Inhibition of Rearrangements in Stannane-Mediated Radical Reduction Reactions by Catalytic Quantities of Diphenyl Diselenide. An Example of Polarity Reversal Catalysis

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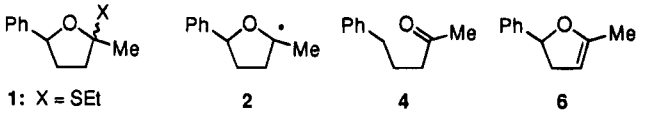
The presence of only 10 mol % of PhSeH, PhSeSePh (reduced *in situ* to PhSeH), and, to a lesser extent, PhSH has a dramatic effect on the efficiency of stannane-mediated free radical rearrangement reactions owing to the superior hydrogen donating qualities of PhSeH and PhSH. Slow radical rearrangements can be prevented altogether, and the yields of even moderately rapid rearrangements significantly diminished. The addition of 10 mol % of PhSeSePh to stannane-mediated aryl radical cyclizations is advantageous as the initial, rapid, 5-hexenyl rearrangement is not impaired but the subsequent, slower neophyl rearrangement is effectively minimized, resulting in the formation of vastly improved 5-exo/6-endo ratios.

Since their introduction into radical chemistry by Clive,[1] alkyl aryl selenides have enjoyed wide popularity as alternatives to alkyl halides in the stannane-mediated generation of alkyl radicals for use in simple reduction reactions and in radical rearrangements.[2] This popularity stems from (i) their ease of introduction in a number of olefin functionalization and cyclofunctionalization reactions;[3] (ii) their ready reaction with stannyl, and tris(trimethylsilyl)silyl, radicals at a convenient rate;[4,5] and (iii) the stability of the carbon–selenium bond, as compared with that of the corresponding alkyl halides, which enables them to be isolated, purified and if necessary carried through diverse reaction sequences unchanged. This comparative stability toward nucleophilic displacement is nicely illustrated by the use of acyl aryl selenides for the generation of acyl radicals.[6–8] Here, we describe the detrimental effect of minor amounts of diphenyl diselenide on stannane mediated rearrangments of alkyl, aryl, and acyl radicals and illustrate how advantage may be taken of this effect in the suppression of unwanted radical rearrangements.

In the course of a recent mechanistic investigation, we had occasion to prepare the 2-(ethylthio)tetrahydrofuran **1** and to study its reaction with triphenyltin hydride, giving mixtures of the reduced product **3** and the ring-opened ketone **4** resulting from quenching and fragmentation of the intermediate radical **2**, respectively (Table 1, entry 1).[9] The thioglycoside **1**[9] reacts relatively slowly with stannyl radicals, prompting us to prepare, in a follow-up investigation, the analogous selenoglycoside **5** in the hope of obtaining a smoother, cleaner reaction. In the event, reaction of **5** with triphenyltin hydride, under identical conditions to those applied to **1**, resulted in a clean reaction with the only observable radical product being the tetrahydrofuran **3** (Table 1, entry 2). Minor amounts of the elimination product **6** were also found but this presumably arises by a polar mechanism. Apparently, the chemistry of the intermediate radical **2** was a factor of its source, **1** or **5**. Closer inspection revealed all samples of **5** to be contaminated with between 5 and 10% of diphenyl diselenide from which it could not be completely purified by column chromatography owing to its partial decomposition on silica gel.



1: X = SEt
3: X = H
5: X = SePh

2 **4** **6**

We hypothesized that the diselenide was rapidly reduced by the stannane to give PhSeH which, with its superior hydrogen-donating abilities (Table 2), quenched the radical **2** (eq 1) before it could undergo fragmentation. The availabilty of only a catalytic quantity of PhSeH in the reaction medium requires a further rapid reaction whereby the radical PhSe• abstracts

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Table 1. Effect of Additives on Bu_3SnH-Mediated Radical Rearrangements

entry	substr	additive (mol %)	substr concn (M)	concn of Bu_3SnH (M)	addition time (h)[a]	products (ratio)
1[b,c]	**1**		0.015	0.02	18	**3:4** (50:50)
2[c]	**5**	PhSeSePh (5–10)	0.02	0.04	16	**3:4** (>95:5)
3	**7**		0.03	0.036	3 (1)	**8:9** (89:11)
4	**7**	PhSeH (10)	0.03	0.036	3 (1)	**8:9** (<5:95)
5	**7**	PhSeSePh (10)	0.03	0.036	3 (1)	**8:9** (<5:95)
6	**7**	PhSH (10)	0.03	0.036	3 (1)	**8:9** (10:90)
7	**10**		0.025	0.03	4 (1)	**11:12** (47:53)
8	**10**	PhSeH (10)	0.025	0.03	4 (1)	**11:12** (13:87)
9	**13**		0.10	0.10	2 (0.5)	**14:15** (100:0)
10	**13**	PhSeSePh (10)	0.10	0.10	2 (0.5)	**14:15** (82:18)
11	**13**		0.20	0.20	0.1 (0.5)	**14:15** (100:0)
12	**13**	PhSeSePh (10)	0.20	0.20	0.1 (0.5)	**14:15** (58:42)
13	**16**		0.20	neat	0[d] (2)	**17:18** (100:0)
14	**16**	PhSeH (10)	0.20	neat	0[d] (2)	**17:18** (82:18)
15	**23**		0.025	neat	0[d] (3)	**24:25** (53:47)
16	**23**	PhSeSePh (10)	0.025	neat	0[d] (3)	**24:25** (46:54)
17	**27**		0.025	neat	0[d] (3)	**24:25** (60:40)
18	**27**	PhSeSePh (10)	0.025	neat	0[d] (3)	**24:25** (80:20)
19	**27**		0.01	neat	0[d] (3)	**24:25** (20:80)
20	**27**	PhSeSePh (10)	0.01	neat	0[d] (3)	**24:25** (90:10)

[a] Numbers in parentheses indicate hours of additional reflux time after the addition of stannane was complete. [b] Taken from ref 9. [c] Ph_3SnH was used in place of Bu_3SnH in these experiments. [d] Indicates mixing of neat stannane with the substrate before heating to reflux.

Table 2. Second-Order Rate Constants for H-Transfer to Primary Alkyl Radicals at 25 °C

entry	hydrogen atom donor	rate (k_{25}), M^{-1} s^{-1}	ref
1	Bu_3SnH	2.4×10^6	11
2	PhSeH	2.1×10^9	12
3	PhSH	1.4×10^8	13

hydrogen from the stannane, regenerating PhSeH and the stannyl radical required for abstraction of the radical precursor (eq 2). The overall scheme (eqs 1–3) closely resembles that for the catalysis by thiols of the reduction of alkyl halides by trialkylsilanes demonstrated by Roberts and dubbed polarity reversal catalysis.[10]

$$R^\bullet + PhSeH \rightarrow RH + PhSe^\bullet \quad (1)$$

$$PhSe^\bullet + Bu_3SnH \rightarrow PhSeH + Bu_3Sn^\bullet \quad (2)$$

$$Bu_3Sn^\bullet + RX \rightarrow Bu_3SnX + R^\bullet \quad (3)$$

Comparison of the rates of trapping of primary alkyl radicals by Bu_3SnH[11] and PhSeH[12] at 25 °C (Table 2, entries 1 and 2) indicates that, if eq 2 is rapid, the presence of only 5% of PhSeH (or its precursor PhSeSePh) as a contaminant in the radical precursor will result in a 50-fold increase in the rate of radical trapping. This increase in rate will significantly inhibit many radical rearrangement reactions and will be very effective in preventing slower rearrangements, such as the fragmentation of radical **2**. It also seems apparent from the work of Roberts[10] that thiols should have a similar, but smaller, effect. Comparison of entries 1 and 3[13] in Table 2 suggests that 5 mol % of thiophenol should accelerate the trapping of alkyl radicals 3-fold.

In order to provide support for the above hypothesis, PhSeSePh was treated in C_6D_6 at room temperature with 1 molar equiv of triphenyltin hydride. Within 5 min, complete consumption of the diselenide (decolorization) was evident as was the clean formation of PhSeH (sharp singlet at δ_H 1.18 which coincided exactly with that of an authentic sample[14]). At this stage it is not clear whether this reaction (eq 4) proceeds via a radical or hydridic mechanism.

$$R_3SnH + PhSeSePh \rightarrow Re_3SnSePh + PhSeH \quad (4)$$

To further investigate this hypothesis, we first turned to the reaction of acetobromoglucose (**7**) with tributyltin hydride and AIBN, which constitutes a very practical synthesis of peracetylated 2-deoxyglucopyranose (**8**).[15] Dropwise addition of Bu_3SnH and AIBN to **7** over 3 h resulted in clean conversion to **8** with only 10% of the reduction product **9** formed (Table 1, entry 3). The inclusion of 10 mol % of either PhSeH or PhSeSePh in the reaction mixture resulted in the complete suppression of the migration reaction (Table 1, entries 4 and 5). Thiophenol was also effective in significantly reducing the extent of this relatively slow radical migration (Table 1, entry 6). Comparison of entries 7 and 8 (Table 1) demonstrates the efficiency of PhSeH in suppressing the migration of diphenylphosphatoxy groups[16] in β-(phosphatoxy)alkyl radicals. Competition reactions in this laboratory have shown that the migration of $(PhO)_2P(O)O$ is at least 100 times faster than that of the $CH_3C(O)O$ group,[17] and so it is not surprising that PhSeH is

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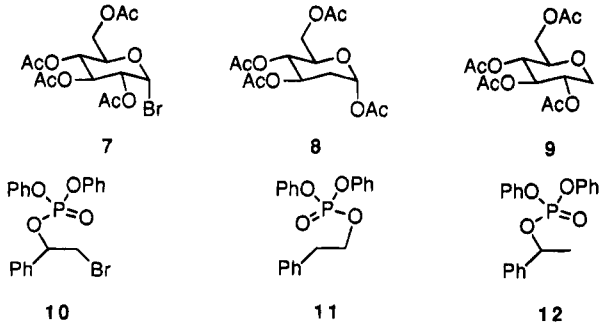
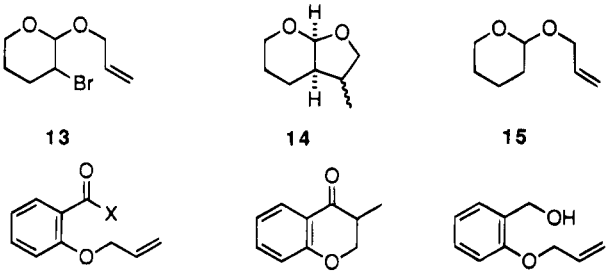
marginally less effective at suppressing the β-(phosphatoxy)alkyl migration than the β-(acyloxy)alkyl migration (cf. entries 4 and 8, Table 1).



7 8 9

10 11 12

Turning to radical cyclization reactions, we next studied the effect of PhSeSePh on the stannane-mediated ring closure of **13**.[18] In the absence of PhSeSePh, dropwise addition of Bu_3SnH over 2 h resulted in essentially quantitative formation of the cyclized product **14**, whereas addition of 10 mol % of PhSeSePh enabled trapping of 18% of the uncyclized radical (Table 1, entries 9 and 10). When the reaction was operated at double the initial concentration and with rapid addition of Bu_3SnH, the reduction product **15** was still not observed in the absence of PhSeSePh but was formed in 42% yield when 10% of PhSeSePh was included (Table 1, entries 11 and 12). Acyl radical cyclizations are also affected: thus in the absence of PhSeH the acyl selenide **16**[7d] gave essentially 100% of the ring-closed product **17** on treatment with Bu_3SnH and AIBN and none of the reduced product **19** (Table 1, entry 13), whereas inclusion of 10 mol % of PhSeH resulted in the formation of 18% of the benzyl alcohol **18** (Table 1, entry 14). Clearly, **18**, identified by comparison with an authentic sample, results from the *in situ* reduction of the noncyclized product **19**, possibly via the intermediacy of a selenoacetal.



13 14 15

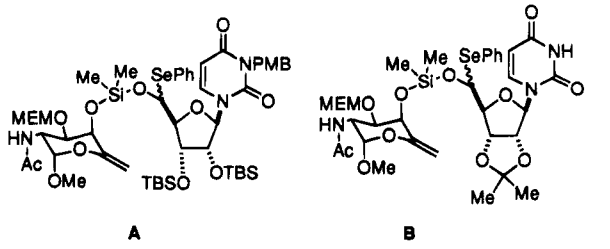
16: X = SePh
19: X = H

17 18

Each of the above examples serves to illustrate the detrimental effect of only minor amounts of PhSeSePh, PhSeH, or PhSH on stannane-mediated radical rearrangement reactions. Slow rearrangements can be suppressed altogether, and the yields of even relatively rapid rearrangements significantly diminished. The take home lesson is evidently that, when using selenides and even sulfides as radical precursors in conjunction with stannanes, and presumably silanes, as radical precursors in rearrangement reactions, time spent in assuring rigorous absence of diselenides or thiols from the substrate will be rewarded by higher yields of the rearranged product.[19]

The question arises as to how the above observations might be turned to advantage. A good candidate is a situation whereby an initial fast and desirable radical rearrangement is followed by a second, slower, and undesirable rearrangement. This situation is well known to occur with 5-hexenyl cyclizations of vinyl[20] and aryl radicals[21] which, following an initial 5-exo-trigonal cyclization, are prone to a slower neophyl-type rearrangement resulting in mixtures of five- and six-membered ring products. One such example is the aryl bromide **20**[21] which, on treatment with Bu_3SnH, gives mixtures of **21** and **22** with lower concentrations of stannane favoring the latter. Mindful of the apparent incompatibilty of aryl aldehydes with our Bu_3SnH/PhSeSePh system *vide supra* (Table 1, entry 14), **20** was oxidized with an activated MnO_2/KCN couple in methanol, according to Corey,[22] to give the ester **23** in excellent yield. Dropwise addition of Bu_3SnH and AIBN to a 0.025 M solution of **23** in benzene at reflux resulted in the formation of **24** and **25** in the ratio 53:47 (Table 1, entry 15). Contrary to our expectations, inclusion of 10 mol % of PhSeSePh in the initial reaction mixture resulted in only a minor change in the product ratio (Table 1, entry 16). Noticing the precipitation of metallic selenium in the reaction mixture, we reasoned that the cleavage of the Ph–Se bond by the stannane was competing with that of the less reactive Ar–Br bond, resulting in irreversible removal of the PhSeSePh/PhSeH from the system. We therefore hypothesized that use of the more reactive iodide **27** should remedy the problem. Alkylation of 2-iodoisovanillin[23] gave the aldehyde **26** which was oxidized to **27** in excellent yield. Treatment of a 0.025 M solution of **27** in benzene at reflux with Bu_3SnH and AIBN gave a 60:40 mixture of **24** and **25** (Table 1, entry 17), reflecting

(19) Although we have not made an extensive search, it is likely that other examples of radical cyclizations either failing or giving low yields due to the presence (unappreciated) of minor quantites of diaryl diselenide can be found in the literature. One apparent example (Myers, A. G.; Gin, D. Y.; Rogers, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4697 and references therein) that appeared whilst this work was in progress, concerns the 7-endo cyclizations of **A** and **B**. With **A**, a chromatographically stable, pure substance, the reaction proceeded according to plan and gave the cyclization product in high yield. However with **B**, which was chromatographically unstable and reported as only 60% pure, the cyclization failed. It was suggested that the more bulky silyl protecting groups in **A** prevented the approach of Bu_3SnH to the initial radical and so permitted the expectedly slow 7-endo cyclization to occur. In light of the observations presented here, it appears much more likely that that the cyclization of **B** was prevented by the presence of PhSeSePh as an impurity, and so of PhSeH, in the reaction mixture.



A B

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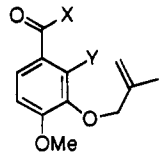
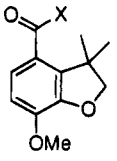
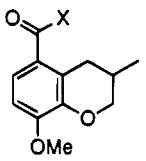
the ratio obtained from the bromide **23**. Inclusion of 10 mol % of PhSeSePh in the initial reaction mixture resulted in an 80:20 ratio of **24** and **25** (Table 1, entry 18), so demonstrating the validity of the concept. By operating at a lower initial concentration of 0.01 M, the effect of the diselenide was rendered even more evident. Thus, without PhSeSePh the ratio of five- to six-membered products was 20:80, while with 10 mol % of PhSeSePh added it was 90:10 (Table 1, entries 19 and 20). Probably, the remaining 10% of the six-membered product in this last run is the result of the direct 6-endo-mode cyclization. Although we have carried out no experiments to this effect, this concept should be readily applicable to vinyl radical cyclizations provided that vinyl iodides and not bromides are used as the radical source.



20: X = H, Y = Br
23: X = OMe, Y = Br
26: X = H, Y = I
27: X = OMe, Y = I



21: X = H
24: X = OMe



22: X = H
25: X = OMe

Finally, we suggest that the use of controlled amounts of PhSeSePh may find use in radical kinetics whereby the rate of a particular cyclization is determined by competition with hydrogen atom abstraction from Bu_3SnH. In such experiments it is customary to work in the presence of a large excess of the stannane, or to stop the reaction at low conversion, so as to be able to assume pseudo-first-order conditions.[24] Conducting the kinetic run in the presence of *n* mol % of PhSeSePh, and hence of *n* mol % of PhSeH as the hydrogen atom donor (where *n* could be chosen to suit the rate of the rearrangement in question), with slow addition of just 1 equiv of stannane, should allow reactions to be run to completion under true first-order conditions for the concentration of PhSeH.

Experimental Section

General. Melting points were recorded on a Thomas hot stage microscope and are uncorrected. ^1H- and ^{13}C-NMR spectra were run in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are downfield from tetramethylsilane as internal standard. All solvents were dried and distilled by standard procedures. All reactions were run under a dry nitrogen or argon atmosphere. THF was distilled, under N_2, immediately prior to use from sodium benzophenone ketyl. Ether refers to diethyl ether. Microanalyses were conducted by Midwest Microanalytical, Indianapolis.

2-Methyl-2-(phenylseleno)-5-phenyltetrahydrofuran (5). A solution of 1-hydroxy-1-phenyl-4-pentanone[9] (178 mg, 1 mmol) in THF (10 mL) was treated with 4-Å molecular sieves (~0.5 g), benzeneselenol[14] (106 μL, 1 mmol), and $BF_3{\cdot}OEt_2$ (122 μL, 1 mmol), and the resulting mixture was stirred at room temperature for 16 h. Saturated $NaHCO_3$ (15 mL) was then added, and the reaction mixture was extracted with EtOAc (2 × 15 mL). The extracts were washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Column chromatography on silica gel (eluant: hexane then hexane/ether 2/1) gave **5** as a pale yellow oil (268 mg, 85%). ^1H-NMR spectroscopy revealed **5** to consist of an unassigned ~3/1 mixture of anomers and to be contaminated with between 5 and 10 % of PhSeSePh depending on the sample. All attempts at further purification of this compound failed to remove minor amounts of PhSeSePh resulting from decomposition on the column. ^1H NMR: δ 1.83 (minor) and 1.87 (major) (2 × s, 3H); 1.92 (m, 1H), 2.15 (m, 1H), 2.36 (m, 1H), 2.54 (m, 1H), 5.14 (minor) and 5.31 (major) (2 × t, J = 8.4 Hz for minor, 7.4 Hz for major, 1H), 7.2–7.7 (m, 10H). ^{13}C NMR: δ 30.17 (major) and 31.02 (minor), 33.82 (major) and 35.19 (minor), 40.58 (major) and 41.90 (minor), 81.15 (major) and 84.18 (minor), 93.55 (minor) and 93.93 (major), 126.07, 126.68, 127.50 (major) and 127.58 (minor), 127.93 (major) and 128.02 (minor), 128.31 (minor) and 128.39 (major), 128.68 (major) and 128.76 (minor), 136.50 (major) and 136.61 (minor), 141.69 (minor) and 141.86 (major).

Methyl 2-Bromo-3-(methallyloxy)-4-methoxybenzoate (23). A mixture of **20**[21] (314 mg, 1.1 mmol), freshly activated MnO_2 (1.91 g, 22 mmol), HOAc (172 μL, 3.0 mmol), and KCN (358 mg, 5.5 mmol) in absolute MeOH (10 mL) was stirred at room temperature for 16 h and then poured into water (25 mL) and extracted repeatedly with EtOAc. After the extracts were washed with water and brine and dried (Na_2SO_4), column chromatography on silica gel (eluant: hexane/EtOAc 4/1) gave **23** as a colorless oil (339 mg, 98%). ^1H NMR: δ 1.93 (s, 3H), 3.89 (s, 6H), 4.38 (s, 2H), 4.99 (s, 1H), 5.16 (d, J = 0.9 Hz, 1H), 6.87 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H). ^{13}C NMR: δ 19.86, 52.30, 56.12, 76.49, 110.29, 113.55, 118.77, 124.86, 127.59, 141.26, 146.08, 156.86, 166.30. Anal. Calcd for $C_{13}H_{15}BrO_4$: C, 49.64; H, 4.80. Found: C, 49.26; H, 4.76.

2-Iodo-3-(methallyloxy)-4-methoxybenzaldehyde (26). A stirred solution of 2-iodoisovanillin[23] (1.11 g, 4 mmol) in dry DMF (20 mL) was treated portionwise at room temperature with NaH (60% in mineral oil, 200 mg, 5 mmol). When gas evolution had ceased, methallyl chloride (494 μL, 5 mmol) was added by syringe and the reaction mixture was brought to 70 °C for 4 h before it was cooled to room temperature, diluted with water (30 mL), and extracted with EtOAc (3 × 20 mL). The extracts were washed with water and brine, dried (Na_2SO_4), evaporated, and then subjected to chromatography on silica gel (eluant: hexane/EtOAc 2/1) to give **26** as pale yellow needles (1.25 g, 94%): mp 65–66 °C. ^1H-NMR: δ 1.96 (s, 3H), 3.94 (s, 3H), 4.01 (s, 2H), 5.03 (s, 1H), 5.20 (s, 1H), 6.97 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 10.03 (s, 1H). ^{13}C-NMR: δ 19.99, 56.18, 76.32, 100.58, 111.79, 113.64, 127.26, 129.00, 140.97, 147.64, 157.71, 195.11. Anal. Calcd for $C_{12}H_{13}IO_3$: C, 43.40; H, 3.95. Found: C, 43.48; H, 3.89.

Methyl 2-Iodo-3-(methallyloxy)-4-methoxybenzoate (27). The ester **27** was prepared from aldehyde **26** (665 mg) exactly as described for the preparation of **23** from **20**. After chromatography on silica gel (eluant: hexane/EtOAc 4/1), it was isolated as a pale yellow oil (698 mg, 96%). ^1H NMR: δ 1.95 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 4.37 (s, 2H), 5.01 (s, 1H), 5.20 (s, 1H), 6.89 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H). ^{13}C NMR: δ 20.00, 52.24, 56.02, 76.05, 94.70, 111.29, 113.41, 127.65, 128.13, 141.14, 148.49, 155.16, 166.70. Anal. Calcd for $C_{13}H_{15}IO_4$: C, 43.11; H, 4.17. Found: C, 43.08; H, 4.11.

Reaction of 5 with Ph_3SnH. To a solution of **5** (containing approximately 5–10% of PhSeSePh) (190 mg, 0.6 mmol) in benzene (30 mL) at reflux under Ar was added a solution of Ph_3SnH (262 mg, 0.9 mmol) and AIBN (10 mg, 0.06 mmol) in benzene (20 mL) dropwise over 16 h with the aid of a motor-driven syringe pump. After a further 2 h at reflux, the reaction mixture was allowed to cool to room temperature and the volatiles were removed under vacuum. Inspection of the crude reaction mixture by ^1H-NMR spectroscopy revealed the reduction product **3**[9,25] (>95%) and the elimination product **6**[26] (<5%). No evidence was found for formation of the ketone **4**.[9]

Reaction of Acetobromoglucose (7) with Bu_3SnH. The β-(Acyloxy)alkyl Rearrangement. A solution of Bu_3SnH (105 mg, 0.36 mmol) and AIBN (2.5 mg, 0.015 mmol) in benzene (10 mL) was added dropwise over 3 h with the aid of a motor-driven syringe pump to a solution of **7**[27] (123 mg, 0.30 mmol) in benzene (10 mL) at reflux under Ar. After a further

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1 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. Examination of the crude reaction mixture by ^{1}H NMR revealed complete conversion of the substrate and formation of the products **8** and **9** in the ratio 89:11 (Table 1, entry 3) with spectral data identical to that described in the literature.[15] Similar experiments were conducted in the presence of PhSeH (10 mol %), PhSeSePh (10 mol %), and PhSH (10 mol %) added to the initial benzene solution of **7** with the results described in entries 4–6, respectively, of Table 1.

Reaction of 2-Bromo-1-phenylethyl Diphenyl Phosphate (10) with Bu_3SnH. The β-(Phosphatoxy)alkyl Rearrangement. A solution of Bu_3SnH (87 mg, 0.3 mmol) and AIBN (2 mg, 0.015 mmol) in benzene (10 mL) was added dropwise over 4 h with the syringe pump to a solution of **10**[16a] (108 mg, 0.25 mmol) at reflux under Ar in benzene (10 mL). After a further 1 h at reflux, the reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. Examination of the crude reaction mixture by ^{1}H NMR revealed complete consumption of the substrate and formation of the products **11** and **12** in the ratio 47:53 (Table 1, entry 7) with spectral data identical to those of authetic samples.[16a] When the reaction was repeated in the presence of 10 mol % of PhSeH in the initial solution of **10**, the final ratio of **11**:**12** was 13:87 (Table 1, entry 8).

Reaction of 3-Bromo-2-(allyloxy)tetrahydropyran (13) with Bu_3SnH. The 5-Hexenyl Rearrangement. To a solution of **13**[18] (221 mg, 1.0 mmol) in benzene (10 mL) at reflux under Ar was added, by means of a syringe pump, a solution of Bu_3SnH (350 mg, 1.2 mmol) and AIBN (8.2 mg, 0.05 mmol) in benzene (12 mL) dropwise over 2 h. After a further 30 min at reflux, the reaction mixture was cooled to room temperature and the solvent removed under vacuum. ^{1}H-NMR spectroscopy indicated that the cyclized product **14**[18] was formed essentially quantitatively and as a 5:1 mixture of diastereomers. The anomeric hydrogen in the major and minor diastereomers had δ 5.28 (d, J = 3.8 Hz) and 5.00 (d, J = 3.6 Hz), respectively (Table 1, entry 9). A similar experiment was conducted with 10 mol % of PhSeSePh added to the initial benzene solution of **13** with the result described in Table 1, entry 10. In a second set of experiments, Bu_3SnH (350 mg, 1.2 mmol) and AIBN (8.2 mg, 0.05 mmol) in benzene (6 mL) were added to a solution of **13** (221 mg, 1.0 mmol) in benzene (5 mL) at reflux over 6 min followed by heating to reflux for 30 min with the result outlined in Table 1, entry 11. In the presence of 10 mol % of PhSeSePh, these conditions gave the result of entry 12, Table 1.

Reaction of *Se*-Phenyl *O*-Allylselenosalicylate (16) with Bu_3SnH. An Acyl Radical Cyclization. A solution of **16**[7d] (63 mg, 0.20 mmol), Bu_3SnH (70 mg, 0.24 mmol), and AIBN (3.3 mg, 0.02 mmol) in benzene (10 mL) was heated to reflux for 2 h. After the solution was cooled to room temperature, the solvent was removed *in vacuo*. Examination of the crude reaction mixture by ^{1}H NMR revealed the essentially quantitative formation of the cyclization product **17** (Table 1, entry 13).[7d] When the reaction was conducted in the presence of 10 mol % of PhSeH, the crude reaction mixture was found to consist of **17** and the reduction product **18** in the ratio 82:18. The benzyl alcohol **18**[28] was identified by comparison with an authentic sample prepared by $LiAlH_4$ reduction of ethyl *O*-allylsalicylate. ^{1}H NMR: δ 4.60 (dt, J = 5.1, 1.5 Hz, 2H), 4.72 (s, 2H), 5.30 (dq, J = 10.5, 1.4 Hz, 1H), 5.42 (dq, J = 17.3, 1.6 Hz), 6.01–6.13 (m, 1H), 6.86–7.30 (m, 4H).

Reaction of Methyl 2-Iodo-3-(methallyloxy)-4-methoxybenzoate (27) with Bu_3SnH. The Neophyl Rearrangement. Isolation of 4-Carbomethoxy-2,3-dihydro-3,3-dimethyl-7-methoxybenzofuran (24) and 5-Carbomethoxy-2,3-dihydro-3-methyl-8-methoxybenzopyran (25). A solution of **27** (181 mg, 0.50 mmol), Bu_3SnH (175 mg, 0.60 mmol), and AIBN (8.2 mg) in benzene (20 mL) was irradiated with a 250-W sunlamp for 3 h in such a way that the heat generated by the lamp maintained the solution at gentle reflux. After removal of the solvent *in vacuo*, ^{1}H-NMR examination revealed a clean reaction mixture consisting only of **24** and **25** in the ratio of 60:40 (Table 1, entry 17). The reaction mixture was taken up in CH_2Cl_2 (1 mL), treated with Et_3N (1 drop),[29] and charged onto a silica gel column. Elution first with hexane and then with CH_2Cl_2 gave first **24** as a colorless oil (69 mg, 58%). ^{1}H NMR: δ 1.49 (s, 6H), 3.87 (s, 3H), 3.92 (s, 3H), 4.28 (s, 2H), 6.77 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 8.6 Hz). ^{13}C NMR: δ 25.48, 44.36, 51.60, 55.87, 86.08, 109.99, 119.67, 125.02, 137.63, 148.14, 148.57, 166.44. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.07; H, 6.90. Further elution gave **25** as a white crystalline solid (44 mg, 37%): mp 66–67 °C (needles from hexane). ^{1}H NMR: δ 1.07 (d, J = 6.7 Hz, 3H), 2.11 (m, 1H), 2.69 (dd, J = 9.8 and 17.9 Hz), 3.30 (ddd, J = 2.2, 5.5 and 17.8 Hz), 3.73 (t, J = 10.0 Hz), 3.85 (s, 3H), 3.92 (s, 3H), 4.29 (ddd, J = 2.2, 3.3 and 10.3 Hz, 1H), 6.74 (d, J = 8.6 Hz), 7.58 (d, J = 6.8 Hz, 1H). ^{13}C NMR: δ 17.05, 26.68, 32.33, 51.60, 55.87, 71.62, 107.69, 121.61, 123.89, 124.93, 144.02, 152.65, 167.37. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.77; H, 6.77. In a parallel experiment PhSeSePh (10 mol %) was added to the initial reaction mixture, resulting in the formation of **24** and **25** in the ratio of 80:20 (Table 1, entry 18). A second set of experiments was conducted in the identical manner using **27** (73 mg, 0.20 mmol), Bu_3SnH (70 mg, 0.24 mmol), and AIBN (3.3 mg, 0.02 mmol) in benzene (20 mL), resulting in the formation of **24** and **25** in the ratio of 20:80 in the absence of PhSeSePh and 90:10 in the presence of 10 mol % of PhSeSePh (Table 1, entries 19 and 20).

Reaction of Methyl 2-Bromo-3-(methallyloxy)-4-methoxybenzoate (23) with Bu_3SnH. The reaction of **23** with Bu_3SnH was conducted as described above for **27** with the results listed in Table 1, entries 15 and 16.

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Supplementary Material Available: Copies of ^{1}H- and ^{13}C-NMR spectra of **5** (2 pages). This material is contained in 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.

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