H, Si-t-Bu), 1.50–2.60 (14 H, H-2's, tetrahydropyranyl), 3.53–4.21 (7 H, H-4', H-5's, tetrahydropyranyl), 4.52–4.67 (1 H, H-3'), 5.45–5.62 (1 H, H-1'), 5.72–5.90 (1 H, tetrahydropyranyl), 6.10–6.27 (1 H, tetrahydropyranyl), 8.11–8.14 (4 s, 1 H, H-5).

3-[2'-Deoxy-5'-*O*-[(1,1-dimethylethyl)dimethylsilyl]-3'-*O*-[phenoxy(thiocarbonyl)]-β-D-ribofuranosyl]-1-(tetrahydropyran-2-yl)-7-[(tetrahydropyran-2-yl)oxy]pyrazolo[4,3-*d*]pyrimidine (29). A solution of **28** (172 mg, 0.32 mmol) and pyridine (0.4 mL) in dry CH_2Cl_2 (6 mL) was cooled to 0 °C, and phenoxythiocarbonyl chloride (89 μL, 0.64 mmol) was added. The reaction mixture was stirred under nitrogen at room temperature for 5 h at which time TLC indicated that reaction was complete. $CHCl_3$ was then added, and the mixture was washed with cooled dilute hydrochloric acid followed by water and aqueous sodium bicarbonate. The organic phase was then dried over sodium sulfate, and the volatiles were removed. The resulting residue was separated by preparative TLC (ethyl acetate–hexane, 6:1) to give 201 mg (93%) of **29** (a mixture of two pairs of diastereoisomers) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.12 (6 H, Si-Me's), 0.88 (9 H, Si-t-Bu), 1.50–3.21 (14 H, H-2's, tetrahydropyranyl), 3.59–4.48 (7 H, H-4', H-5's, tetrahydropyranyl), 5.44–5.62 (1 H, H-1'), 5.70–6.00 (2 H, H-3', tetrahydropyranyl), 6.20–6.38 (1 H, tetrahydropyranyl), 7.09–7.50 (5 H, phenyl), 8.11–8.17 (4 s, 1 H, H-5).

3-[2',3'-Dideoxy-5'-*O*-[(1,1-dimethylethyl)dimethylsilyl]-β-D-ribofuranosyl]-1-(tetrahydropyran-2-yl)-7-[(tetrahydropyran-2-yl)oxy]pyrazolo[4,3-*d*]pyrimidine (30). To a solution of **29** (94 mg, 0.14 mmol) and 2,2'-azobis(2-methylpropionitrile) (18 mg, 0.11 mmol) in dry toluene (5 mL) was added a solution of tri-*n*-butyltin hydride (188 μL, 0.7 mmol) in toluene (1 mL). The reaction mixture was heated at 80 °C for 15 h. The volatiles were then removed, and the residue was separated by preparative TLC (ethyl acetate–$CHCl_3$–hexane, 2:1:4) to afford 63 mg (86%) of **30** (a mixture of two pairs of diastereoisomers) as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 0.11 (6 H, Si-Me's), 0.85 (9 H, Si-t-Bu), 1.50–2.70 (16 H, H-2's, H-3's, tetrahydropyranyl), 3.60–4.30 (7 H, H-4', H-5's, tetrahydropyranyl), 5.19–5.34 (1 H, H-1'), 5.84–5.94 (1 H, tetrahydropyranyl), 6.18–6.28 (1 H, tetrahydropyranyl), 8.06–8.09 (4 s, 1 H, H-5).

3-(2',3'-Dideoxy-β-D-ribofuranosyl)-1-(tetrahydropyran-2-yl)-7-[(tetrahydropyran-2-yl)oxy]pyrazolo[4,3-*d*]pyrimidine (31). To a solution of **30** (89 mg, 0.17 mmol) in tetrahydrofuran (5 mL) was added a 1 M solution of tetra-*n*-butylammonium fluoride in tetrahydrofuran (0.33 mL, 0.33 mmol). The mixture was stirred at room temperature, and desilylation was complete in 30 min based on TLC. The solvent was removed and the residue was separated by preparative TLC (ethyl acetate–hexane, 1:1) to give 65 mg (94%) of **31** (a mixture of two pairs of diastereoisomers) as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 1.50–2.70 (16 H, H-2's, H-3's, tetrahydropyranyl), 3.62–4.30 (7 H, H-4', H-5's, tetrahydropyranyl), 5.16–5.28 (1 H, H-1'), 5.78–5.88 (1 H, tetrahydropyranyl), 6.14-6.25 (1 H, tetrahydropyranyl), 8.09–8.12 (4 s, 1 H, H-5).

3-(2',3'-Dideoxy-β-D-ribofuranosyl)pyrazolo[4,3-*d*]pyrimidin-7-one (2',3'-Dideoxyformycin B, 3). A mixture of **31** (41 mg, 0.10 mmol) and pyridinium *p*-toluenesulfonate (12 mg, 0.048 mmol) in methanol (4.5 mL) and water (0.5 mL) was stirred at 50 °C for 2 d. Volatiles were then removed, and the residue was separated by preparative TLC (1:1:1 acetone–ethyl acetate–CH_2Cl_2) to yield 21 mg (88%) of **3** as a colorless solid: ^{1}H NMR (DMSO-d_6) δ 1.95–2.39 (m, 4 H, H-2's, H-3's), 3.40, 3.56 (dd's, 2H, $J_{4',5'a}$ = 4.4 Hz, $J_{4',5'b}$ = 3.9 Hz, $J_{5'a,5'b}$ = 11.5 Hz, H-5's), 4.01–4.12 (m, 1 H, H-4'), 5.13 (dd, 1 H, $J_{1',2'a}$ = 6.3 Hz, $J_{1',2'b}$ = 8.1 Hz, H-1'), 7.86 (s, 1 H, H-5); ^{13}C NMR (DMSO-d_6) δ 27.94, 31.26 (C-2', C-3'), 64.27 (C-5'), 74.39, 80.16 (C-1', C-4'), 126.15 (C-7a), 136.24 (C-3a), 144.01, 144.61 (C-3, C-5), 155.70 (C-7); HRMS calcd for $C_{10}H_{12}N_4O_3$ + H^+ 237.0985, found 237.0990.

Acknowledgment. We thank Dr. K. A. Watanabe of the Sloan-Kettering Memorial Cancer Center for an authentic sample of 2'-deoxypseudouridine and Dr. Andre Rosowsky of the Dana Farber Cancer Institute for an authentic sample of 2'-deoxyformycin B. We thank the National Institutes of Health for financial support.

Registry No. **1**, 39967-60-7; **2**, 42821-83-0; **3**, 142189-82-0; **4**, 52522-99-3; **5**, 1191-99-7; **6**, 142189-83-1; **7**, 142189-84-2; **8**, 696-07-1; **9**, 142189-85-3; **10**, 142189-86-4; **11**, 130277-32-6; **13**, 142189-87-5; **14**, 13877-55-9; **16**, 142189-88-6; **18**, 142189-89-7; **19**, 142189-90-0; **20** (isomer 1), 142189-91-1; **20** (isomer 2), 142235-94-7; **20** (isomer 3), 142235-95-8; **20** (isomer 4), 142235-96-9; **21**, 142189-92-2; **22**, 142189-93-3; **23** (isomer 1), 142189-94-4; **23** (isomer 2), 142235-97-0; **23** (isomer 3), 142235-98-1; **23** (isomer 4), 142235-99-2; **24**, 142189-95-5; **25**, 142189-96-6; **26** (isomer 1), 142189-97-7; **26** (isomer 2), 142236-00-8; **26** (isomer 3), 142236-01-9; **26** (isomer 4), 142236-02-0; **27**, 142189-98-8; **28** (isomer 1), 142189-99-9; **28** (isomer 2), 142236-03-1; **28** (isomer 3), 142236-04-2; **28** (isomer 4), 142236-05-3; **29** (isomer 1), 142190-00-9; **29** (isomer 2), 142236-06-4; **29** (isomer 3), 142236-07-5; **29** (isomer 4), 142236-08-6; **30** (isomer 1), 142190-01-0; **30** (isomer 2), 142236-09-7; **30** (isomer 3), 142236-10-0; **30** (isomer 4), 142236-11-1; **31** (isomer 1), 142190-02-1; **31** (isomer 2), 142291-60-9; **31** (isomer 3), 142236-12-2; **31** (isomer 4), 142236-13-3.

Synthesis of γ- and δ-Lactones by Free-Radical Annelation of *Se*-Phenyl Selenocarbonates

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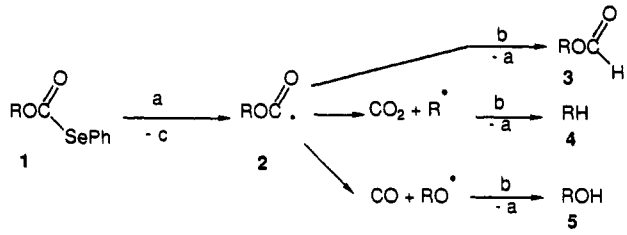
A general method for the synthesis of γ- and δ-lactones through the intramolecular addition of alkoxycarbonyl radicals, formed by reaction of *Se*-phenylselenocarbonates with *n*-Bu_3SnH, onto carbon–carbon multiple bonds is described. This free-radical cyclization is characterized by high regioselectivity favoring exo addition and by a high ratio of cyclization to reduction. Monocyclic, fused bicyclic, and spirocyclic lactones are formed in good to excellent yield. Use of allyltri-*n*-butyltin as a chain-transfer agent in the place of *n*-Bu_3SnH affords the corresponding 3-butenyl lactones.

The recent advances in synthetic free-radical chemistry are largely due to an increased understanding, and subsequent synthetic application, of the factors affecting the selectivity of free-radical reactions.[1,2] The reaction of

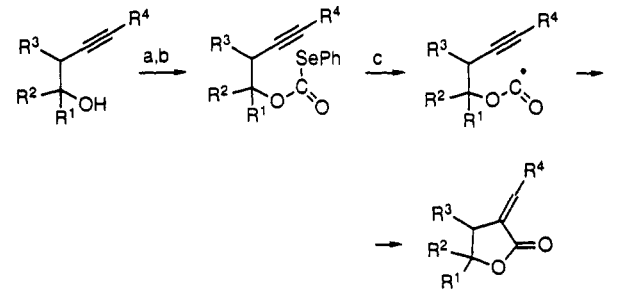
0022-3263/92/1957-4696$03.00/0

Scheme I[a]



[a] Key: (a) $Bu_3Sn^{\bullet}$; (b) Bu_3SnH; (c) $Bu_3SnSePh$.

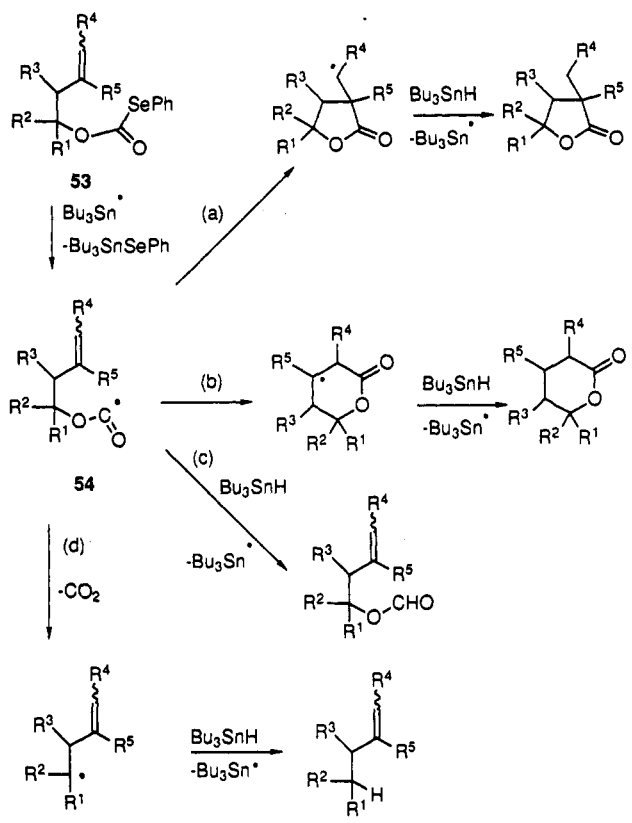
Scheme II[a]



[a] Key: (a) $COCl_2$; (b) PhSeH; (c) Bu_3SnH, AIBN.

selenocarbonates with tri-*n*-butyltin hydride illustrates how free-radical processes can be controlled and effectively used for synthetic purposes. Graf and co-workers studied the AIBN-catalyzed reaction of a series of selenocarbonates derived from steroidal alcohols with *n*-Bu_3SnH in boiling aromatic solvents.[3] Under these conditions the carbon–selenium bond of the selenocarbonates **1** is cleaved to give alkoxycarbonyl radicals **2** which can lead either to formates **3** through hydrogen atom abstraction or to alkanes **4** and alcohols **5** through degradation followed by hydrogen atom abstraction (Scheme I). High selectivity in favor of the formation of formates **3** relative to alkanes **4** and alcohols **5** was observed in reactions of some primary and secondary selenocarbonates **1** (R = $R'CH_2$ or R'_2CH) at 80 °C. Selectivity was reversed by increasing the reaction temperature to 144 °C. In a preliminary paper we have demonstrated that alkoxycarbonyl radicals **2** may be efficiently trapped if a carbon–carbon triple bond is introduced in the residue "R" in a position that allows a 5-*exo*-*dig* addition.[4] Thus, selenocarbonate derivatives of homopropargylic alcohols undergo a *n*-Bu_3SnH–AIBN-induced cyclization to α-alkylidene-γ-butyrolactones in excellent yields (Scheme II). The successful intramolecular addition of oxycarbonyl radicals to triple bonds, including nonactivated triple bonds, served as a test case indicating that 4-alkyl-γ-butyrolactones should also be accessible through addition to similarly positioned double bonds. Indeed, our

Scheme III



early paper was followed by other reports from this[5-7] and other[8-10] laboratories on the synthesis of lactones through the homolytic cyclization of various seleno esters. In the present paper we present a full account on the synthesis of γ- and δ-lactones through the free-radical cyclization of unsaturated selenocarbonates.[11]

Se-Phenyl selenocarbonates were prepared from the chloroformates of the corresponding alcohols and phenylselenol,[3] except for *Se*-phenyl selenocarbonates of tertiary alcohols which were derivatized as (alkoxycarbonyl)imidazolides before reaction with phenylselenol. Yields, which were not optimized, are given in Table I with additional data in the Experimental Section.

The results obtained in the reactions of *Se*-phenyl selenocarbonates derived from 21 different unsaturated alcohols with *n*-Bu_3SnH (stoichiometric amount) and AIBN (catalytic amount) in boiling benzene or toluene are summarized in Table I. The numbers in square brackets in the column "procedure" indicate the initial concentration of selenocarbonate in experiments in which all the reagents were mixed at the start, while the numbers in parentheses give the time of addition of individual solutions of *n*-Bu_3SnH and AIBN to a boiling solution of selenocarbonate in benzene (slow addition). Scheme III describes some of the theoretically possible reaction paths of intermediate alkoxycarbonyl radicals of type **54** generated by the reaction of *O*-alk-3-enyl phenyl selenocarbonates **53** and

(1) For reviews on synthetic free-radical chemistry see: (a) Hart, D. J. *Science* **1984**, *223*, 883. (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergammon Press: Oxford, 1986. (c) Curran, D. P. *Synthesis* **1988**, *417*, 489. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541.

(2) For reviews on selectivity in free-radical reactions see: (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925. (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (d) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553. (e) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969. (f) Minisci, F.; Citterio, A. *Adv. Free-Radical Chem.* **1980**, *6*, 65. (g) Rüchardt, C. *Top. Curr. Chem.* **1980**, *88*, 1. (h) Stork, G. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 149. (i) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401.

(3) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328.

(4) Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1986**, *27*, 641.

(5) Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1988**, *29*, 2581.

(6) Bachi, M. D.; Bosch, E. *Heterocycles* **1989**, *28*, 579.

(7) Bachi, M. D.; Bosch, E.; Denenmark, D.; Girsh, D. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer Academic Publishers: Boston, 1989; p 125.

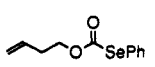
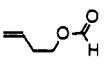
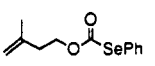
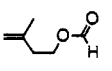
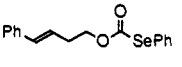
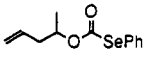
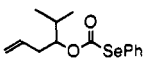
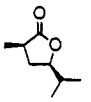
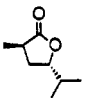
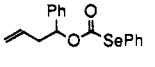
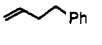
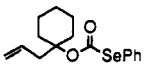
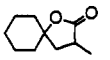
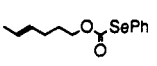
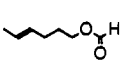
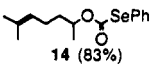
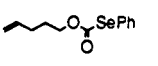
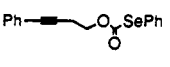
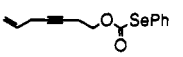
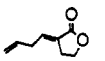
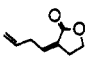
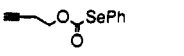
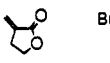
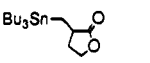
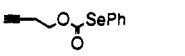
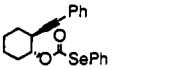
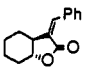
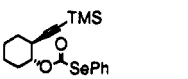
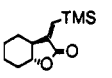
(8) Singh, A. K.; Bakshi, R. K.; Corey, E. J. *J. Am. Chem. Soc.* **1987**, *109*, 6187.

(9) Boger, D. L.; Mathvink, R. *J. Am. Chem. Soc.* **1990**, *112*, 4008.

(10) Astley, M. P.; Pattenden, G. *Synlett* **1991**, 335.

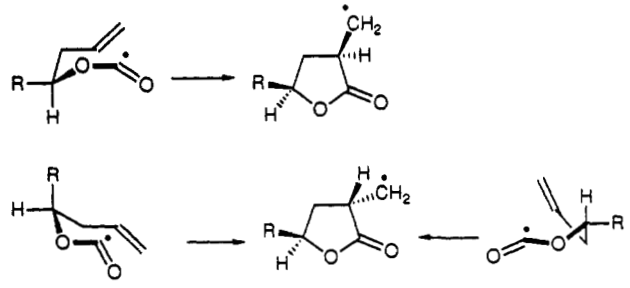
(11) This material is taken from the Ph.D. thesis of Eric Bosch, The Weizmann Institute of Science, Rehovot, 1989.

Table I. Reactions of *O*-Alkenyl and *O*-Alkynyl Seleno Carbonates with *n*-Bu_3SnH and AIBN. Synthesis of Lactones

	seleno carbonate (yield)[a]	procedure[b] $[c_0]/(t_{add})$	product (yield)[c]		isol.[d]
(1)	 **6** (79%)	[0.02M]	 **27** (92%)	 **49** (nil)	A
(2)	**6**	[neat]	**27** (55%)	**49** (45%)[e]	
(3)	 **7** (76%)	[0.02M]	 **28** (99%)	 **50** (nil)	A
(4)	**7**	[1.0M]	**28** (25%)	**50** (75%)[e]	
(5)	 **8** (79%)	[0.02M]	 **29** (80%)[f]		B
(6)	 **9** (83%)	[0.02M]	 **30a** (61%)[g]	 **30b** (31%)[g]	A
(7)	 **10** (81%)	[0.02M]	 **31a** (68%)[g]	 **31b** (22)[g]	A
(8)	 **11** (84%)	[0.02M]	 **52** (74%)		A
(9)	 **12** (71%)	[0.02M]	 **32** (95%)		B
(10)	 **13** (94%)	[0.02M]	 **33** (74%)	 **51** (18%)[e]	C&A
(11)	**13**	(2 h)	**33** (91%)	**51** (3%)[e]	C&A
(12)	 **14** (83%)	(2 h)	 **34** (86%)		C&A
(13)	 **15**(73%)	(2 h)	 **35** (55%)[h]		A
(14)	 **16** (83%)	(2 h)	 **36** (87%)		C&B
(15)	**16**	[0.02M]	**36** (95%)		C&B
(16)	 **17** (84%)	(2 h)	 **37a** (70%)	 **37b** (11%)[i]	B
(17)	 **18** (67%)	[0.02M][j]	 **38** (26%)	 **39** (3%)	A&B
(18)	 **18**	(2 h)	 **36** (19%)		B
(19)	 **19** (84%)	(2 h)	 **40a** (75%)	 **40b** (15%)	B
(20)	 **20** (66%)	(2 h)	 **41a** (78%)	**41b** (15%)[i]	B
(21)	**21** (89%)	(2 h)	**42a** (16%)[g]	**42b** (23%)[g]	B
			43 (53%)[g]		
(22)	**22** (91%)	(2 h)	**44a** (84%)	**44b** (8%)	B
(23)	**23** (53%)[h]	[0.02M][j]	**45** (55%)		B
(24)	**24** (79%)	(30 min)	**46a** (73%)	**46b** (17%)	B
(25)	**25** (89%)	(2 h)	**47** (79%)		B
(26)	**26** (60%)	(2 h)/[0.005M]	**48a** (36%)	**48b** (46%)	B

[a] Isolated, unoptimized yield, from corresponding alcohol. [b] $[c_0]$ represents initial concentration of Bu_3SnH when all reagents were mixed on starting the reaction, (t_{add}) represents time of addition of solutions of Bu_3SnH and AIBN. Unless otherwise stated reactions were performed in benzene at 80 °C. [c] Unless otherwise stated yields of isolated product (>95% pure) are given. [d] Isolation procedures: A, distillation; B, chromatography; C, fractionation between hexane and MeCN. [e] By comparison of NMR of crude product to NMR of an authentic sample. [f] 88% by GC and NMR analyses. [g] The isomers were not separated. Ratio estimated by GC–MS and NMR analyses. [h] ca. 90% pure, yield estimated by NMR of crude product. [i] ca. 85% pure, yield estimated by NMR of crude product. [j] Reaction performed in toluene during 8 h.

Scheme IV

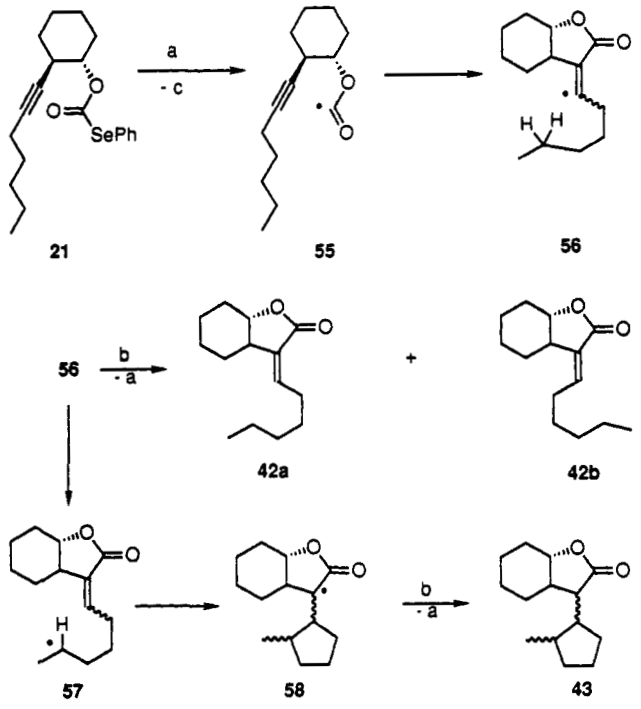


R = Me, i-Pr

Bu_3SnH/AIBN. Experimental results for these reactions are given in entries 1–9 of Table I. The parent compound **6** undergoes an exclusive exo addition (path a) on reaction at 0.02 M initial concentration (entry 1). The γ-butyrolactone **27** constitutes the major reaction product (path a), even when the reaction is performed at high initial *n*-Bu_3SnH concentration (entry 2), although in this case it is accompanied by the formyl ester **49** (path c). Endo ring closure (path b) and decarboxylation (path d) do not occur. This reaction pattern parallels that of the reactive vinyl radicals where cyclization predominates over direct hydrogen abstraction even in concentrated solutions[12,13] and contrasts with the cyclization of hexenyl radicals where low concentrations of Bu_3SnH are essential to ensure high yields of cyclization.[2a] The high preference for 5-exo cyclization of carbonyl radicals **54** is clearly manifested by the quantitative cyclization of the selenocarbonate **7** into the 3,3′-dimethyl lactone **28** (entry 3). This result indicates that carbonyl radical cyclizations, similar to vinyl and aryl radical cyclizations,[14] are significantly less subject to steric interference than alkyl radicals which are generally retarded by substitution at the site of addition to the double bond.[2a] Cyclization of selenocarbonate **9** led to a 2/1 mixture of cis and trans isomers of the 3,5-dimethyl lactone **30** (entry 6).[15] Such a cis selectivity is consistent with that predicted by both Beckwith's[2b] and Houk's[16] force field models for intramolecular alkenyl radical additions. On the basis of these models the cis isomers would arise from that pseudochair transition state where the R group adopts the equatorial position (Scheme IV). The minor isomer would either be formed from the corresponding chair where the R group adopts the axial position or from the boat transition state with R equatorial. As expected, the diastereoisomeric ratio is enhanced when the methyl group is replaced by the bulkier isopropyl group as in selenocarbonate **10** (entry 7). Excellent cyclization yields are also observed in the reactions of selenocarbonates derived from tertiary alcohols (entry 9). Decarboxylation of the intermediate alkoxycarbonyl radical (cf. Scheme III path d) was only observed with selenocarbonate **11** (entry 8). In this example, a highly stabilized secondary benzylic radical is formed by elimination of carbon dioxide.[17]

The high yields observed in the δ-lactonization of selenocarbonates **13** and **14** and the high lactone vs open-chain formyl ratio (e.g., **33**/**51**) indicate that the rate of 6-*exo-trig*

Scheme V[a]



[a] Key: (a) $Bu_3Sn^{\bullet}$; (b) Bu_3SnH; (c) $Bu_3SnSePh$.

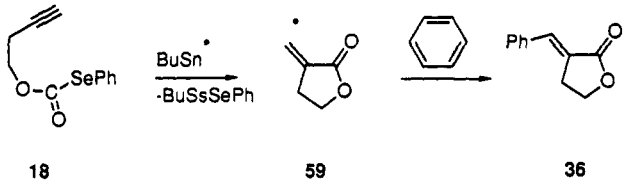
addition of the alkoxycarbonyl radical is sufficiently higher than the rate of intramolecular 1,5 hydrogen atom transfer as to make this process synthetically useful. However, in order to minimize intermolecular hydrogen transfer from the Bu_3SnH the reactions are better performed under high-dilution conditions (cf. entries 10 and 11).

The high preference for exo-cyclizations over other possible competitive reactions (e.g., as in Scheme III) of alkoxycarbonyl radicals is also manifested by their intramolecular addition to carbon–carbon triple bonds. Thus, the Bu_3SnH/AIBN-induced carbolactonization of selenocarbonates derived from homopropargylic alcohols proceeds in excellent yield and provides a useful method for the synthesis of monocyclic and bicyclic α-alkylidene γ-lactones (entries 14–24). The method is also suitable for selenocarbonates derived from tertiary alcohols having a high intrinsic risk for decarboxylation (entry 24). The ratio between *E*/*Z* stereoisomers about the exocyclic double bond is strongly affected by the nature of the substituents.[18] Due to the planar nature of the α-benzylidene γ-lactone molecule **36** and the possible nonbonded interaction of the phenyl group with the carbonyl oxygen atom in the *Z*-isomer, only the *E*-isomer was obtained (entries 14–15). The *E*-isomer predominates also for the benzylidene lactones **40**. The lower selectivity observed in this case is probably due to some oppositely directed nonbonded interaction with the methylene group of the fused cyclohexane ring. Due to its tetrahedral structure the TMS group experiences stronger repulsion from the adjacent cyclohexane methylene group when in the *E* configuration than from the oxygen carbonyl when in the *Z* configuration; consequently, the *E*/*Z* ratio in the fused bicyclic (trimethylsilyl)methylidene lactones **41** and **44** is inverted with respect to that observed for the benzylidene lactones **40**. As there is no steric interference between the TMS

(12) Beckwith, A. L. K.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525.
(13) Stork, G.; Mook, R. *Tetrahedron Lett.* **1986**, *27*, 4529.
(14) Stork, G.; Bain, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.
(15) For NMR data of cis and trans disubstituted lactones see: Hussain, S. A. M. T.; Ollis, W. D.; Smith, C. S., J. F. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1480.
(16) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959.
(17) For a similar decarboxylation see: Beak, P.; Moje, S. W. *J. Org. Chem.* **1974**, *39*, 1320.

(18) Stereochemistry was determined by NMR. A downfield shift of 0.6–1.0 ppm is observed for the olefinic proton of the *E*-isomer as compared with the corresponding proton in the *Z*-isomer of the α-alkylidene γ-lactones. See Experimental Section.

Scheme VI



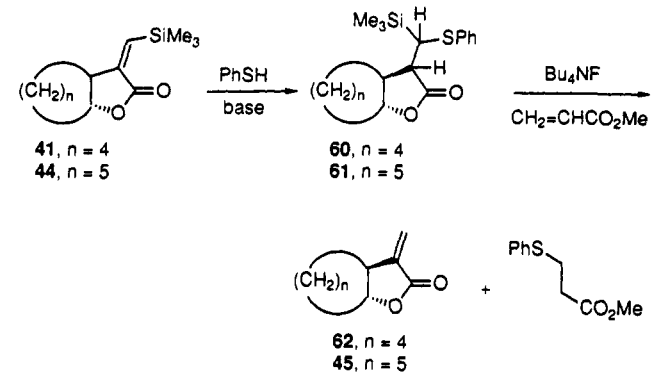
18 59 36

group and the cyclohexane methylene group in the spirolactone **46** the *E*-isomer is predominantly obtained.

High yields of α-alkylidene γ-lactones may also be obtained from starting materials carrying an alkyl substituent on the acetylene (Table I, entry 16). However, if the alkyl group is *n*-butyl or a longer alkyl group, competitive reactions may occur as shown for selenocarbonate **21** (Scheme V and entry 21 of Table I). In this reaction, in addition to the (*E*)- and (*Z*)-hexylidene lactones **42**, six diastereoisomers of the tricyclic lactone **43** were obtained.[19] Evidently, the alkoxycarbonyl radical **55** readily cyclizes; however, the radical **56** formed on cyclization is apparently partitioned between reduction by *n*-Bu_3SnH to give the alkylidene lactones **42** and 1,5-hydrogen atom abstraction to form the secondary radical **57**. This radical is then well positioned to cyclize onto the activated double bond to give, through radical **58**, the tricyclic lactones **43**.

While most of the reactions studied led to formation of α-alkylidene γ-lactones in excellent yields, the reactions involving the parent compound **18** and compound **23** afforded the corresponding α-methylene lactones **38** and **45** in poor to moderate yields when reacted with *n*-Bu_3SnH under the standard conditions. Compounds **18** and **23** carry an unsubstituted acetylenic function, their reaction intermediates are reactive terminal vinyl radicals, and their expected products contain an activated terminal double bond. All these species are highly susceptible to competitive secondary reactions. Indeed, in a reaction of selenocarbonate **18**, performed in toluene under standard conditions (Table I, entry 17), the α-methylene lactone **38** was accompanied by the adduct **39** of **38** and *n*-Bu_3SnH. In another reaction (Table I, entry 18) performed by the high-dilution technique only the benzylidene lactone **36** deriving from the reaction of the reactive vinyl radical **59** and benzene, the reaction solvent, was isolated (Scheme VI). It is noted that the more sterically congested α-methylene lactone **45** was obtained in higher, though still modest, yield (Table I, entry 23). The wide interest in α-methylene γ-lactones due to their presence in many biologically active compounds[20] led us to investigate their preparation from their TMS derivatives which are readily available by the method described above (cf. Table I, entries 20, 22, 24, and 26). As conventional methods for desilylation were found to be ineffective for the removal of a TMS group located on the β-position of an α,β-unsaturated carbonyl system we developed a new desilylation procedure.[5] Accordingly, phenylthio was added to the α-(trimethylsilyl)methylene lactones **41**, and the resulting adduct **60** was treated with tetrabutylammonium fluoride and methyl acrylate to give the α-methylene γ-lactone **62** (Scheme VII). The fused bicyclic α-methylene γ-lactone

Scheme VII

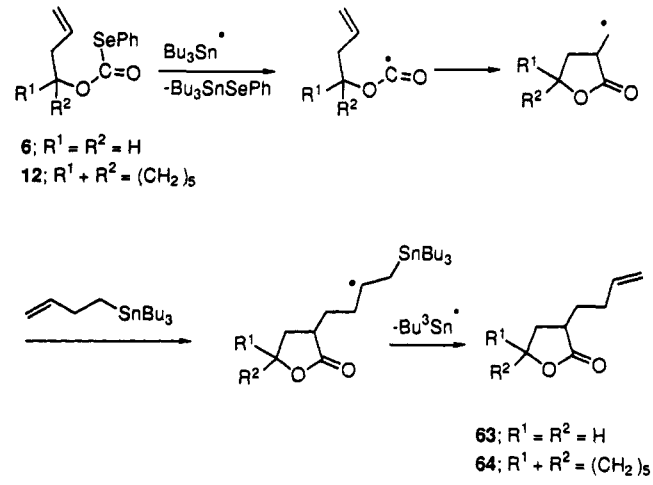


41, n = 4
44, n = 5

60, n = 4
61, n = 5

62, n = 4
45, n = 5

Scheme VIII



6; $R^1 = R^2 = H$
12; $R^1 + R^2 = (CH_2)_5$

63; $R^1 = R^2 = H$
64; $R^1 + R^2 = (CH_2)_5$

45 was similarly obtained from the α-(trimethylsilyl)-methylene lactones **44** in excellent yield.[21]

Although it was postulated that 6-(π-*exo*)-*exo*-*dig* cyclizations of carbonyl and vinyl radicals are not favored reactions,[22] we examined the feasibility of this type of cyclization. As models we used (alkynyloxy)carbonyl radicals generated by homolysis of the carbon–selenium bond in the selenocarbonates **25–26** (Table I, entries 25–26). We were gratified to find that 6-*exo*-*dig* cyclization of these (alkynyloxy)carbonyl radicals is feasible. Indeed, the yield of δ-lactone formation is high for ring closure onto aryl- or silyl-substituted triple bonds.

Free radicals generated on the exocyclic carbon during the lactonization may be efficiently trapped by allyltri-*n*-butylstannane,[23,24] thus forming α-homoallyl lactones. For example, reaction of the selenocarbonate **6** with allyltri-*n*-butyltin (2 equiv) and AIBN (0.2 equiv) afforded the α-homoallyl γ-lactone **63** (76%) (Scheme VIII), along with α-methyl butyrolactone **27** (7%). Similarly, the selenocarbonate **12** was converted into the spirolactone **64** (73%).

In summary, we have developed an efficient method for the synthesis of γ- and δ-lactones through the intramolecular addition of alkoxycarbonyl radicals, formed by reaction of *Se*-phenyl selenocarbonates with *n*-Bu_3SnH, onto carbon–carbon multiple bonds. These free-radical reactions are characterized by high regioselectivity favoring

(19) Product separation is extremely difficult. The composition of the reaction mixture was determined by a combination of repeated flash chromatographies, elemental analyses, and NMR and GC–MS spectroscopy, as described in the Experimental Section. Formate formation through hydrogen transfer to the incipient radical **60** was excluded due to the absence of the characteristic resonance of the formate hydrogen at δ 8.05–8.10.

(20) Hoffmann, H. M. R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94.

(21) For a discussion on desilylation of a TMS group located on the β-position of an α,β-unsaturated carbonyl system, see ref 5.

(22) Crich, D; Fortt, S. M. *Tetrahedron Lett.* **1987**, *28*, 2895.

(23) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Michael, R. W.; Wiley, R. *Tetrahedron* **1985**, *41*, 4079.

(24) Moriya, O.; Kakihana, M.; Urata, Y.; Sugizaki, T.; Kageyama, T.; Uneo, Y.; Endo, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1401.

exo addition and by a high ratio of cyclization to reduction. Monocyclic, fused bicyclic, and spirocyclic lactones are formed in good to excellent yield. Use of allyltri-*n*-butyltin as chain transfer agent in the place of *n*-Bu_3SnH affords the corresponding 3-butenyl lactones.

Experimental Section

General Procedures. Unless otherwise stated all solvents were dried by conventional methods and the reactions were performed in flame- or oven-dried glassware under an atmosphere of argon. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F-254). "Standard workup" refers to partition of the reaction mixture (1 mmol) between EtOAc (70 mL) and water (30 mL), washing the organic layer with cold dilute HCl (30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), brine (30 mL), and water (30 mL), drying over $MgSO_4$, and evaporation of the solvent. Flash chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh). Preparative TLC was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F-254). Products were distilled with a Büchi kugelrohr apparatus, and the temperatures refer to the oven temperature. Proton NMR spectra were measured in $CDCl_3$ on a Bruker WH-270 spectrometer or a Varian FT-80A spectrometer. All chemical shifts are reported in ppm units downfield from Me_4Si. IR were measured on a Nicolet MX-100 or a Mattson Fourier transform spectrometer. High-resolution mass spectra were determined on a Varian MAT731 spectrometer. Low-resolution mass spectra were performed on a Finnigan 4500 GC–MS spectrometer and are reported in mass units with the relative intensities in parentheses. Elemental analyses were performed by the microanalytical laboratory of the Hebrew University, Jerusalem. Alkenyl and alkynyl alcohols which were not commercially available were prepared by conventional methods. Unless otherwise stated the purity of all title compounds was judged to be >95% by ^1H NMR spectral determination.

General Procedure for the Preparation of *Se*-Phenyl Selenocarbonates Derived from Either Primary or Secondary Alcohols. Chloroformates of primary alcohols were prepared by adding the alcohol to a cold (5 °C) 10 wt % solution of phosgene (1.3 equiv) in benzene. The solution was warmed to room temperature and stirred overnight. The excess phosgene was removed by bubbling a stream of dry argon through the reaction mixture, and the solvent was then evaporated to give the crude chloroformate. The chloroformate could be distilled under vacuo. For the preparation of chloroformates of secondary alcohols, triethylamine (1.2 equiv) was added dropwise to the reaction mixture described above. The excess phosgene was removed as before, and the solution was diluted with dry ether and filtered over Celite. Evaporation of the solvent gave the crude chloroformate. A solution of phenylselenol,[25] 8 mmol in benzene (25 mL), and pyridine (0.6 mL) was added to a solution of the chloroformate, derived from a primary or a secondary alcohol (6 mmol, 1 M) in benzene. After 1 h the mixture was diluted with dry ether and filtered over Celite. The solvent was evaporated, and flash chromatography of the residue yielded the *Se*-phenylselenocarbonate. Under these conditions the excess phenylselenol was recovered as diphenyl diselenide. Yields of products are given in Table I; their characterization is based on the analytical data given below.

General Procedure for the Preparation of *Se*-Phenyl Selenocarbonates Derived from Tertiary Alcohols. Sodium hydride (0.16 mmol) was added to a stirred solution of the alcohol (1.22 mmol) in THF (7 mL). After gas evolution had ceased carbonyl diimidazole (1.36 mmol) was added. The mixture was stirred for 24 h, and then a solution of phenylselenol (2.5 mmol) in benzene was added. Stirring at room temperature was continued for an additional 3 h. The solvent was evaporated, and flash chromatography of the residue (hexane/EtOAc (35:1)) followed by distillation at 80 °C (0.03 mmHg) yielded the selenocarbonate. Yields of products are given in Table I; their characterization is based on the analytical data given below.

(25) Smith, A. B.; Scarbrough, R. M. *Tetrahedron Lett.* 1978, 1649.

***O*-But-3-en-1-yl *Se*-phenyl selenocarbonate (6)**: distilled at 76 °C (0.2 mmHg); IR (film) 3078, 3062, 2983, 2960, 1729 vs (C=O), 1644, 1581, 1479, 1441, 1119–1114 vs, 1075, 741, and 690 cm^{-1}; ^1H NMR δ 2.43 (q, J = 6.7 Hz, 2 H, CCH_2C), 4.30 (t, J = 6.7 Hz, 2 H, CH_2O), 5.08–5.15 (m, 2 H, C=CH_2), 5.68–5.83 (m, 1 H, C*H*=CH_2), 7.28–7.42 (m, 3 H), 7.60–7.67 (m, 2 H); exact mass calcd for $C_{11}H_{12}O_2Se$ m/e 256.0002, found m/e 256.0068.

***O*-(3-Methylbut-3-en-1-yl) *Se*-phenyl selenocarbonate (7)**: IR (film) 3062, 2973, 1729 s (C=O), 1652, 1440, 1114, 1074, and 740 cm^{-1}; ^1H NMR δ 1.74 (s, 3 H, CH_3), 2.38 (t, J = 6.8 Hz, 2 H, CCH_2C), 4.36 (t, J = 6.8 Hz, 2 H, CH_2O), 4.73 (d, J = 0.7 Hz, 1 H, C=C*H*H), 4.82 (d, J = 1.3 Hz, 1 H, C=CH*H*), 7.24–7.25 (m, 1 H), 7.35–7.37 (m, 2 H), 7.59–7.63 (m, 2 H); mass spectrum m/e 270 (M^+, 0.2), 157 (3), 77 (12), 69 (100). Anal. Calcd for $C_{12}H_{14}O_2Se$: C, 53.54; H, 5.24. Found: C, 53.24; H, 5.02.

***O*-((*E*)-4-Phenylbut-3-en-1-yl) *Se*-phenyl selenocarbonate (8)**: IR (film) 3064, 3027, 2956, 2898, 1728 vs, br (C=O), 1578, 1495, 1479, 1440, 1130 vs, 1074, 1001, 966, 740, and 691 cm^{-1}; ^1H NMR δ 2.58 (br q, J = 6.8 Hz, 2 H, CCH_2C), 4.36 (t, J = 6.7 Hz, 2 H, CH_2O), 6.11 (dt, J = 15.9, 7.0 Hz, 1 H, C=C*H*CH_2), 6.46 (d, J = 15.9 Hz, 1 H, PhCH), 7.20–7.41 (m, 8 H), 7.58–7.61 (m, 2 H); mass spectrum m/e 157 (PhSe, 6), 131 (77), 130 (47), 115 (21), 91 (100), 77 (31), 51 (28). Anal. Calcd for $C_{17}H_{16}O_2Se$: C, 61;71; H, 4.86. Found: C, 61.64; H, 4.87.

***O*-Pent-4-en-2-yl *Se*-phenyl selenocarbonate (9)**: IR (film) 3079, 2972, 1747 vs, 1653, 1457, 1378, 1288–1231 vs, 1142, 1029, and 895 cm^{-1}; ^1H NMR δ 1.30 (d, J = 6.3 Hz, 3 H, CH_3), 2.28–2.42 (m, 2 H, CCH_2C), 5.04–5.15 (m, 3 H, C=CH_2 and HCO), 5.66–5.81 (m, 1 H, CH_2=C*H*), 7.32–7.42 (m, 3 H), 7.60–7.66 (m, 2 H).

***O*-(5-Methylhex-1-en-4-yl) *Se*-phenyl selenocarbonate (10)**: IR (film) 3078, 2967, 1729 s (C=O), 1142, 1118, 740 cm^{-1}; ^1H NMR δ 0.91 (apparent t, J = 6 Hz, 6 H, 2×CH_3), 1.81–1.93 (m, 1 H, CH_3CH), 2.34 (br t, J = 7 Hz, 2 H, CH_2CO), 4.86–4.93 (m, 1 H, CHO), 5.09 (br d, J = 9 Hz, 1 H, *trans*-CH=CH'H), 5.10 (br d, J = 17 Hz, 1 H, *cis*-CH=CH'*H*), 5.67–5.82 (m, 1 H, C*H*=CH_2), 7.28–7.39 (m, 3 H), 7.61–7.64 (m, 2 H). Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.88; H, 6.29.

***O*-(1-Phenylbut-3-en-1-yl) *Se*-phenyl selenocarbonate (11)**: IR (film) 3065, 3036, 2917, 1729 s (C=O), 1117 vs, 1074, 741, 699, and 691 cm^{-1}; ^1H NMR δ 2.52–2.76 (m, 2 H, CCH_2C), 5.08 (d, J = 11.2 Hz, 1 H, *trans*-C=CHH), 5.09 (d, J = 16.1 Hz, 1 H, *cis*-C=CHH), 5.60–5.75 (m, 1 H, CH=CH_2), 5.88 (m, 1 H, CHO), 7.27–7.41 (m, 8 H), 7.58–7.61 (m, 2 H). Anal. Calcd for $C_{17}H_{16}O_2Se$: C, 61.64; H, 4.87. Found: C, 61.39; H, 5.02.

***O*-(1-Allylcyclohex-1-yl) *Se*-phenyl selenocarbonate (12)**: IR (film) 2938, 2863, 1728 s (C=O), 1711 sh, 1449, 1163, 1112 vs, 1075, 922, 831, 740, and 690 cm^{-1}; ^1H NMR δ 1.19–1.63 (m, 8 H), 2.19 (br d, apparent J = 12 Hz, 2 H), 2.65 (d, J = 7.3 Hz, 2 H, CH_2CH=C), 5.07–5.14 (m, 2 H, C=CH_2), 5.79 (ddd, J = 18, 12, 7 Hz, C*H*=CH_2), 7.33–7.37 (m, 3 H), 7.60–7.64 (m, 2 H); exact mass calcd for C_9H_{15} (M – OC(O)SePh) m/e 123.1174, found m/e 123.1215. Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.42; H, 6.24. Found: C, 59.38; H, 6.45.

***O*-((*E*)-Hex-4-en-1-yl) *Se*-phenyl selenocarbonate (13)**: distilled at 100 °C (0.2 mmHg); IR (film) 2960, 2938, 2919, 1728 vs (C=O), 1581, 1479, 1441, 1135–1108 vs, 1075, 1023, 968, 740, and 690 cm^{-1}; ^1H NMR δ 1.64 (br d, J = 5.5 Hz, 3 H, CH_3), 1.67–1.77 (m, 2 H), 1.99–2.07 (m, 2 H), 4.25 (t, J = 6.6 Hz, 2 H, CH_2O), 5.34–5.49 (m, 2 H), 7.28–7.43 (m, 3 H), 7.61–7.64 (m, 2 H). Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.11; H, 5.70. Found: C, 55.42; H, 5.88.

***O*-(6-Methylhept-5-en-2-yl) *Se*-phenyl selenocarbonate (14)**: IR (film) 3076, 2977, 2931, 1728 s (C=O), 1440, 1380, 1119 s, 1061, 740 cm^{-1}; ^1H NMR δ 1.30 (d, J = 6.3 Hz, 3 H, $CHCH_3$), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.49–1.73 (m, 2 H), 1.98–2.06 (m, 2 H), 5.00–5.09 (m, 1 H, C=CH), 7.33–7.40 (m, 3 H), 7.61–7.64 (m, 2 H). Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 56.19; H, 6.74. Found: C, 56.62; H, 6.33.

***O*-Pent-4-en-1-yl *Se*-phenyl selenocarbonate (15)**: IR (film) 2974, 1728 s (C=O), 1121 s, 1070, 1022 cm^{-1}; ^1H NMR δ 1.71–1.82 (m, 2 H, $CH_2CH_2CH_2$), 2.07–2.15 (m, 2 H, C=CCH_2), 4.27 (t, J = 6.5 Hz, 2 H, CH_2O), 4.98–5.07 (m, 2 H, C=CH_2), 5.70–5.85 (m, 1 H, C*H*=CH_2), 7.32–7.43 (m, 3 H), 7.61–7.67 (m, 2 H). Anal. Calcd for $C_{12}H_{14}O_2Se$: C, 53.54; H, 5.24. Found: C, 53.86; H, 5.35.

***O*-(4-Phenylbut-3-yn-1-yl) *Se*-phenyl selenocarbonate (16)**: distilled at 105 °C (0.4 mmHg); IR (film) 3062, 2960, 2240 w, 1727

s (C=O), 1597, 1490, 1440, 1120 s br, 757, 740, 690 cm^{-1}; ^1H NMR δ 2.80 (t, J = 6.9 Hz, 2 H, CH_2CH_2O), 4.43 (t, J = 6.9 Hz, 2 H, CH_2O), 7.27–7.42 (m, 8 H), 7.61–7.64 (m, 2 H); mass spectrum m/e 330 (M^+, ^{80}Se, 0.4), 328 (M^+, ^{78}Se, 0.28), 129 (91), 128 (M – PhSeC(=O)OH, 100), 127 (31), 77 (30); exact mass calcd for $C_{17}H_{14}O_2Se$ m/e 330.0159, found m/e 330.0200. Anal. Calcd for $C_{17}H_{14}O_2Se$: C, 62.01; H, 4.29. Found: C, 61.86; H, 4.30.

***O*-Hept-6-en-3-yn-1-yl *Se*-phenyl selenocarbonate (17)**: distilled at 95 °C (0.06 mmHg); IR (film) 2962, 2927, 1728 vs (C=O), 1642, 1114, 740, 690 cm^{-1}; ^1H NMR δ 2.58 (tt, J = 7.0, 2.3 Hz, 2 H, CCH_2CH_2O), 2.93–2.95 (m, 2 H, CH_2CH_2OC), 4.33 (t, J = 7.0 Hz, 2 H, CH_2O), 5.11 (dd, J = 9.9, 1.6 Hz, 1 H, *trans*-CH=CH*H*), 5.32 (dd, J = 16.9, 1.6 Hz, 1 H, *cis*-CH=CH*H*), 5.81 (m, 1 H, CH=CH_2), 7.32–7.40 (m, 3 H), 7.61–7.64 (m, 2 H). Anal. Calcd for $C_{14}H_{14}O_2Se$: C, 57.35; H, 4.81. Found: C, 57.10; H, 4.84.

***O*-But-3-yn-1-yl *Se*-phenyl selenocarbonate (18)**: IR (film) 3296, 3060, 2880, 2065 w, 1727 s (C=O), 1578, 1132–1117 br s, 740 cm^{-1}; ^1H NMR (80 MHz) δ 2.01 (t, J = 2.7 Hz, 1 H, HCC), 2.58 (td, J = 6.9, 2.7 Hz, 2 H, CH_2CH_2O), 4.34 (t, J = 6.9 Hz, 2 H, CH_2O), 7.32–7.43 (m, 3 H), 7.54–7.69 (m, 2 H); mass spectrum m/e 254 (M^+, ^{80}Se, 1.6), 129 (10), 78 (13), 77 (20); exact mass calcd for $C_{11}H_{10}O_2Se$ m/e 253.9846, found m/e 253.9832. Anal. Calcd for $C_{11}H_{10}O_2Se$: C, 52.19; H, 3.98. Found: C, 52.15; H, 4.08.

***O*-[*trans*-2-(Phenylethynyl)-1-cyclohex-1-yl] *Se*-phenyl selenocarbonate (19)**: distilled at 110 °C (0.5 mmHg); IR (film) 3058, 2939, 2862, 2236 w, 1728 s (C=O), 1598, 1580, 1129–1106 br s cm^{-1}; ^1H NMR δ 1.28–1.54 (m, 4 H), 1.57–1.75 (m, 2 H), 1.98–2.12 (m, 2 H), 2.75 (ddd, J = 9.3, 8.5, 3.8 Hz, 1 H, C*H*CCPh), 5.04 (ddd, J = 8.5, 8.4, 3.5 Hz, 1 H, CHO), 7.25–7.43 (m, 8 H), 7.58–7.62 (m, 2 H); exact mass calcd for $C_{14}H_{15}$ (M – OC(=O)SePh) m/e 183.1174, found m/e 183.1135. Anal. Calcd for $C_{21}H_{20}O_2Se$: C, 65.80; H, 5.26. Found: C, 65.50; H, 5.25.

***O*-[*trans*-2-[(Trimethylsilyl)ethynyl]cyclohex-1-yl] *Se*-phenyl selenocarbonate (20)**: distilled at 77 °C (0.05 mmHg); IR (film) 3061, 2941 s, 2863, 2178 s (C≡C), 1728 s (C=O), 1580, 1250, 1139 vs, 1107 vs, 845 s ($Si(CH_3)_3$) cm^{-1}; ^1H NMR δ 0.16 (s, 9 H, $Si(CH_3)_3$), 1.23–1.52 (m, 6 H), 1.59–1.67 (m, 2 H), 1.89–1.96 (m, 1 H), 2.00–2.07 (m, 1 H), 2.56 (td, J = 8.7, 4.1 Hz, 1 H, CCCH), 4.95 (td, J = 8.4, 3.8 Hz, 1 H, CHO), 7.32–7.38 (m, 3 H), 7.64–7.66 (m, 2 H); exact mass calcd for $C_{11}H_{19}Si$ (M – OC(=O)SePh) m/e 179.1255, found m/e 179.1236. Anal. Calcd for $C_{18}H_{24}O_2SeSi$: C, 56.96; H, 6.38. Found: C, 57.25; H, 6.49.

***O*-(*trans*-2-Hept-1-ynylcyclohexyl) *Se*-phenyl selenocarbonate (21)**: distilled at 77 °C (0.3 mmHg); IR (film) 2936, 2861, 1730 s (C=O), 1580, 1439, 1132–1113 br s cm^{-1}; ^1H NMR δ 0.89 (t, J = 6.9 Hz, 3 H, CH_3), 1.22–1.56 (m, 10 H), 1.62–1.66 (m, 2 H), 1.84–1.91 (m, 1 H), 1.99–2.06 (m, 1 H), 2.14 (td, J = 6.9, 1.9 Hz, 2 H, CH_2CH_2CC), 2.51 (m, 1 H, CCC*H*CHO), 4.90 (td, J = 8.2, 3.7 Hz, 1 H, CHO), 7.32–7.38 (m, 3 H), 7.61–7.65 (m, 2 H); exact mass calcd for $C_{20}H_{26}O_2Se$ m/e 378.1098, found m/e 378.1166. Anal. Calcd for $C_{20}H_{26}O_2Se$: C, 63.65; H, 6.94. Found: C, 64.02; H, 6.97.

***O*-[*trans*-2-[(Trimethylsilyl)ethynyl]cycloheptyl-1-yl] *Se*-phenyl selenocarbonate (22)**: distilled at 105 °C (0.4 mmHg); IR (film) 2933 s, 2863, 2173 s (C≡C), 1729 s (C=O), 1580, 1249, 1123 vs, 843 vs ($Si(CH_3)_3$) cm^{-1}; ^1H NMR δ 0.15 (s, 9 H, $Si(CH_3)_3$), 1.45–1.70 (m, 7 H), 1.74–1.86 (m, 2 H), 1.90–2.00 (m, 1 H), 2.82 (ddd, J = 7.7, 7.1, 3.0 Hz, 1 H, CCCH), 5.13 (ddd, J = 7.1, 7.1, 3.5 Hz, 1 H, CHO), 7.30–7.41 (m, 3 H), 7.61–7.65 (m, 2 H). Anal. Calcd for $C_{19}H_{26}O_2SeSi$: C, 58.00; H, 6.66. Found: C, 58.35; H, 6.70.

***O*-(*trans*-2-Ethynylcyclohept-1-yl) *Se*-phenyl selenocarbonate (23)**: distilled at 60 °C (0.05 mmHg) (ca. 90% pure); IR (film) 3299, 2934, 2863, 1727 s (C=O), 1123 cm^{-1}; ^1H NMR δ 1.46–2.01 (m, 10 H, CH_2), 2.14 (d, J = 2.5 Hz, 1 H, CCH), 2.80–2.86 (m, 1 H, CCCH), 5.15 (td, J = 7.1, 3.4 Hz, 1 H, CHO), 7.30–7.45 (m, 3 H), 7.61–7.68 (m, 2 H); exact mass calcd for $C_{16}H_{18}O_2Se$ m/e 322.0472, found m/e 322.0505.

***O*-[*trans*-1-[3-(Trimethylsilyl)prop-2-yn-1-yl]cyclohex-1-yl] *Se*-phenyl selenocarbonate (24)**: pale yellow oil; IR ($CHCl_3$) 2942, 2866, 2178, 1722 s (C=O), 1157 s, 1122 s, 846 s (C=O) cm^{-1}; ^1H NMR δ 0.20 (s, 9 H, $Si(CH_3)_3$), 1.25–1.28 (m, 1 H), 1.45–1.64 (m, 7 H), 2.23–2.26 (m, 2 H), 2.88 (s, 2 H, $CH_2CCSiMe_3$), 7.31–7.39 (m, 3 H), 7.63–7.67 (m, 2 H); exact mass calcd for $C_{12}H_{21}Si$ (M – OC(=O)SePh) m/e 193.1411, found m/e 193.1340. Anal. Calcd for $C_{19}H_{26}O_2SeSi$: C, 58.00; H, 6.66. Found: C, 58.18; H, 6.60.

***O*-(5-Phenylpent-4-yn-1-yl) *Se*-phenyl selenocarbonate (25)**: distilled at 79 °C (0.01 mmHg); IR (film) 3059, 2958, 1726 vs (C=O), 1490, 1479, 1440, 1123 cm^{-1}; ^1H NMR δ 1.93–2.02 (m, 2 H, CH_2H_2O), 2.50 (t, J = 6.9 Hz, 2 H, CH_2CC), 4.43 (t, J = 6.2 Hz, 2 H, CH_2O), 7.26–7.39 (m, 8 H), 7.61–7.65 (m, 2 H). Anal. Calcd for $C_{18}H_{16}O_2Se$: C, 62.98; H, 4.70. Found: C, 62.67; H, 4.85.

***O*-[*trans*-2-[3-(Trimethylsilyl)-2-propyn-1-yl]cyclohex-1-yl] *Se*-phenyl selenocarbonate (26)**: IR (film) 3062, 2939, 2861, 2177 (C≡C), 1731 (C=O), 1731 (C=O), 1250, 1137, 1114, 845 ($SiMe_3$) cm^{-1}; ^1H NMR δ 0.15 (s, 9 H, $SiMe_3$), 1.35–1.44 (m, 4 H), 1.62–1.76 (m, 3 H), 1.98–2.18 (m, 3 H), 2.43 (dd, J = 3.5, 16.8 Hz, 1 H, C*H*HCC), 4.62–4.72 (m, 1 H, CHO), 7.31–7.42 (m, 3 H), 7.60–7.65 (m, 2 H). Anal. Calcd for $C_{19}H_{26}O_2SeSi$: C, 58.01; H, 6.67. Found: C, 57.75; H, 6.63.

General Procedures for the Cyclization of Unsaturated Phenyl Selenocarbonates. Two general procedures were used for the cyclization of selenocarbonates. I. A solution of the phenyl selenocarbonate (1 mmol), *n*-Bu_3SnH (1.1–1.2 equiv), and AIBN (0.15 equiv) in benzene was boiled until TLC indicated complete consumption of the phenyl selenocarbonate. The initial concentration of *n*-Bu_3SnH is given in square brackets in the column "procedure" in Table I. II. Individual solutions of *n*-Bu_3SnH (1.2 equiv) and AIBN (0.15 equiv) in 10 mL of benzene were slowly added to a boiling 0.02 M solution of the phenyl selenocarbonate in benzene. The addition time is given in parentheses in the column "procedure" in Table I. The mixture was then refluxed until TLC indicated complete consumption of the phenyl selenocarbonate.

Several procedures were used for isolation of the products. Procedure A. With low molecular weight products the solvent was distilled from the reaction mixture at atmospheric pressure. Two consecutive bulb to bulb distillations afforded pure lactonic products. Procedure B. With relatively high molecular weight products the solvent was evaporated under vacuum, and the products were isolated by flash chromatography. Under these conditions a large part of the selenium was recovered as diphenyl diselenide. Procedure C. After evaporation of the solvent under vacuum the residue was dissolved in acetonitrile (80 mL) and washed with hexane (6 × 20 mL). The residue obtained after evaporation of the acetonitrile was further purified by either procedure A or procedure B (column "isol." in Table I). Yields of products are given in Table I; their characterization is based on the analytical data given below.

3-Methylbutyrolactone (27):[26] IR (film) 2978, 1767 vs (C=O), 1382, 1223, 1178 s, 1137, and 1024 cm^{-1}; ^1H NMR δ 1.29 (d, J = 7.0 Hz, 3 H, CH_3), 1.85–2.00 (m, 1 H, 4-CH), 2.39–2.50 (m, 1 H, 4-CH′), 2.54–2.66 (ddq, J = 10.2, 8.7, 7.0 Hz, 1 H, 3-CH), 4.14–4.24 (m, 1 H, 5-CH), 4.31–4.38 (m, 1 H, 5-CH′); exact mass calcd for $C_5H_8O_2$ m/e 100.0524, found m/e 100.0561.

3,3′-Dimethylbutyrolactone (28):[27] IR (film) 2968, 2931, 1769 vs (C=O), 1204, 1107, and 1029 cm^{-1}; ^1H NMR δ 1.28 (s, 6 H, $(CH_3)_2$), 2.12 (t, J = 6.9 Hz, 2 H, CCH_2C), 4.27 (t, J = 6.9 Hz, 2 H, CH_2O); exact mass calcd for $C_6H_{10}O_2$ m/e 114.0680, found m/e 114.0677.

3-Benzyl-4,5-furan-2(3*H*)-one (29): colorless oil; IR (film) 3027, 2915, 1770 vs, 1603, 1454, 1375, 1205, 1185 and 1150 s, 1023 s, and 702 cm^{-1}; ^1H NMR δ 1.92–2.07 (m, 1 H, 4-CH), 2.19–2.31 (m, 1 H, 4′-CH), 2.75 (dd, J = 13.2, 9.4 Hz, 1 H, PhC*H*H′), 2.81–2.91 (m, 1 H, 3-CH), 3.25 (dd, 1 H, J = 13.2, 3.5 Hz, PhC*H*H′), 4.10–4.27 (m, 2 H, CH_2O), 7.19–7.37 (m, 5 H, ArH); mass spectrum m/e 176 (M^+, 11), 148 (20), 147 (20), 104 (22), 91 (100), 65 (33), 51 (25); exact mass calcd for $C_{11}H_{12}O_2$ m/e 176.0837, found m/e 176.0899. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.28; H, 7.04.

3,5-Dimethylbutyrolactone (30). 30a,b:[15] IR (film, mixture) 2978, 2937, 2879, 1773 vs (C=O), 1458, 1389, 1351, 1184, 1124, 1045, and 953 cm^{-1}. **30a**: ^1H NMR δ 1.27 (d, J = 7.0 Hz, 3 H, CH_3CC=O), 1.42 (d, J = 6.1 Hz, 3 H, CH_3CHO), 1.42–1.55 (m, 1 H), 2.52 (ddd, J = 11, 8, 5 Hz, 1 H), 2.64–2.78 (m, 1 H), 4.44–4.52 (m, 1 H, HCO); mass spectrum m/e 114 (M^+, 0.5), 99 (6), 71 (6), 70 (54), 55 (100). **30b**: ^1H NMR (partial) δ 1.28 (d, J = 7.3 Hz,

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3 H, $CH_3CHC{=}O$), 1.38 (d, J = 6.3 Hz, 3 H, CH_3CHO), 2.03–2.09 (m, 1 H), 2.61–2.78 (m, 1 H), 4.64–4.71 (m, 1 H, HCO); mass spectrum m/e 114 (M^+, 0.5), 99 (8), 71 (5), 70 (59), 55 (100). **30a,b**: exact mass calcd for $C_6H_{10}O_2$ (mixture) m/e 114.0680, found m/e 114.0634.

3-Methyl-5-isopropylbutyrolactone (31). 31a,b: IR (film, mixture) 2969, 1770 s (C=O), 1193, 1171, 1021, 995 cm^{-1}. **31a**: ^1H NMR δ 0.92 (d, J = 6.8 Hz, 3 H, $CH(CH_3)CH_3$), 1.04 (d, J = 6.6 Hz, 3 H, $CH(CH_3)CH_3$), 1.27 (d, J = 7.0 Hz, 3 H, CH_3CH), 1.60–1.98 (m, 2 H), 2.38–2.48 (m, 1 H), 2.60–2.73 (m, 1 H), 3.99–4.08 (m, 1 H, CHO). **31b**: ^1H NMR (partial) δ 0.93 (d, J = 6.7 Hz, 3 H, $CH(CH_3)CH_3$), 1.01 (d, J = 6.8 Hz, $CH(CH_3)CH_3$), 1.29 (d, J = 7.3 Hz, 3 H, CH_3CH), 2.13–2.18 (m, 1 H), 4.18–4.28 (m, 1 H, CHO). **31a,b**: exact mass calcd for $C_8H_{14}O_2$ m/e 142.0993, found m/e 142.0464.

3-Methylspirocyclohexyl-1,5-butyrolactone (32).[28] The lactone was recrystallized from hexane/benzene as colorless prisms: mp 70 °C (benzene/hexane); IR (CH_2Cl_2) 2942, 2865, 1761 s (C=O), 1452, 1208, and 966 cm^{-1}; ^1H NMR δ 1.27 (d, J = 7.15 Hz, 3 H, CH_3), 1.50–1.77 (m, 11 H), 2.34 (dd, J = 12.7, 9.2 Hz, 1 H, *cis*-C*H*HCHCH$_3$), 2.78 (ddq, J = 10.8, 9.2, 7.2 Hz, 1 H, C*H*CH$_3$); mass spectrum m/e 168 (M^+, 3), 125 (51), 82 (24), 67 (27), 55 (100). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.46; H, 9.26.

3-Ethylvalerolactone (33):[29,30] IR (film) 2963, 2939, 1737 vs (C=O), 1159, 1087, 1051 cm^{-1}; ^1H NMR δ 0.99 (t, J = 7.4 Hz, 3 H, CH_3), 1.51–1.64 (m, 2 H), 1.84–1.97 (m, 3 H), 2.01–2.14 (m, 1 H), 2.37–2.44 (m, 1 H), 4.28–4.32 (m, 2 H, CH_2O); mass spectrum m/e 128 (M^+, 0.5), 100 (61), 70 (17), 69 (15), 56 (53), 55 (100); exact mass calcd for $C_7H_{12}O_2$ m/e 128.0836, found 128.0778.

3-Isopropyl-6-methylvalerolactone (34): IR (film, mixture) 2962, 2877, 1728 s (C=O), 1459, 1388 and 1371 ($CH(CH_3)_2$), 1188, 1090 cm^{-1}; ^1H NMR δ (major isomer) 0.92 (d, J = 6.9 Hz, 3 H), 0.97 (d, J = 7.1 Hz, 3 H), 1.36 (d, J = 6.3 Hz, 3 H, OCHC*H*$_3$), 1.49–1.73 (m, 2 H), 1.80–2.04 (m, 2 H), 2.22–2.58 (m, 2 H), 4.30–4.40 (m, 1 H, CHO); (minor isomer-partial spectrum) 1.01 (d, J = 6.7 Hz, 3 H), 1.37 (d, J = 6.2 Hz, 3 H, OCHC*H*$_3$), 4.42–4.51 (m, 1 H, CHO); mass spectrum m/e (major) 156 (M^+, 7), 114 (100), 84 (34), 73 (64), 69 (92); (minor) 156 (M^+, 6), 114 (100), 84 (33), 73 (67), 69 (78).

3-Methylvalerolactone (35):[26] ca. 90% pure; IR (film) 2939, 1733 s cm^{-1}; ^1H NMR δ 1.26 (d, J = 6.9 Hz, 3 H, CH_3), 1.73–2.18 (m, 4 H), 2.64 (m, 1 H), 4.22–4.34 (m, 2 H, CH_2O); exact mass calcd for $C_6H_{10}O_2$ m/e 114.0680, found m/e 114.0668.

3-Benzylidenebutyrolactone (36):[31,32] mp 116.5–117.5 °C (lit.[32] mp 115.5 °C); IR (CCl_4) 2926, 1766 s (C=O), 1657, 1178, 1035 cm^{-1}; ^1H NMR δ 3.25 (td, J = 7.3, 2.9 Hz, 2 H, C*H*$_2$CH$_2$O), 4.46 (t, J = 7.3 Hz, 2 H, CH_2O), 7.37–7.52 (m, 5 H, ArH), 7.58 (t, J = 2.9 Hz, 1 H, C=CHPh); mass spectrum m/e 174 (M^+, 62), 173 (49), 129 (42), 116 (82), 115 (M – CH_3OCO, 100), 63 (36), 58 (41), 51 (55); exact mass calcd for $C_{11}H_{10}O_2$ m/e 174.0681, found m/e 174.0678.

Alkylidene Lactone 37. (a) **37a**: IR (film) 2981, 2916, 1751 vs (C=O), 1681, 1653, 1378, 1195, 1025 cm^{-1}; ^1H NMR δ 2.86–2.92 (m, 4 H), 4.39 (t, J = 7.4 Hz, 2 H, C*H*$_2$O), 5.10 (dm, J = 10 Hz, 1 H, *trans*-CH=C*H*H), 5.11 (dm, J = 17 Hz, 1 H, *cis*-CH=CH*H*), 5.82 (m, 1 H, C*H*=CH$_2$), 6.79 (tt, J = 7.5, 2.8 Hz, 1 H, CH$_2$C=C*H*CH$_2$); mass spectrum m/e 138 (M^+, 1), 110 (10), 91 (11), 79 (100), 77 (33); exact mass calcd for $C_8H_{10}O_2$ m/e 138.0681, found m/e 138.0680. (b) **37b**: ca. 85% pure; IR (film) 2942, 2912, 1749 vs (C=O), 1675, 1631, 1375, 1246, 1027 cm^{-1}; ^1H NMR δ 2.93 (m, 2 H), 3.49 (m, 2 H), 4.33 (m, 2 H, CH_2O), 5.05 (dm, J = 10 Hz, 1 H, *trans*-CH=CHH), 5.10 (d, J = 17 Hz, 1 H, *cis*-CH=CHH), 5.85 (m, 1 H, CH=CH$_2$), 6.23 (brt, J = 7.5 Hz, 1 H, CH$_2$C=CHCH$_2$); exact mass calcd for $C_8H_{10}O_2$ m/e 138.0681, found m/e 138.0659.

3-Methylenebutyrolactone (38):[32,33] IR (film) 2929, 1766 s (C=O), 1667, 1265 cm^{-1}; ^1H NMR δ 2.96–3.03 (m, 2 H, C*H*$_2$CH$_2$O), 4.38 (t, J = 7.3 Hz, 2 H, CH_2O), 5.68 (t, J = 2.5 Hz, 1 H, C=C*H*H), 6.26 (t, J = 2.9 Hz, C=CH*H*); exact mass calcd for $C_5H_6O_2$ m/e 98.0367, found m/e 98.0364.

3-[(Tributylstannyl)methyl]butyrolactone (39): IR (film) 2957, 2925 s, 1771 s (C=O), 1179, 1138, 1025 cm^{-1}; ^1H NMR δ 0.76–1.01 (m, 15 H), 1.17–1.37 (m, 8 H), 1.42–1.53 (m, 6 H), 1.80–1.95 (m, 1 H), 2.38–2.48 (m, 1 H), 2.60–2.73 (m, 1 H), 4.11–4.20 (m, 1 H), 4.29–4.36 (m, 1 H). Anal. Calcd for $C_{17}H_{34}O_2Sn$: C, 52.47; H, 8.81. Found: C, 53.20; H, 8.64.

Benzylidene Lactone 40.[34] (a) **40a**: recrystallized from benzene/hexane as colorless needles; mp 144–146 °C (lit.[34] mp 146–147.5 °C); IR (CCl_4) 2941 s, 2863, 1766 vs (C=O), 1654, 1189, 1116, 1025 s cm^{-1}; ^1H NMR δ 1.30–1.46 (m, 2 H), 1.56–1.66 (m, 2 H), 1.84–2.06 (m, 2 H), 2.14–2.29 (m, 2 H), 2.53–2.62 (m, 1 H, C*H*CHO), 3.79 (ddd, J = 10.7, 10.7, 3.6 Hz, 1 H, CHO), 6.60 (d, J = 2.8 Hz, 1 H, CHPh), 7.30–7.43 (m, 3 H), 7.82–7.85 (m, 2 H); mass spectrum m/e 228 (M^+, 32), 184 (M – CO_2, 45), 141 (86), 129 (73), 128 (73), 115 (88), 104 (43), 91 (100), 77 (55); exact mass calcd for $C_{15}H_{16}O_2$ m/e 228.1150, found m/e 228.1136. (b) **40b**: IR (CCl_4) 3028, 2943 s, 2870, 1767 vs (C=O), 1667 s, 1187, 1017 cm^{-1}; ^1H NMR δ 0.95 (m, 1 H), 1.29 (m, 2 H), 1.63 (m, 2 H), 1.84 (m, 1 H), 2.19 (mt, J = 14.2 Hz, 2 H), 2.71 (dddd, J = 11.3, 10.7, 3.35, 2.7 Hz, 1 H, C*H*CHO), 3.75 (ddd, J = 10.8, 10.7, 3.5 Hz, 1 H, CHO), 7.30–7.52 (m, 5 H, ArH), 7.61 (d, J = 3.35 Hz, 1 H, CHPh); mass spectrum m/e 228 (M^+, 50), 184 (M – CO_2, 43), 141 (89), 129 (78), 128 (76), 115 (99), 91 (100), 77 (59). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.67; H, 7.22.

Alkylidene Lactone 41. (a) **41a** was recrystallized from hexane as white plates: mp 1070.5–108.5 °C; IR (CCl_4) 2946, 1777 vs (C=O), 1248, 1126, 1018 vs cm^{-1}; ^1H NMR δ 0.21 (s, 9 H, $Si(CH_3)_3$), 1.23–1.42 (m, 3 H), 1.57–1.63 (qd, J = 11.6, 3.4 Hz, 1 H), 1.84–1.88 (m, 1 H), 1.93–1.97 (m, 1 H), 2.07 (d, J = 12.0 Hz, 1 H), 2.24 (br d, J = 11.0 Hz, 1 H), 2.41 (dddd, J = 10.7, 10.6, 2.7, 2.1 Hz, 1 H, CCCH), 3.71 (ddd, J = 10.6, 10.3, 3.6 Hz, 1 H, CHO), 6.07 (d, J = 2.7 Hz, 1 H, C=CH); mass spectrum m/e 210 (17), 209 (M – CH_3, 97), 83 (81), 75 (100), 73 (74), 59 (34); exact mass calcd for $C_{12}H_{20}O_2Si$ m/e 224.1234, found m/e 2214.1306. Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.53; H, 9.03. (b) **41b**: ca. 85% pure; IR (CCl_4) 2951, 1766 sh, 1751 s (C=O), 1216 vs cm^{-1}; ^1H NMR δ 0.19 (s, 9 H, $Si(CH_3)_3$), 1.32–1.49 (m, 2 H), 1.59–1.69 (m, 2 H), 1.85–1.99 (m, 2 H), 2.22–2.34 (m, 2 H), 2.44 (br t, J = 9 Hz, 1 H, CCCH), 3.72 (br t d, J = 10.9, 3.7 Hz, 1 H, CHO), 6.84 (d, J = 3.2 Hz, 1 H, C=CH); mass spectrum m/e 224 (M^+, 2), 209 (53), 75 (87), 73 (100), 67 (75); exact mass calcd for $C_{12}H_{19}O_2Si$ (M – H), $C_{11}H_{17}O_2Si$ (M – CH_3) and C_3H_9Si m/e 223.1144, 209.0998, and 73.0473, found m/e 223.1113, 209.1048, and 73.0483, respectively.

Cyclization Products of *Se*-Phenyl Selenocarbonate (21). Flash chromatography gave two major groups of compounds. The first group comprised mainly **42b** (23%): IR (film) 2931, 2862, 1761 (C=O), 1682, 1125, 1085, 1018 cm^{-1}; ^1H NMR δ 0.89 (t, J = 6.6 Hz, 3 H, CH_3), 1.22–1.96 (m, 12 H), 2.05 (br, d, J = 11.2 Hz, 1 H), 2.19–2.24 (m, 1 H), 2.32–2.40 (m, 1 H), 2.59–2.67 (m, 2 H), 3.65 (td, J = 11.0, 3.6 Hz, 1 H, HCO), 5.87 (td, J = 7.7, 2.7 Hz, 1 H, HC=C); mass spectrum m/e 222 (M^+, 7), 109 (23), 95 (16), 93 (15), 91 (23), 81 (29), 79 (39), 67 (100); exact mass calcd for $C_{14}H_{22}O_2$ m/e 222.1619, found m/e 222.1616. This isomer was contaminated with isomers of the tricyclic compound **43**. **Isomer a** (13%): ^1H NMR (partial spectrum) δ 0.82 (d, J 7.1 = Hz); mass spectrum m/e 222 (M^+, 0.3), 140 (100), 95 (27), 82 (43), 81 (51), 80 (36), 79 (31), 68 (46), 67 (100). **Isomer b** (2%): ^1H NMR (partial spectrum) δ 0.96 (d, J = 6.7 Hz); mass spectrum m/e 140 (100), 95 (23), 82 (34), 81 (43), 80 (40), 79 (27), 68 (48), 67 (86). The mixture containing compounds **42b** and **43a–b** was analyzed for carbon and hydrogen content. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.90; H, 10.02. The second portion contained mainly **42a** (16%): IR (film) 2946, 2864, 1762, 1683, 1211, 1026 cm^{-1}; ^1H NMR δ 0.89 (t, J = 6.7 Hz, 3 H, CH_3), 1.27–2.49 (m, 17 H), 3.70 (td, J = 10.9, 3.6 Hz, 1 H, HCO), 6.63 (td, J = 7.8, 2.9 Hz, HC=C); mass spectrum m/e 222 (M^+, 2), 152 (17), 95 (32), 91 (22), 84 (21), 82 (25), 81 (41), 79 (53), 77 (24), 68 (23), 67 (100); exact mass calcd for $C_{14}H_{22}O_2$ m/e 222.1619,

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found m/e 222.1640. The following isomers of **43** were identified. **Isomer c** (7%): ^{1}H NMR (partial spectrum) δ 0.78 (d, J = 7.1 Hz); mass spectrum m/e 222 (M^+, 0.4), 140 (60), 95 (26), 82 (65), 81 (53), 80 (28), 79 (28), 68 (38), 67 (100). **Isomer d** (2%): ^{1}H NMR (partial spectrum) δ (d, J = 7.1 Hz); mass spectrum m/e 140 (100), 95 (24), 82 (36), 81 (45), 80 (42), 79 (27), 73 (25), 68 (50), 67 (89). **Isomer e** (1%): ^{1}H NMR (partial spectrum) δ 0.82 (d, J = 7.1 Hz); mass spectrum m/e 140 (100), 95 (19), 81 (39), 80 (33), 79 (24), 73 (21), 68 (42), 67 (92). **Isomer f** (7%): ^{1}H NMR (partial spectrum) δ 1.00 (d, J = 6.4 Hz); mass spectrum m/e 140 (66), 95 (27), 82 (51), 81 (54), 80 (28), 79 (29), 68 (37), 67 (100). The fraction containing compounds **42a** and **43c–f** was analyzed for carbon and hydrogen content. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.48; H, 9.98. The fraction eluted between these portions contained the following isomers of **43**: **a**, **c**, **e**, **f** in yields of 3, 1, 12, and 4%, respectively. Overall yields were thus: **42b** (23%), **42a** (16%), and isomers of **43** (53%). All these yields were estimated by a combination of NMR and GC–MS.

Alkylidene Lactone 44. (a) **44a** was recrystallized from benzene/hexane and obtained as colorless plates: mp 108.5–109.5 °C; IR (CCl_4) 2938 s, 2864, 1765 vs (C=O), 1742 sh, 1247, 1167, 1012 cm^{-1}; ^{1}H NMR δ 0.20 (s, 9 H, $Si(CH_3)_3$), 1.31–1.82 (m, 8 H), 2.05–2.17 (m, 1 H), 2.33–2.41 (m, 1 H), 2.72 (dddd, J = 10.1, 9.7, 4.9, 3.1 Hz, 1 H, C=CC*H*CHO), 4.15 (ddd, J = 9.7, 9.7, 4.2 Hz, 1 H, CHO), 6.18 (d, J = 3.1 Hz, 1 H, C=CHSiMe$_3$); mass spectrum m/e 225 (4), 224 (14), 223 ($M^+ - CH_3$, 74), 143 (25), 83 (35), 75 (100), 73 (46). Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.60; H, 9.50. (b) **44b** was recrystallized from benzene/hexane and obtained as colorless needles: mp 127–128 °C; IR (CCl_4) 2940, 2867, 1770 vs (C=O), 1251, 1218, 1177, 1024 cm^{-1}; ^{1}H NMR δ 0.22 (s, 9 H, $Si(CH_3)_3$), 1.43–1.82 (m, 8 H), 2.21–2.32 (m, 1 H), 2.33–2.39 (m, 1 H), 2.81 (dddd, J = 11.5, 8.4, 4.5, 3.4 Hz, 1 H, C=CC*H*CHO), 4.17 (ddd, J = 10.3, 8.5, 3.8 Hz, 1 H, CHO), 6.93 (d, J = 3.4 Hz, 1 H, C=CHSiMe$_3$); mass spectrum m/e 237 [$(M - 1)^+$, 0.5], 223 (48), 83 (18), 75 (100), 73 (88). Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.69; H, 9.27.

Methylene Lactone 45:[35] IR (film) 2929 s, 2861, 1767 s (C=O), 1661, 1455, 1263, 1152, 1125, 100 cm^{-1}. ^{1}H NMR δ 1.40–1.80 (m, 7 H), 2.12–2.20 (m, 1 H), 2.34–2.40 (m, 2 H), 2.74–2.79 (m, 1 H), 4.14 (br t, J = 9.7, 4.5 Hz, 1 H, CHO), 5.54 (d, J = 3.3 Hz, 1 H, C=CHH), 6.18 (d, J = 3.3 Hz, 1 H, C=CHH); mass spectrum m/e 166 (M^+, 1), 95 (20), 82 (37), 81 (33), 79 (45), 67 (65), 55 (56), 54 (100); exact mass calcd for $C_{10}H_{14}O_2$ m/e 166.0993, found m/e 166.0978.

Alkylidene Lactone 46. (a) **46a** was then distilled at 66 °C (0.1 mmHg) and obtained as white crystals: IR ($CHCl_3$) 3012, 2941 s, 2863, 1743 s (C=O), 1633, 1309, 1272, 1253, 1147, 842 (C=O) cm^{-1}; ^{1}H NMR δ 0.18 (s, 9 H, $Si(CH_3)_3$), 1.51–1.60 (m, 6 H), 1.72–1.81 (m, 4 H), 2.67 (d, J = 2.8 Hz, 2 H, CH=CCH_2), 6.92 (t, J = 2.8 Hz, 1 H, CH=CCH_2); mass spectrum m/e 238 (M^+, 1), 223 (19), 112 (11), 97 (32), 75 (43), 73 (100); exact mass calcd for $C_{13}H_{22}O_2Si$ m/e 238.1389, found m/e 238.1401. Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.77; H, 9.36. (b) **46b** was distilled at 73 °C (0.15 mmHg) and obtained as white crystals: IR ($CHCl_3$) 3015, 2940, 2862, 1754 s (C=O), 1634, 1322 s, 1309 s, 1248 s, 863 s, 844 s ($Si(CH_3)_3$) cm^{-1}; ^{1}H NMR δ 0.20 (s, 9 H, $Si(CH_3)_3$), 1.44–1.52 (m, 4 H), 1.57–1.60 (br d, J = 10 Hz, 1 H), 1.68–1.77 (m, 5 H), 2.71 (d, J = 2.4 Hz, 2 H, CH=CCH_2), 6.34 (t, J = 2.4 Hz, 1 H); mass spectrum m/e 223 (54), 143 (20), 83 (19), 81 (17), 77 (10), 75(100); exact mass calcd for $C_{12}H_{19}O_2Si$ ($M - CH_3$) m/e 223.1154, found m/e 223.1178.

3-Benzylidenevalerolactone (47):[32] IR (film) 2958, 1709 vs (C=O), 1613, 1261, 1173, 1122 cm^{-1}; ^{1}H NMR δ 1.96–2.02 (m, 2 H, C*H*$_2$CH$_2$O), 2.89 (td, J = 6.5, 2.3 Hz, 2 H, CH$_2$C=C), 4.40 (t, J = 5.3 Hz, 2 H, CH$_2$O), 7.35–7.46 (m, 5 H), 7.93 (t, J = 2.3 Hz, 1 H, PhCH); mass spectrum m/e 188 (M^+, 49), 187 (100), 129 (38), 128 (29), 115 (61), 102 (32), 91 (29), 77 (27); exact mass calcd for $C_{12}H_{12}O_2$ m/e 188.0837, found m/e 188.0850.

(Trimethylsilyl)methylene Lactones 48. (a) **48a**: IR (film) 3057, 2940, 2863, 1715 s (C=O), 1247, 1195, 844 ($SiMe_3$) cm^{-1}: ^{1}H NMR δ 0.16 (s, 9 H, $Si(CH_3)_3$), 1.02–1.50 (m, 4 H), 1.57–1.77 (m, 2 H), 1.82–1.87 (m, 2 H), 2.11–2.17 (m, 1 H), 2.33 (ddd, J = 2.5, 12.5, 16.2 Hz, C*H*HC=C), 2.64 (ddd, J = 1.2, 4.7, 16.2 Hz, CH*H*C=C), 3.86–3.96 (m, 1 H, CHO), 6.21–6.23 (m, 1 H, C=CH). (b) **48b**: IR (film) 2939, 2864, 1717 s (C=O), 1251, 1225, 1198, 1178, 864, 840 ($SiMe_3$) cm^{-1}; ^{1}H NMR δ 0.18 (s, 9 H, $Si(CH_3)_3$), 1.05–1.90 (m, 8 H), 2.13–2.18 (m, 1 H), 2.25 (md, J = 13 Hz, 1 H), 2.71 (dd, J = 4.5, 16.4 Hz, 1 H), 3.89–3.98 (m, 1 H, CHO), 7.24 (br s, 1 H, C=CH). Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.48; H, 9.31. Found: C, 65.25; H, 8.97.

Deprotection of (Trimethylsilyl)methylene Lactones 41 and 44. Preparation of Methylene Lactone 62. (a) Phenylthio Adduct 60. A solution of **41a** (41 mg, 0.2 mmol) in ethanol (2 mL) was added to a solution of sodium phenyl thiolate (0.8 mmol) in ethanol (4 mL). After 16 h the reaction was quenched with acetic acid and extracted with ether, and the organic layer washed with brine and water. After evaporation of the solvent preparative TLC (hexane/EtOAc (15:1)) yielded the lactone **60** (48 mg, 77%, 87% based on converted **41**) as a white powder which was recrystallized from hexane as white prisms: mp 108–109.5 °C; IR (CCl_4) 3076, 2947, 2863, 1779 vs (C=O), 1584, 1254 s, 1037 cm^{-1}; ^{1}H NMR δ 0.23 (s, 9 H, $Si(CH_3)_3$), 1.06–1.54 (m, 4 H), 1.64–1.73 (m, 1 H), 1.84–1.99 (m, 2 H), 2.05 (d, J = 12.2 Hz, 1 H, PhSCHCHC*H*), 2.67 (dd, J = 12.5, 2.5 Hz, 1 H, PhSCHC*H*), 3.06 (d, J = 2.5 Hz, 1 H, PhSCH), 3.62 (ddd, J = 10.4, 9.8, 3.6 Hz, 1 H, CHO), 7.15–7.21 (m, 1 H), 7.26–7.32 (m, 2 H), 7.34–7.39 (m, 2 H); mass spectrum m/e 334 (M^+, 2), 252 (21), 237 (21), 79 (15), 75 (20), 73 (100); exact mass calcd for $C_{18}H_{26}O_2SSi$ m/e 334.1422, found m/e 334.1400. **(b) Reaction of Lactone 60 with Desiccated Tetrabutylammonium Fluoride and Methyl Acrylate.** A solution of anhydrous tetrabutylammonium fluoride (47 mg, 0.18 mmol) in THF (0.2 mL) was added to a stirred solution of the lactone **60** (31 mg, 0.09 mmol) and methyl acrylate (0.1 mL, 1.1 mmol) in THF (0.2 mL). After 10 min the mixture was evaporated. Preparative TLC (hexane/EtOAc (6:1)) yielded (a) methyl 3-(phenylthio)propionate (15.5 mg, 93%) as a pale orange oil and (b) α-methylene lactone **62**[35] (12 mg, 83%) as a clear oil: IR (film) 2935, 1773 cm^{-1}; ^{1}H NMR δ 1.30–1.75 (m, 4 H), 1.82–1.99 (m, 2 H), 2.10–2.15 (m, 1 H), 2.23–2.29 (m, 1 H), 2.38–2.46 (m, 1 H), 3.71 (td, J = 11.0, 3.7 Hz, 1 H, CHO), 5.38 (d, J = 3.2 Hz, 1 H, C=CHH), 6.07 (d, J = 3.2 Hz, 1 H, C=CHH); mass spectrum m/e 152 (M^+, 2), 124 (40), 96 (45), 79 (49), 67 (100).

Preparation of Methylene Lactone 45. (a) Phenyl Thiol Adduct 61. Phenyl thiol (0.52 mL, 5.1 mmol) and triethylamine (0.62 mL, 4.5 mmol) were added to a stirred solution of **44** (0.786 g, 3.3 mmol) in THF (12 mL) at room temperature. After 2.5 h the reaction mixture was neutralized with acetic acid. Water (25 mL) was added, and the mixture extracted with ether (3 × 80 mL). The organic layer was washed with $NaHCO_3$ (20 mL) and brine (20 mL) and dried and the solvent evaporated. Flash chromatography (hexane/EtOAc (20:1)) yielded the lactone **61** (1.09 g, 95%) as a white powder which was recrystallized from hexane as white needles: mp 108.5–109 °C; IR (CCl_4) 2940 s, 2863, 1767 vs (C=O), 1253 s, 1179 s, 1008, 843 s ($Si(CH_3)_3$) cm^{-1}; ^{1}H NMR δ 0.25 (s, 9 H, $Si(CH_3)_3$), 1.19–1.68 (m, 8 H), 2.04–2.12 (m, 1 H), 2.26–2.39 (m, 2 H), 2.71 (dd, J = 11.8, 2.4 Hz, 1 H, PhSCHC*H*C=O), 3.01 (d, J = 2.4 Hz, 1 H, PhSCH), 4.00 (td, J = 9.9, 4.6 Hz, 1 H, CHO), 7.15–7.21 (m, 1 H), 7.28–7.31 (m, 2 H), 7.37–7.40 (m, 2 H); exact mass calcd for $C_{19}H_{28}O_2SSi$ m/e 348.1579, found m/e 348.1616. Anal. Calcd for $C_{19}H_{28}O_2SSi$: C, 65.47; H, 8.09; S, 9.20. **(b) Reaction of Lactone 61 with Desiccated Tetrabutylammonium Fluoride and Methyl Acrylate.** The lactone **61** (22.8 mg, 0.066 mmol) was treated with methyl acrylate (0.07 mL, 0.7 mmol) and anhydrous tetrabutylammonium fluoride (29 mg, 0.11 mmol) in THF (0.1 mL) as described for the preparation of **62**. Preparative TLC with hexane/EtOAc (8:1) as eluant gave (a) methyl-3-(phenylthio)propionate (12 mg, 94%) [IR (film) 2930, 1740 s (C=O), 1585, 1247, 1174, 1145 cm^{-1}; ^{1}H NMR δ 2.63 (t, J = 7.4 Hz, 2 H, CH_2CO_2Me), 3.17 (t, J = 7.4 Hz, 2 H, $PhSCH_2$), 3.68 (s, 3 H, CO_2CH_3), 7.20–7.38 (m, 5 H, Ph); mass spectrum m/e 196 (M^+, 40), 136 (32), 123 (55), 109 (52), 77 (32), 65 (73), 59 (100)] and (b) α-methylene lactone **45** (10.8 mg, 93%) as a clear oil (for analytical data see above).

3-(3-Butenyl)butyrolactone (63). A solution of selenocarbonate **6** (139 mg, 0.55 mL), allyltributyltin (0.3 mL, 1 mmol), and AIBN (10 mg) in benzene (0.5 mL) was boiled for 1 h. The solvent was evaporated, the residue was dissolved in acetonitrile

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(30 mL), and the organotin compounds were extracted with hexane (3 × 30 mL). NMR analysis of the acetonitrile portion revealed a 10:1 ratio of **63**:**27**. The products consisting of **63** (76%) and **27** (7%) were distilled to give **63**: IR (film) 3081, 2982, 2936, 2920, 1769 s (C=O), 1642 (CH=CH_2), 1170, 1026 cm^{-1}; ^1H NMR δ 1.48–1.59 (m, 1 H), 1.86–2.28 (m, 4 H), 2.35–2.46 (m, 1 H), 2.49–2.59 (m, 1 H), 4.15–4.24 (m, 1 H, CH*H*O), 4.36 (dt, J = 8.8, 2.6 Hz, 1 H, CH*H*O), 5.01–5.11 (m, 2 H, C=CH_2), 5.72–5.87 (tdd, J = 17, 10.4, 6.6 Hz, 1 H, C*H*=CH_2); mass spectrum m/e 140 (M^+, 0.5), 86 (100), 67 (12), 55 (33); exact mass calcd for $C_8H_{12}O_2$ m/e 140.0837, found m/e 140.0860.

3-But-3-enylspirocyclohexyl-1,5′-butyrolactone (64). Prepared by reaction of selenocarbonate **12** with allyltributyltin as described above for the preparation of **63**: IR (film) 3078, 2938, 2862, 1767 s (C=O), 1451, 1202, 1132, 951 cm^{-1}; ^1H NMR δ 1.26–1.75 (m, 13 H), 2.00–2.33 (m, 3 H), 2.65–2.78 (m, 1 H), 5.01 (d, J = 9.9 Hz, 1 H, *trans*-CH=C*H*H), 5.06 (d, J = 15.8 Hz, 1 H, *cis*-CH=CH*H*), 5.72–5.86 (m, 1 H, C*H*=CH_2); exact mass calcd for $C_{13}H_{20}O_2$ m/e 208.1463, found m/e 208.1585.

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Supplementary Material Available: Proton NMR spectra of compounds **6**, **9**, **23**, **31a,b**, **34**, **37a**, **46b**, **48a**, **60**, **63**, and **64** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

The Electrochemical Reductive Trimethylsilylation of Aryl Chlorides: A Good Route to Aryltrimethylsilanes and a Novel Route to Tris(trimethylsilyl)cyclohexadienes†

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The electroreductive trimethylsilylation of aryl chlorides R–C_6H_4Cl (R = H, *o*-Me, *m*-Me, *p*-Me) can be controlled so as to give, in good yields, either the corresponding aryltrimethylsilanes (products of the reduction of the carbon–chlorine bond) or mixtures of *cis*- and *trans*-tris(trimethylsilyl)cyclohexa-1,3(or 1,4)-dienes (products of the successive reduction of the carbon–chlorine bond and the partial reduction of the aromatic ring). Which of the two products is formed depends upon how much electricity is passed during the constant current electrolysis, in a one-compartment cell equipped with a sacrificial aluminum anode, of an aryl chloride in 80:20 THF/HMPA solution that also contains Et_4NBF_4 as the supporting electrolyte and excess Me_3SiCl. The electroreductive trimethylsilylation of phenyltrimethylsilane gave, in 62% yield, a mixture of three 3,5,6-tris(trimethylsilyl)-cyclohexa-1,3-dienes, of which the trans, pseudo a-a isomer constituted 89%. Such products cannot be obtained by the chemoreductive trimethylsilylation of phenyltrimethylsilane. The electroreductive trimethylsilylation of benzene and toluene produced the corresponding bis(trimethylsilyl)cyclohexa-1,4-dienes. The regio- and stereochemical outcomes of the electroreductive trimethylsilylation of the various substrates can be explained in terms of the electronic and steric effets of the substituents originally attached to the aromatic ring and the steric effects of the trimethylsilyl groups that are subsequently attached.

Introduction

In reporting the results of our studies of the use of organosilicon compounds in organic synthesis, we have described the application of allyl-, vinyl-, and phenylsilanes in the preparation of functionalized organic compounds.[1,2] We have since focused our efforts on developing electrochemical methods for silylating aryl halides R–C_6H_4–X (R = H, *o*-, *m*-, *p*-Me; X = Cl, Br), benzene, toluene, and phenyltrimethylsilane. Such methods would obviate the use of chemical reducing agents like metallic lithium or sodium.

Only a few reports of the electroreductive silylation of organic halides have so far appeared. Shono et al.[3] obtained benzyltrimethylsilanes and allyltrimethylsilanes by the electrolysis of benzyl chlorides and allyl halides, respectively, in the presence of chlorotrimethylsilane (Me_3SiCl). The electrolyses were performed in a two-compartment cell equipped with platinum electrodes. However, when the diaphragm that separated the anodic and cathodic compartments was removed, both trimethylsilylation and chlorination took place. Yoshida et al.[4] succeeded in electroreductively silylating allyl chlorides, vinyl halides, and aryl iodides. However, attempts to electroreductively silylate aryl chlorides (the least expensive aryl halides) and alkyl halides failed. In any event, the method could not be easily modified so as to permit preparative-scale silylations.

As for our work, we have described a very selective electroreductive silylation of polychloromethanes[5] and have reported the first results of attempts to electroreductively silylate benzyl chloride, phenyl bromide, and phenyl

† This article is dedicated to Professor Ulrich Wannagat, on the occasion of his 70th birthday, in recognition of his outstanding research in Organometallic Chemistry.

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