Polarity-Reversal-Catalyzed Hydrostannylation Reactions: Benzeneselenol-Mediated Homolytic Hydrostannylation of Electron-Rich Olefins

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Dedicated to the memory of Professor *Hanns Fischer*. We take for granted his many contributions to the field of radical chemistry. I am particularly indebted to his careful and patient explaining to me of the 'persistent radical effect' over a drink, on a balmy New Hampshire evening.

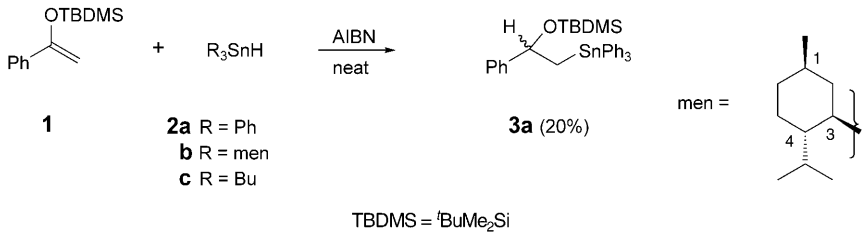
Addition of 10 mol-% of diphenyl diselenide to hydrostannylation reactions involving electron-rich olefins results in a dramatic improvement in yield. For example, reaction of α-{[(*tert*-butyl)dimethylsilyl]-oxy}styrene (**1**) with triphenylstannane (**2a**; 1.1 equiv.) in the presence of PhSeSePh and 2,2′-azobis[2-methylpropanenitrile] (AIBN) affords {2-{[(*tert*-butyl)dimethylsilyl]oxy}-2-phenylethyl}triphenylstannane (**3a**) in 95% yield after 2 h. This reaction presumably benefits, by the increased rate of H-atom transfer, from the *in situ* generated polarity-reversal catalyst, benzeneselenol.

Introduction. – Intermolecular free-radical additions of stannyl radicals to multiple bonds have emerged as important methods for the preparation of tetraorganylstannanes which can be reacted further to afford new C–C bonds through a variety of transition-metal-mediated coupling processes [1]. As part of an ongoing research program exploring new stereoselective free-radical processes [2], we were interested in the hydrostannylation of silyl enol ethers with chiral trialkylstannanes.

Previous work suggested to us that free-radical hydrostannylation reactions involving trialkylstannanes proceeded most efficiently with electron-deficient olefins [3], with few examples of olefins bearing electron-donating groups providing synthetically useful outcomes [4]. This guiding principle was indeed found to operate for reactions involving α-{[(*tert*-butyl)dimethylsilyl]oxy}styrene (={1-{[(*tert*-butyl)dimethylsilyl]oxy}ethenyl}benzene; **1**). Overnight reaction of **1** with triphenylstannane (**2a**; 1.1 equiv.) in the presence of 2,2′-azobis[2-methylpropanenitrile] (AIBN) at 80° and in the absence of solvent afforded a 20% yield of the desired stannane, {2-{[(*tert*-butyl)dimethylsilyl]-oxy}-2-phenylethyl}triphenylstannane (**3a**), while the sterically more demanding chiral stannane tri[(1*R*,3*R*,4*S*)-menthyl]stannane (=tris[(1*R*,2*S*,5*R*)-2-(1-methylethyl)-5-methylcyclohexyl]stannane; **2b**) [5] returned only starting material after prolonged

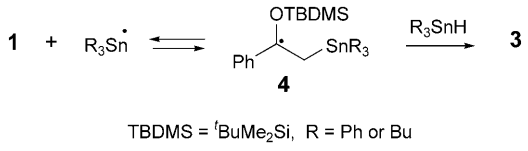
heating with **1** at 140° in the absence of solvent, even when large excesses of stannane **2b** (5 equiv.) were employed (*Scheme 1*)[1]).

Scheme 1



While steric factors are undoubtedly partly responsible for these outcomes, it is quite likely that reversible fragmentation is also responsible for the problems that we encountered in these systems. It is well established that hydrostannylation reactions of medial alkenes can be problematic because the addition of the nucleophilic stannyl radical to the alkene is a reversible process [4]. In other words, the rate of (reversible) β-fragmentation of the adduct radical **4** is competitive with H-atom abstraction from the stannane (*Scheme 2*).

Scheme 2



Roberts demonstrated that trialkylsilanes, in the presence of a catalytic amount of a thiol, are capable of reducing alkyl halides and other precursors [6]. Dubbed 'polarity-reversal catalysis' by *Roberts*, the success of this chemistry, has been attributed to favorable polar effects in the transition state for H-atom transfer from an S- to a C-centered radical (*e.g.*, **5**) over the less favorable transition state (*e.g.*, **6**) and has been supported by computational-chemistry techniques [7]. A similar catalytic phenomenon has been described by *Crich* and co-workers for reactions involving stannanes catalyzed by benzeneselenol, a technique that effectively extends the kinetic range of stannane-mediated reactions [8]. It is interesting to note that *Roberts* showed that alkenes could be easily hydrosilylated by using silane/thiol mixtures [9].

[1]) It is interesting to note that the analogous trimethylsilyl enol ether product 2-{[(trimethylsilyl)oxy]-2-phenylethyl}triphenylstannane failed to survive either of these reaction conditions.

Given this rich history, we were surprised to discover that, apart from one example that utilized Bu_3SnH/ArSH to double hydrostannylate terminal alkynes [10], polarity-reversal catalysis has, to the best of our knowledge, not been applied to hydrostannylation chemistry of alkenes. We now report that hydrostannylation of olefins, especially electron-rich alkenes can be significantly improved by the introduction of a polarity-reversal catalyst (benzeneselenol) into the reaction mixture.

Results and Discussion. – We began this study by examining the reaction of α-{[(*tert*-butyl)dimethylsilyl]oxy}styrene (**1**) with tributylstannane (**2c**) at 80° in the absence of solvent (AIBN initiator). Benzeneselenol (PhSeH) was generated by the *in situ* method described by *Crich* and co-workers [8], that is by the rapid ionic reaction of diphenyl diselenide with **2c** (*Scheme 3*). The outcomes of this initial investigation are listed in *Table 1*.

Scheme 3

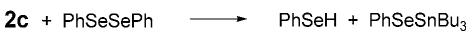


Table 1. *Reaction of Tributylstannane* (**2c**) *with Enol Ether* **1** *in the Presence of Diphenyl Diselenide* (see text)

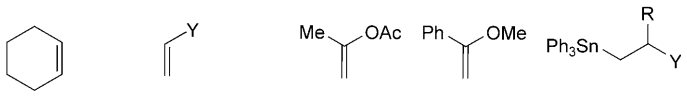
Entry	**2c**[a])	PhSeSePh[a])	**2c** (effective)[b])	Yield of **3c**[c]) [%]
1	0.97	0.08	0.89	30
2	1.05	0.05	1.0	43
3	1.05	0.08	0.97	55
4	1.50	0.11	1.39	99
5	1.31	0.14	1.17	87

[a]) Equiv. relative to **1**. [b]) Adjusted taking *Scheme 3* into account. [c]) Isolated yield.

Inspection of *Table 1* reveals that good yields are possible for the hydrostannylation of **1** without the need for forcing conditions, with *ca.* 10% PhSeSePh and 1.2–1.4 effective equiv. of Bu_3SnH providing yields of tributyl{2-{[(*tert*-butyl)dimethylsilyl]oxy}-2-phenylethyl}stannane (**3c**) approaching quantitative. It should be noted that in the absence of added catalyst, no reaction was observed even when 1.5 equiv. of the Bu_3SnH was used. Presumably, this reaction benefits by the improved rate of H-atom transfer from benzeneselenol to **4** [11], resulting in reduced competition from the reversible fragmentation depicted in *Scheme 2*.

We next turned our attention to the reaction of substrates **1**, and **7**–**14** with triphenylstannane (**2a**). The results of experiments in which these substrates were treated with 1.1 and 0.1 equiv. of **2a** and PhSeSePh, respectively, in the presence of AIBN at 80° and in the absence of solvent are reported in *Table 2*.

The data presented in *Table 2* clearly highlight the beneficial effect that addition of diphenyl diselenide, through its action as the polarity-reversal catalyst, benzeneselenol, has on the electron-rich olefins in this study. As expected, *Entries 2–4* show that hydrostannylation reactions in which either electron-deficient (see **8** and **9**) or unsubstituted terminal (see **10**) olefins are employed derive no benefit through the introduction of a polarity-reversal catalyst. We were surprised to discover that the hydrostannylation of



7 **8** Y = CN, **9** Y = CO_2Me, **10** Y = $(CH_2)_4Me$, **11** Y = Ph, **12** Y = $O(CH_2)_2OH$ **13** **14** **15**

Table 2. *Reaction of Triphenylstannane* (**2a**; 1.1 equiv.) *with Substrates* **1** *and* **7**–**14** *at 80°* (AIBN) *in the Absence of Solvent* (see text)[a])

Entry	Substrate[b])	Yield of **3a** or **15**[c])[d]) [%]	Yield of **3a** or **15**[d])[e]) [%]
1	**7**	trace	trace
2	**8**	95	98
3	**9**	94	97
4	**10**	96	93
5	**11**	92	63
6	**12**	94	77
7	**13**	78	44
8	**14**	90	71
9	**1**	95	20

[a]) All reactions were performed at 80±3° for 2.5 h under stirring. [b]) Equiv. of reagent given relative to this substrate. [c]) 10 mol-% of PhSeSePh added. [d]) Isolated yield. [e]) No catalyst added.

styrene (**11**) afforded stannane **15** (R = H, Y = Ph) in moderate yield after 40 min, together with an unidentified by-product that may well be oligomeric in nature. The formation of this by-product is completely suppressed by the addition of 10 mol-% of PhSeSePh to the reaction mixture, affording the desired hydrostannylated product in 92% yield in under 10 min. It is interesting to note that attempts to hydrostannylate styrene and diethenylbenzene can be inefficient [4], but can be assisted by the addition of *Lewis* acid catalysts [12] or sonication [13].

Entries 6–10 demonstrate the beneficial effect that the addition of PhSeSePh has on chemistry involving electron-rich olefins, with the most dramatic improvement observed for reactions involving the (*tert*-butyl)dimethylsilyl ether **1**, in which the yield rose from 20% to 95% after 2.5 h when 10 mol-% of PhSeSePh was included. It is interesting to note that the hydrostannylation of vinyl acetate with triisobutylstannane has been reported to proceed in 92% yield after 22 h at 50° [14].

The typical procedure (see *Exper. Part*) involved addition of diphenyl diselenide (0.1 equiv.) to a homogeneous mixture of triphenylstannane (**2a**; 1.1 equiv.), olefin **1** (1.0 equiv.), and a few crystals of AIBN under Ar, followed by heating to 80° for 2.5 h. The product **3a** was isolated directly from the reaction mixture by flash chromatography. This procedure deserves comment. In previous, uncatalyzed experiments in which large excesses of stannane were employed, tedious workup conditions that included several repeated chromatographic purification steps were necessary to obtain a product of acceptable purity. The conditions described above are a significant

improvement in that high-purity product is obtained after a single purification step, largely because the by-product $PhSeSnPh_3$ behaves discreetly upon chromatography.

Finally, our inability to improve the outcome of the reaction involving cyclohexene (*Table 2*, *Entry 1*) deserves comment. As previously discussed, medial alkenes are hydrostannylated inefficiently, an outcome ascribed to competitive reversible fragmentation of the adduct radical. We suggest that $Ph_3Sn^{\bullet}$ undergoes competitive homolytic substitution at the Se-atom in benzeneselenol with expulsion of phenyl radical, and it is this chemistry that dominates to the exclusion of homolytic addition to cyclohexene.

While we were initially surprised that polarity-reversal catalysis was unable to disrupt this competitive equilibrium, our hypothesis is supported by available rate-constant data. While, to the best of our knowledge, no rate data exist for the addition of triphenylstannyl radicals to cyclohexene, based on data available for related systems [15], this radical is likely to add to cyclohexene with a rate constant several orders of magnitude slower than those for the analogous reactions involving terminal olefins, and with a rate constant about one order of magnitude slower than that for homolytic substitution at the Br-atom in bromobenzene [16]. *Crich* and co-workers had noted that 'the catalytic species, PhSeH, itself is more rapidly cleaved by Bu_3SnH than aryl bromides' [17].

In conclusion, we have demonstrated that homolytic hydrostannylation reactions of electron-rich alkenes derive considerable benefit, through improved yield as well as reaction and purification conditions, by inclusion of benzeneselenol as polarity-reversal catalyst.

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Experimental Part

*{2-{[(*tert-*Butyl)dimethylsilyl]oxy}-2-phenylethyl}triphenylstannane* (**3a**). Diphenyl diselenide (0.1 equiv.) was added to a homogeneous mixture of triphenylstannane (**2a**; 1.1 equiv.), **1** (1.0 equiv.), and a few crystals of AIBN, under Ar. The resulting yellow soln. rapidly became colorless. The mixture was heated for 2.5 h at 80° and then cooled. The resulting residue was purified by flash chromatography (*Scharlau* silica gel *60* (230–400 mesh), hexanes/AcOEt (1% Et_3N) 10:1): **3a** (95%). Colorless oil. IR (neat): 3064, 2953, 1950, 1877, 1817, 1429, 1219, 1074, 1060. ^{1}H-NMR (400 MHz, $CDCl_3$): −0.77 (*s*, 3 H); −0.81 (*s*, 3 H); 0.74 (*s*, 9 H); 2.10 (*dd*, *J* = 7.6, 12.8, 1 H); 2.19 (*dd*, *J* = 13.2, 4.8, 1 H); 5.21 (*dd*, *J* = 7.2, 5.2, 1 H); 7.16–7.20 (*m*, 4 H); 7.27–7.41 (*m*, 15 H); 7.60–7.63 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): −4.9; −4.7; 18.3; 25.9 (3 C); 26.6; 73.8; 126.0; 127.0; 128.2; 128.3 (6 C); 128.5; 137.0 (6 C); 139.4 (3 C); 146.6. ^{119}Sn-NMR (150 MHz, $CDCl_3$): 124.8 ($(Bu_3Sn)_2O$ δ 82). Anal. calc. for $C_{32}H_{38}OSiSn$: C 65.65, H 6.54, Sn 20.28; found: C 65.68, H 6.53, Sn 20.35.

REFERENCES

[1] M. W. Carland, C. H. Schiesser , 'Synthetic uses of R_3MH (Me = Ge, Sn, Pb)', in 'The Chemistry of Organic Germanium, Tin and Lead Compounds', Vol. 2, Ed. Z. Rappoport, John Wiley & Sons, Chichester, 2002, and refs. cit. therein.

[2] D. Dakternieks, A. Duthie, L. Zeng, V. T. Perchyonok, C. H. Schiesser, *Tetrahedron: Asymmetry* **2004**, *15*, 2547; L. Zeng, V. T. Perchyonok, C. H. Schiesser, *Tetrahedron: Asymmetry* **2004**, *15*, 995; D. Dakternieks, V. T. Perchyonok, C. H. Schiesser, *Tetrahedron: Asymmetry* **2003**, *14*, 3057; D. Dakternieks, K. Dunn, V. T. Perchyonok, C. H. Schiesser, *Chem. Commun.* **1999**, 1665.

[3] D. P. Curran, G. Gualtieri, *Synlett* **2001**, 1038; S. D. Mandolesi, L. C. Koll, J. C. Podestá, *J. Organomet. Chem.* **1999**, *587*, 74.
[4] A. G. Davies, 'Organotin Chemistry', Wiley-VCH, Chichester, 2004; see also: S. Tanaka, T. Nakamura, H. Yorimitsu, H. Shinokubo, K. Oshima, *Org. Lett.* **2000**, *2*, 1911; D. P. Curran, S. Hadida, S.-Y. Kim, Z. Luo, *J. Am. Chem. Soc.* **1999**, *121*, 6607.
[5] D. Dakternieks, K. Dunn, C. H. Schiesser, E. R. T. Tiekink, *J. Organomet. Chem.* **2000**, *605*, 209.
[6] B. P. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25, and refs. cit. therein.
[7] C. H. Schiesser, M. A. Skidmore, *J. Chem. Soc., Perkin Trans. 2* **1998**, 2329.
[8] D. Crich, X. Hao, M. Lucas, *Tetrahedron* **1999**, *55*, 14251; D. Crich, J.-T. Hwang, H. Liu, *Tetrahedron Lett.* **1996**, *37*, 3105; D. Crich, X-Y. Jiao, Q. Yao, J.-S. Harwood, *J. Org. Chem.* **1996**, *61*, 2368; D. Crich, Q. Yao, *J. Org. Chem.* **1995**, *60*, 84.
[9] M. B. Haque, B. P. Roberts, D. A. Tocher, *J. Chem. Soc., Perkin Trans. 1* **1998**, 2881; H. S. Dang, B. P. Roberts, *Tetrahedron Lett.* **1995**, *36*, 2875.
[10] J.-C. Meurice, M. Vallier, M. Ratier, J.-C. Duboudin, M. Pétraud, *J. Organomet. Chem.* **1997**, *587*, 67.
[11] M. Newcomb, S.-Y. Choi, J. H. Horner, *J. Org. Chem.* **1999**, *64*, 1225; M. Newcomb, *Tetrahedron* **1993**, *49*, 1151.
[12] V. Gevorgyan, J.-X. Liu, Y. Yamamoto, *Chem. Commun.* **1998**, 37.
[13] E. Nakamura, Y. Imanishi, D. Machii, *J. Org. Chem.* **1994**, *59*, 8178.
[14] W. P. Neumann, H. Niermann, R. Sommer, *Liebigs Ann. Chem.* **1962**, *659*, 27.
[15] K. U. Ingold, J. Lusztyk, J. C. Scaiano, *J. Am. Chem. Soc.* **1984**, *106*, 343.
[16] D. P. Curran, C. P. Jasperse, M. J. Totleben, *J. Org. Chem.* **1991**, *56*, 7169.
[17] D. Crich, J.-T. Hwang, S. Gastaldi, F. Recupero, D. J. Wink, *J. Org. Chem.* **1999**, *64*, 2877.

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