfonium iodide (2.4 g, 12 mmol) in DMSO (10 mL) was added dropwise, with stirring. After 1 min, 2-iodoacetophenone (2.5 g, 10 mmol) was rapidly added. After 5 min, the solution was warmed to room temperature and stirring continued for a further 5 h. Water (20 mL) was added, the mixture was extracted with ether (4×), the combined organic phases were washed with water (10×) and dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was separated by flash chromatography (2% ether/petroleum ether) to give the title compound as a colorless oil (1.7 g, 64%): ^{1}H NMR (CCl_4) δ 1.57 (s, 3H), 2.63 (d, J = 5 Hz, 1H), 2.87 (d, J = 5 Hz, 1H), 6.6–7.7 (m, 4H); mass spectrum m/z (rel inten) 260 (3), 105 (18), 91 (100). HRMS calcd for C_9H_9IO ($M^{+\cdot}$) 259.9700, found 259.9703.

1-(2-Iodophenyl)-1-phenyloxirane (17d). The title compound was prepared in analagous fashion to that described for **17b**, using sodium hydride (250 mg, 10 mmol), DMSO (5 mL), THF (10 mL), trimethylsulfonium iodide (2.1 g, 10 mmol) in DMSO (8 mL), 2-iodobenzophenone (2.7 g, 9 mmol) and isolated after flash chromatography (1.5% ether/petroleum ether) as a colorless solid (1.1 g, 40%): mp = 40–41 °C; ^{1}H NMR (CCl_4) δ 3.1 (d, J = 5 Hz, 1H), 3.25 (d, J = 5 Hz, 1H), 6.6–7.8 (m, 9H); mass spectrum m/z (rel inten) 322 (23), 195 (31), 165 (98), 105 (31), 91 (100); HRMS calcd for $C_{14}H_{11}IO$ ($M^{+\cdot}$) 321.9856, found 321.9847. Anal. Calcd for $C_{14}H_{11}IO$: C, 52.2; H, 3.4%. Found: C, 51.5; H, 3.4%.

General Procedure for the Reaction of Oxiranes 11 and 17 with Sodium Benzylselenoate: Reaction of (2-Iodoethenyl)oxirane (11a). Sodium borohydride (120 mg, 3.2 mmol) was added, in portions, to a suspension of dibenzyl diselenide (580 mg, 1.7 mmol) in dry ethanol (8 mL) until the characteristic yellow diselenide color had disappeared. (2-Iodoethenyl)oxirane (**11a**) (550 mg, 2.8 mmol) was added and the resultant orange solution stirred for 30 min. Water (15 mL) was added, the mixture was extracted with ether (3×), the combined organic phases were washed with saturated sodium chloride and dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was separated by flash chromatography (17% ether/petroleum ether) to give as the product of higher R_f, 1-(benzylseleno)-4-iodobut-3-en-2-ol (**12a**) (120 mg, 12%) as a pale oil, bp ~ 140 °C/0.75 mm (Kügelrohr); ^{1}H NMR ($CDCl_3$) δ 2.57 (dd, J = 9.0, 13.0 Hz, 1H), 2.58 (s(br), 1H), 2.80 (dd, J = 3.9, 13.0 Hz, 1H), 3.86 (s, 2H), 4.45 (m, 1H), 6.26–6.38 (m, 2H), 7.22–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 27.6, 30.5, 73.0, 83.0, 96.2, 127.0, 128.7, 129.0, 141.8; ^{77}Se NMR(C_6H_6) δ 197.7; mass spectrum m/z (rel inten) 368 (0.02), 241 (6), 91 (100). Anal. Calcd for $C_{11}H_{13}IOSe$: C, 36.0; H, 3.6%. Found C, 35.8; H, 3.5%.

The product of lower R_f was assigned to be 2-(benzylseleno)-4-iodobut-3-en-1-ol (**13a**) (513 mg, 50%) and was isolated as a pale oil which rapidly decomposed on standing: ^{1}H NMR ($CDCl_3$) δ 2.35 (s (br), 1H), 3.61 (d, J = 6 Hz, 2H), 3.8–4.1 (m, 3H), 6.2–6.5 (m, 2H), 7.2–7.5 (m, 5H).

Reaction of 1-(2-Iodoethenyl)-1-methyloxirane (11b): following the general procedure using sodium borohydride (120 mg, 3.2 mmol), dibenzyl diselenide (580 mg, 1.7 mmol), 1-(2-iodoethenyl)-1-methyloxirane (**11b**) (600 mg, 2.8 mmol), and dry ethanol (8 mL). Purification of the crude product by flash chromatography (17% ether/petroleum ether) yielded 1-(benzylseleno)-4-iodo-2-methylbut-3-en-2-ol (**12b**) as a pale oil (570 mg, 53%): bp ~ 130 °C/ 0.75 mm (Kügelrohr); ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3H), 2.77 (s, 1H), 2.80 (d, J = 12.8 Hz, 1H), 3.03 (d, J = 12.8 Hz, 1H), 3.85 (s, 2H), 6.29 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 8.6 Hz, 1H), 7.2–7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.9, 28.9, 37.3, 73.7, 96.1, 126.9, 128.6, 128.9, 145.0; ^{77}Se NMR(C_6H_6) δ 194.4; mass spectrum m/z (rel inten) 255 (10, [M − I$^+$]), 197 (22), 91 (100). Anal. Calcd for $C_{12}H_{15}IOSe$: C, 37.8; H, 4.0%. Found: C, 37.7; H, 4.0%.

Reaction of 2-(Iodophenyl)oxirane (17a): following the general procedure using (2-iodophenyl)oxirane (**17a**) (1.3 g, 5.3 mmol), dibenzyl diselenide (900 mg, 3.0 mmol), sodium borohydride (200 mg, 5.3 mmol), and dry ethanol (10 mL). After

(50) Minh, T. Q.; Christiaens, L.; Renson, M. *Tetrahedron* **1972**, *28*, 5379.
(51) Auwers, K.; Lechner, M.; Bundesmann, H. *Chem. Ber.* **1925**, *58*, 36.
(52) Gore, P. H.; Thorburn, S.; Weyell, D. J. *J. Chem. Soc. Perkin Trans. 1* **1973**, 2940.

workup, the residue was separated by flash chromatography (10% ether/petroleum ether) to afford, as the product of higher R_f, 2-(benzylseleno)-1-(2-iodophenyl)ethanol (**18a**) as a pale oil (1.1 g, 52%): ^{1}H NMR ($CDCl_3$) δ 2.51 (dd, J = 9.0, 13.3 Hz, 1H), 2.90 (d, 1.8 Hz, 1H), 2.97 (dd, J = 3.3, 13.2 Hz, 1H), 3.73 (s, 2H), 4.87 (m, 1H), 6.86 (t, J = 6.6 Hz, 1H), 7.1–7.5 (m, 7H), 7.67 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.6, 32.8, 75.6, 126.8, 126.9, 127.7, 128.5, 128.9, 129.4, 132.5, 138.8, 139.2, 144.5; ^{77}Se NMR(C_6H_6) δ 214.2; mass spectrum m/z (rel inten) 418 (1), 183 (9), 105 (13), 84 (100); HRMS calcd for $C_{15}H_{15}IOSe$ ($M^{+\cdot}$) 417.9334, found 417.9450. Anal. Calcd for $C_{15}H_{15}IOSe$: C, 43.2; H, 3.6%. Found: C, 44.0; H, 3.9%.

The product of lower R_f proved to be 2-(benzylseleno)-2-(2-iodophenyl)ethanol (**19a**) which was isolated as a pale oil (520 mg, 24%): bp ~ 175 °C/ 0.03 mm (Kügelrohr); ^{1}H NMR ($CDCl_3$) δ 3.7–4.0 (m, 5H), 4.42 (m, 1H), 6.85 (t, J = 6.5 Hz), 7.1–7.5 (m, 7H), 7.82 (d, J = 8.0 Hz, 1H); ^{13}C NMR (C_6D_6) δ 28.6, 51.0, 65.2, 127.1, 128.7, 129.1, 133.5, 138.8, 140.4, 142.6; ^{77}Se NMR (C_6H_6) δ 334.6; mass spectrum m/z (rel inten) 418 (1), 118 (12), 108 (96), 79 (100); HRMS calcd for $C_{15}H_{15}IOSe$ ($M^{+\cdot}$) 417.9334, found 417.9433.

Reaction of 1-(2-Iodophenyl)-1-methyloxirane (17b): following the general procedure using 1-(2-iodophenyl)-1-methyloxirane (**17b**) (1.6 g, 6.1 mmol), dibenzyl diselenide (1.16 g, 3.4 mmol), sodium borohydride (260 mg, 6.9 mmol), and dry ethanol (17 mL). After workup, the crude reaction mixture was separated by flash chromatography (10% ether/petroleum ether) to afford 2-(benzylseleno)-1-(2-iodophenyl)-1-methylethanol (**18b**) as a colorless oil (1.65 g, 64%): ^{1}H NMR ($CDCl_3$) δ 1.81 (s, 3H), 3.05 (d, J = 12.8 Hz, 1H), 3.17 (s, 1H), 3.49 (d, J = 11.5 Hz, 1H), 3.61 (d, J = 11.5 Hz, 1H), 3.91 (d, J = 12.8 Hz, 1H), 6.91 (t, J = 7.3 Hz, 1H), 7.2–7.4 (m, 6H), 7.75 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.4, 28.2, 37.5, 74.1, 93.3, 126.9, 127.8, 128.2, 128.5, 128.8, 129.0, 138.8, 142.7, 147.1; mass spectrum m/z (rel inten) 305 (3), 247 (7), 197 (10), 91 (100); HRMS calcd for $C_{16}H_{17}IOSe$ ($[M - I]^+$) 305.0444, found 305.0446.

Reaction of 1-(2-Iodophenyl)-2-methyloxirane (17c): following the general procedure using 1-(2-iodophenyl)-2-methyloxirane (**17c**) (330 mg, 1.3 mmol), dibenzyl diselenide (245 mg, 0.72 mmol), sodium borohydride (65 mg, 1.7 mmol), and dry ethanol (4 mL). After workup, the crude reaction mixture was separated by flash chromatography (20% ether/pertoleum ether) to afford 2-(benzylseleno)-2-(2-iodophenyl)ethanol (**19c**) as a colorless oil (465 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 1.22 (d, J = 5.5 Hz, 3H), 2.23 (s(br), 1H), 3.79 (m, 2H), 4.14 (m, 1H), 4.45 (d, J = 5.5 Hz, 1H), 6.92 (t, J = 7.3 Hz), 7.2–7.4 (m, 6H), 7.64 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H); mass spectrum m/z (rel inten) 432 (4), 132 (79), 91 (100); HRMS calcd for $C_{16}H_{17}IOSe$ ($M^{+\cdot}$) 431.9491, found 431.9461.

Reaction of 1-(2-Iodophenyl)-1-phenyloxirane (17d): following the general procedure using 1-(2-iodophenyl)-1-phenyloxirane (**17d**) (500 mg, 1.5 mmol), dibenzyl diselenide (290 mg, 0.86 mmol), sodium borohydride (70 mg, 1.9 mmol), and dry ethanol (4.5 mL). After workup, the crude reaction mixture was separated by flash chromatography (20% ether/hexane) to afford 2-(benzylseleno)-1-(2-iodophenyl)-1-phenylethanol (**18d**) as a colorless oil (650 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 3.37 (d, J = 13.0 Hz, 1H), 3.63 (m, 2H), 3.80 (d, J = 13.0 Hz, 1H), 6.95 (t, J = 7.7 Hz, 1H), 7.2–7.4 (m, 11H), 7.60 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H); mass spectrum m/z (rel inten) 367 (2, $[M - I]^+$), 276 (19), 261 (43), 105 (81), 91 (100). HRMS calcd for $C_{21}H_{19}IOSe$ ($[M - I]^+$) 367.0601, found 367.0617.

Reaction of 1-(2-Iodophenyl)-2-phenyloxirane (17e): following the general procedure using 1-(2-iodophenyl)-2-phenyloxirane (**17e**) (465 mg, 1.4 mmol), dibenzyl diselenide (285 mg, 0.84 mmol), sodium borohydride (90 mg, 2.0 mmol), and dry ethanol (4 mL). After workup, the crude reaction mixture was separated by flash chromatography (20% ether/petroleum ether) to afford as the product of higher R_f, 2-(benzylseleno)-1-(2-iodophenyl)-2-phenylethanol (**18e**) as a colorless oil (340 mg, 33%): ^{1}H NMR ($CDCl_3$) δ 2.69 (d, J = 3.0 Hz, 1H), 3.65 (d, J = 12.1 Hz, 1H), 3.69 (d, J = 12.1 Hz, 1H), 4.43 (d, J = 5.5 Hz, 1H), 5.34 (dd, J = 3.0, 5.5 Hz), 6.8–7.2 (m, 13H), 7.75 (d, J = 7.7 Hz, 1H); mass spectrum m/z (rel inten) 367 (5, $[M - I]^+$), 276 (9), 165 (24), 105 (23), 91 (100); HRMS calcd for $C_{21}H_{19}IOSe$ ($[M - I]^+$) 367.0601, found 367.0623.

The product of lower R_f proved to be 2-(benzylseleno)-2-(2-iodophenyl)-1-phenylethanol (**19e**) (480 mg, 47%): ^{1}H NMR ($CDCl_3$) δ 2.46 (d, J = 2.6 Hz, 1H), 3.42 (m, 2H), 4.70 (d, J = 7.3 Hz, 1H), 5.02 (dd, J = 2.6, 7.3 Hz), 6.86 (t, J = 7.7 Hz, 1H), 7.1–7.45 (m, 11H), 7.55 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H); mass spectrum m/z (rel inten) 388 (3, $[M - C_7H_6O]^+$), 185 (21), 105 (45), 91 (100); HRMS calcd for $C_{21}H_{19}IOSe$ ($[M - C_7H_6O]^+$) 387.9229, found 387.9221.

Reaction of 1-(Benzylseleno)-4-iodobut-3-en-2-ol (12a) with Tris(trimethylsilyl)silane: Formation of Selenophene (16a). 1-Benzylseleno-4-iodobut-3-en-2-ol (**12a**) (9.2 mg, 24 μmol), azobis(isobutyronitrile) (AIBN) (1 crystal) and tris(trimethylsilyl)silane (TTMSS) (7.7 μL, 25 μmol) were dissolved in benzene (5 mL) and heated, under nitrogen, at 80 °C overnight. GC/MS and ^{77}Se NMR spectroscopy of the crude reaction mixture indicated quantitative formation of selenophene (**16a**). ^{77}Se NMR (C_6H_6) δ 610; mass spectrum m/z (relative intensity) 132 (100), 106 (56), 93 (18), 80 (18). Spectral properties are consistent with previous reports.[34]

Reaction of 1-(Benzylseleno)-4-iodo-2-methylbut-3-en-2-ol (12b) with Tris(trimethylsilyl)silane: Formation of 3-Methylselenophene (16b). Following the procedure outlined above, 1-(benzylseleno)-4-iodo-2-methylbut-3-en-2-ol (**12b**) was quantitatively converted into 3-methylselenophene (**16b**) as evident by GC-MS and ^{77}Se NMR spectroscopy: ^{77}Se NMR (C_6H_6) δ 599; mass spectrum m/z (rel inten) 145 (100), 117 (12), 93 (20). Spectral properties are consistent with previous reports.[34]

1-[2-(Benzylseleno)ethyl]-2-iodobenzene (26). Sodium borohydride (250 mg, 6.6 mmol) was slowly added, under nitrogen, to a stirred suspension of dibenzyl diselenide (1.15 g, 3.4 mmol) in ethanol (60 mL) until the characteristic yellow diselenide color had disappeared. 2-(2-Iodophenyl)ethyl 4-toluenesulfonate (2.45 g, 6.1 mmol) (prepared in general fashion[53] from 2-(2-iodophenyl)ethanol[42] and 4-toluenesulfonyl chloride) in ethanol (20 mL) was added and the reaction stirred at room temperature overnight. The reaction mixture was quenched with 10% hydrochloric acid (100 mL) and extracted with ether (3×). The combined extracts were dried ($MgSO_4$), the solvent removed *in vacuo*, and the residue separated by flash chromatography (1% ether/petroleum ether) to give the title compound as a pale yellow oil (2.2 g, 90%): ^{1}H NMR ($CDCl_3$) δ 2.70–2.75 (m, 2H), 3.01–3.06 (m, 2H), 3.81 (s, 2H), 6.9–7.8 (m, 9H); ^{77}Se NMR C_6H_6) δ 269; HRMS calcd for $C_{15}H_{15}ISe$ ($[M - I]^+$) 275.0337, found 275.0424.

1-(Benzylseleno)-2-phenylethane (28). The title compound was prepared in identical fashion to that described for **26** using 2-phenylethanol and isolated a a pale oil (95%): ^{1}H NMR ($CDCl_3$) δ 2.69–2.74 (m, 2H), 2.87–2.92 (m, 2H), 3.76 (s, 2H), 7.13–7.29 (m, 12H); ^{77}Se NMR C_6H_6) δ 268; HRMS calcd for $C_{15}H_{16}Se$ ($M^{+\cdot}$) 276.0417, found 276.0381.

General Procedure for the Preparation of Benzo[*b*]selenophenes (21). Benzo[*b*]selenophene (21a). 2-(Benzylseleno)-1-(2-iodophenyl)ethanol (**18a**) (200 mg, 480 μmol), TTMSS (120 mg, 480 μmol), and AIBN (ca. 2 mg) were dissolved in benzene (100 mL) and heated at 80 °C, under nitrogen, overnight. The solvent was removed *in vacuo*, dichloromethane (10 mL) and triethylamine (200 μL) were added, and the resultant solution was stirred overnight to remove trace amounts of benzyl iodide. The solution was washed with 10% hydrochloric acid (2×) and water (2×) and dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was separated by flash chromatography (5% ether/petroleum ether) to give the title compound as a white solid (70 mg, 80%) mp = 49–50 °C (lit:[50] mp = 51 °C); ^{1}H NMR ($CDCl_3$) δ 7.2–7.4 (m, 2H), 7.57 (d, J = 5.7 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 124.3, 124.5, 125.3, 125.6, 127.7, 128.6, 141.2, 142.0; ^{77}Se NMR ($CDCl_3$) δ 525; mass spectrum m/z (rel inten) 182 (100), 102 (62), 89 (9). Spectral properties are consistent with previous reports.[34]

3-Methylbenzo[*b*]selenophene (21b): following the general procedure using 2-(benzylseleno)-1-(2-iodophenyl)-1-methylethanol (**18b**) (500 mg, 1.2 mmol), TTMSS (290 mg, 1.2 mmol), AIBN (ca. 5 mg), benzene (230 mL), and triethylamine (800 μL).

(53) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Press: Birmingham, AL, 1989.

The residue was separated by flash chromatography (petroleum ether) to give the title compound as a pale oil which solidified on standing (180 mg, 82%): ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 7.27 (td, J = 7.7, 1.4 Hz, 1H), 7.38 (td, J = 8.0, 1.6 Hz, 1H), 7.52 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.9, 123.2, 124.2, 124.3, 125.9, 126.0, 135.1, 141.4, 141.9; ^{77}Se NMR ($CDCl_3$) δ 487; mass spectrum m/z (rel inten) 196 (64), 115 (100). Spectral properties are consistent with previous reports.[34]

3-Phenylbenzo[*b*]selenophene (21d): following the general procedure using 2-(benzylseleno)-1-(2-iodophenyl)-1-phenylethanol (**18d**) (300 mg, 610 μmol), TTMSS (150 mg, 610 μmol), AIBN (ca. 3 mg) and benzene (120 mL). Evaporation of the solvent *in vacuo* and separation by flash chromatography (hexane) gave the title compound as a low-melting solid (145 mg, 93%): ^{1}H NMR ($CDCl_3$) δ 7.22–7.56 (m, 7H), 7.88 (s, 1H), 7.75–8.0 (m, 2H); ^{77}Se NMR ($CDCl_3$) δ 505; mass spectrum m/z (rel inten) 258 (100), 178 (68), 152 (19). Spectral properties are consistent with previous reports.[34]

2-Phenylbenzo[*b*]selenophene (21e): following the general procedure using 2-(benzylseleno)-1-(2-iodophenyl)-2-phenylethanol (**18e**) (120 mg, 250 μmol), TTMSS (62 mg, 250 μmol), AIBN (ca. 1 mg) and benzene (50 mL). Evaporation of the solvent *in vacuo* and separation by flash chromatography (hexane) gave the title compound as a white solid (55 mg, 86%): mp = 166–167 °C; ^{1}H NMR ($CDCl_3$) δ 6.9–7.9 (m, 10H); ^{77}Se NMR ($CDCl_3$) δ 515; mass spectrum m/z (rel inten) 258 (22), 178 (100). Anal. Calcd for $C_{14}H_{10}Se$: C, 65.4; H, 3.9%. Found C, 65.0; H, 3.7%.

2,3-Dihydrobenzo[*b*]selenophene (27): following the general procedure using 1-(benzylseleno)-2-(2-iodophenyl)ethane (**26**) (240 mg, 600 μmol), TTMSS (185 μL, 600 μmol) and AIBN (ca. 1 mg), benzene (120 mL), and triethylamine (230 μL). The residue was separated by flash chromatography (petroleum ether) to give the title compound as a colorless oil (70 mg, 63%): ^{1}H NMR ($CDCl_3$) δ 3.37–3.39 (m, 4H), 7.05–7.34 (m, 4H); ^{77}Se NMR ($CDCl_3$) δ 322; HRMS calcd for C_8H_8Se ($M^{+\cdot}$) 183.9791, found 183.9795. This compound has previously been prepared,[43] although no details are available.

Reaction of 1-(2-Iodophenyl)-2-(benzylseleno)ethanol (18a) with Tri-*n*-butyltin Hydride: Preparation of 2,3-Dihydro-3-hydroxybenzo[*b*]selenophene (23). 1-(2-Iodophenyl)-2-(benzylseleno)ethanol (**20a**) (100 mg, 240 μmol), tri-*n*-butyltin hydride (65 μL, 240 μmol), and AIBN (ca. 1 mg) were heated, under nitrogen, in benzene (50 mL) overnight. The solvent was removed *in vacuo* and the residue dissolved in ether and stirred with potassium fluoride (100 mg) overnight. After filtration and solvent evaporation, the crude product was separated by preparative TLC (ether) to give the title compound as a pale oil which was contaminated with trace amounts of tri-*n*-butyltin residues (40 mg, 83%): ^{1}H NMR ($CDCl_3$) δ 2.4 (s(br), 1H), 3.31 (dd, J = 3.6, 10.3 Hz, 1H), 3.66 (dd, J = 6.1, 10.3 Hz, 1H), 5.36 (m, 1H), 7.1–7.5 (m, 4H); ^{77}Se NMR ($CDCl_3$) δ 268; mass spectrum m/z (rel inten) 200 (100), 183 (67), 105 (61), 91 (74). Spectral properties are consistent with previous reports.[50]

Acknowledgment. We gratefully acknowledge the Australian Research Council for financial support and Deakin University for the award of an Equity Scholarship to J.E.L.