Tin Radical Addition to Alkynyl Sulfides: Reactivity of the Intermediate Thioalkyl-Substituted β-(Tributylstannyl)vinyl Radicals

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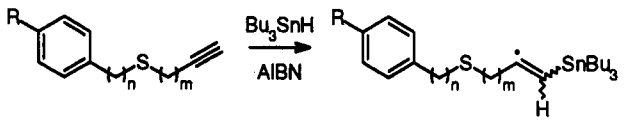
Phenyl and benzyl alkynyl sulfides **1a–g** and **3a**, phenylalkynylamines **19a,b**, ethers **22a,b**, and selenide **31** reacted with tributyltin radicals to give intermediate β-stannylvinyl radicals, whose fate depended on the nature of the side chain. 4-Phenylthio-substituted but-1-en-2-yl radicals underwent stereospecific 5-exo cyclization on the adjacent phenyl ring. The resulting spirocyclohexadienyl radicals gave thiophenes and thiopyrans by carbon–sulfur bond scission or ring expansion on the exocyclic double bond, respectively. Similar behavior was exhibited by the corresponding selenium-containnig radical, which afforded a selenophene almost exclusively. (Benzylthio)alkyl-substituted radicals gave products deriving from intramolecular S_H2 substitution at the sulfur atom, whereas propargyl sulfides yielded a stannylallene via a β-scission reaction. No 6(or more)-membered ring closure was observed with pentynyl and hexynyl phenyl sulfides **1b,c**, which gave only the (*E*)-addition products of tin hydride; oxygen- and nitrogen-containing vinyl radicals also gave the (*E*)-adducts exclusively. An interaction between the unpaired electron orbital and the empty low-energy orbitals of the heteroatom might explain why sulfur and selenium can undergo 5-exo cyclization.

For more than a decade, radical reactions have drawn the attention of organic chemists from both a mechanistic and a synthetic perspective.[1] Vinyl radicals are widely studied intermediates that have been employed in synthetically useful cyclization and annulation reactions. They have usually been generated from vinyl halides by the standard tin hydride approach[2] and from alkynes by addition of carbon-,[3] tin-,[4] sulfur-,[5] or selenium-centered[6] radicals.

In our studies of radical chemistry, we have accomplished annulations that involve the formation of vinyl radicals as the key step. In these reactions, a radical adds intermolecularly to the carbon–carbon triple bond of an alkyne, and the resulting vinyl radical cyclizes onto the aromatic ring present in the first radical.[5c,7]

Scheme 1



1a-g (R = H) **3a** (R = Me) **2a-g** (R = H) **4a** (R = Me)

a: n = 0, m = 2; **b**: n = 0, m = 3; **c**: n = 0, m = 4; **d**: n = 1, m = 2; **e**: n = 1, m = 3; **f**: n = 1, m = 1; **g**: n = 0, m = 1.

In this paper, we report on our research into the reactivity of vinyl radicals that bear a sulfur atom in the side chain[5b,c,8] and describe the behavior of radicals **2a–g**, generated by regioselective addition of stannyl radicals to the appropriate phenylthio- and benzylthio-substituted alkynes **1a–g** (Scheme 1). Our study investigated the feasibility of an intramolecular cyclization onto the adjacent phenyl ring to obtain stannylated sulfur-containing heterocycles. These compounds can be useful precursors of a wide range of derivatives via a tin–lithium exchange reaction or a palladium-mediated coupling with alkyl, vinyl, or acyl halides.[9]

Results and Discussion

Stannyl radicals were generated by the tributyltin hydride method. The reactions were generally carried out

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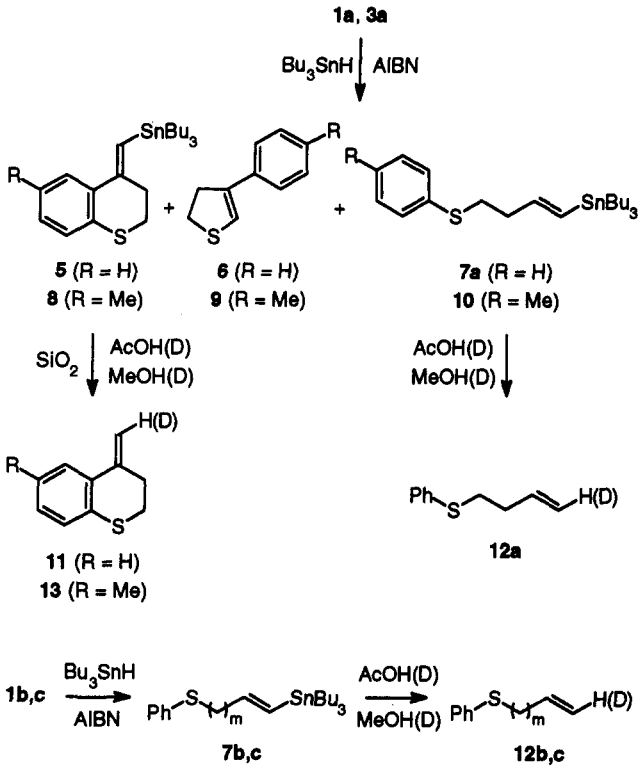
Scheme 2



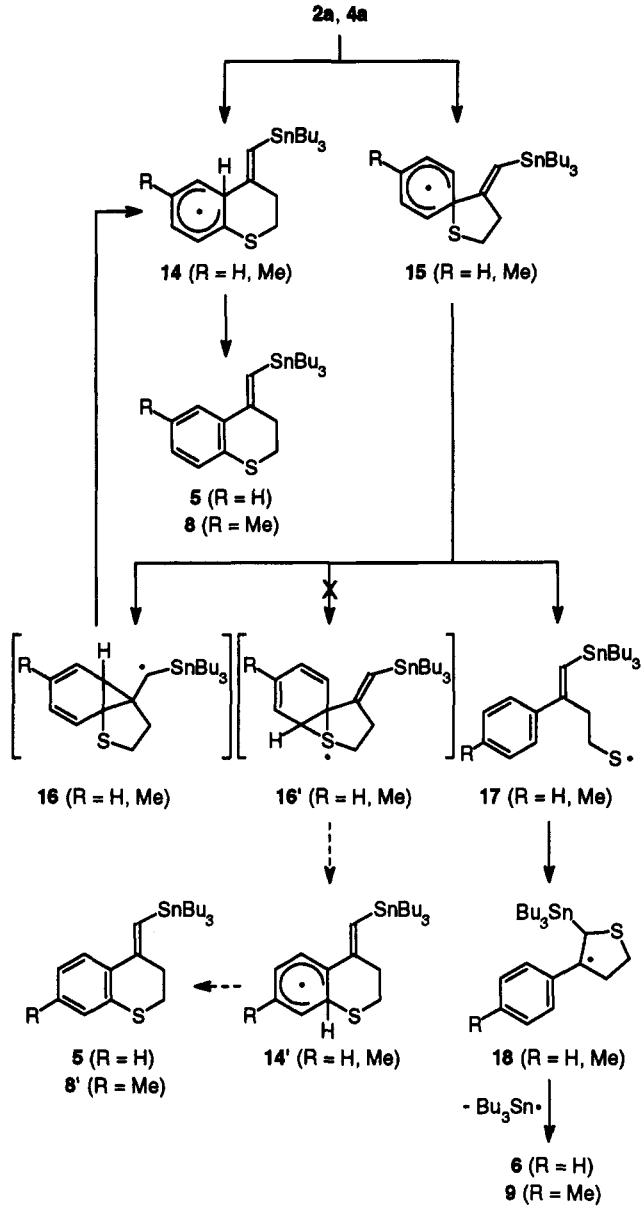
at a very low concentration of hydride to minimize the formation of hydrostannylated products **7**, which arise from a competing hydrogen abstraction reaction of radicals **2** (Scheme 2). This condition was achieved through slow addition of tin hydride to the reaction mixture. In a typical experiment, a benzene solution of equimolar amounts of tributyltin hydride and α,α'-azobisisobutyronitrile (AIBN) was added, by a syringe pump, to a refluxing 0.1 M solution of alkynyl sulfides **1a–g** (1 equiv) and AIBN (0.2 equiv). After 30 min at reflux, the reaction mixture was generally analyzed by GC–MS and ^{1}H NMR and chromatographed on a silica gel column.

The reaction of 4-(phenylthio)but-1-yne (**1a**) furnished thiopyran **5**, thiophene **6**, and alkene **7a** in an apparently 1:2:3 ratio and 85% overall yield. The **5**/**6**/**7a** ratio changed from 1:2:3 to 1:2:1 when we diluted the starting mixture from 0.1 to 0.02 M, whereas a high concentration of tin hydride afforded **7a** almost exclusively.

The stannylated alkene **7a** was the expected addition product derived from radical **2a** through hydrogen atom transfer from tin hydride. In all cases, the (*E*)-adduct greatly predominated over the (Z)-isomer, whose structure was easily deduced by ^{1}H NMR analysis. The ^{1}H NMR spectrum of (*E*)-**7a** was quite puzzling, because the two *trans*-vinylic protons produced a very complicated multiplet at $\delta = 6.0$, which was finally interpreted by computer simulation (see Experimental Section). Structural assignment was made based on chemical evidence: protodestannylation in methanol/acetic acid solution[10] gave **12a**, whereas deuterodestannylation of the reaction mixture in deuterated acetic acid and methanol[10] led to the (*E*)-1-deuterio-substituted (*E*)-[1-D]-**12a**.

The dihydrothiophene **6** was present in the reaction mixture before workup; therefore, the removal of the tributylstannyl group most likely occurred during formation of **6** and not as the result of a subsequent protodestannylation. Compound **6** might arise from radical **2a** through a 5-exo cyclization leading to spirocyclohexadienyl radical **15** (R = H); the thiyl radical **17** (R = H) can easily derive from **15** by subsequent β-scission of the C–S bond (Scheme 3). Cyclization of **17** (R = H) on the adjacent double bond gives the radical intermediate **18** (R = H) and then thiophene **6** by displacement of a tributyltin radical. Product **6** was identified by spectral analysis and Raney-nickel reduction to 2-phenylbutane, as previously described.[11] The rearrangement of **2a** to **17** involves a 1,4-migration of an aryl group from a sulfur atom to a vinylic carbon. In recent years, similar 1,4-aryl migrations have been observed in radical additions of toluenethiols to alkynes[8] and in annulations involving imidoyl radicals.[7a,c] To our knowledge, examples of intramolecular ipso-substitution of thiyl radicals by vinyl radicals have not been reported.

Scheme 3



Formally, thiopyran **5** could arise from **2a** through a 6-membered cyclization on the adjacent phenyl ring and

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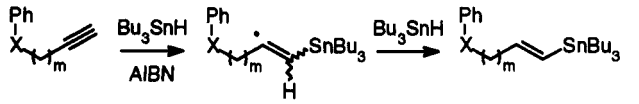
subsequent rearomatization of the resulting cyclohexadienyl radical 14 (R = H). However, 5 was not isolated, because column chromatography caused a complete protodestannylation that led to thiopyran 11, easily identified by spectral analysis and not detected in the crude product before workup (Scheme 2). The ^{1}H NMR spectrum of the reaction mixture showed that the formation of product 5 was stereospecific. The (*E*)-configuration was assigned by performing a deuterodestannylation[10] of the reaction mixture, which resulted in the (*E*)-deuteriothiopyran (*E*)-11-d_1. The observed trans-stereospecificity suggests that radical **2a** can cyclize only in its (*Z*)-configuration, consistent with previously reported results.[4b,c]

In principle, the formation of thiopyran 5 could also occur via the spiro radical 15. Cyclization of 15 on the adjacent sulfur atom could compete with β-scission and lead to the strained radical 16′ and then to the expanded 6-membered radical 14′ by fission of the C–S intraannular bond (Scheme 3). However, this pathway must be rejected, because the reaction of *p*-tolyl butynyl sulfide (**3a**) gave thiophene 9 and adduct 10, as well as thiopyran 8 which is derived from the radical intermediate 14 (R = Me). No trace of the isomer 8′ was detected. Compound 8 destannylated to 13 on a silica gel column, like the related thiopyran 5; 13 was identified by ^{1}H NMR spectroscopy and Raney-nickel reduction to 3-*sec*-butyltoluene. Alternatively, radical 15 could expand to the 6-endo radical 14 by addition to the exocyclic double bond and concomitant 1,2-migration of a carbon-carbon σ-bond. Similar ring expansions of 5-exo- to 6-endo radicals are well documented in cyclizations of β-multiply-bonded alkyl or vinyl radicals.[2d,j,12] Unfortunately, it is not possible to determine the reaction pathway, i.e., whether it is the above route or the direct 6-endo cyclization mode, since both lead to the same radical intermediate 14. However, our statement that the 5-membered spiro radical 15 might be the key intermediate in the formation of both thiopyran (5 and 8) and thiophene (6 and 9) was indirectly supported by reactions of pentynyl and hexynyl sulfides **1b,c**. Under standard conditions, these sulfides gave only the adducts (*E*)-**7b,c**, which derived from the radical intermediates **2b,c** by a hydrogen abstraction reaction. Their structures were assigned by spectral analogies with compound **7a**. The (*E*)-configuration was established for **7b** by a deuterodestannylation reaction leading to the deuterio-substituted (*E*)-[1-D]-**12b**. The absence of any cyclization product arising from radicals **2b,c** would suggest a general incapability of stannylvinyl radicals **2a–c** and **4a** to undergo 6(or more)-membered cyclizations, according to the Baldwin–Beckwith rules for homolytic ring closure.[13,14]

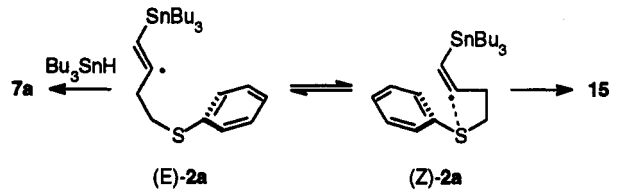
Moreover, we found evidence that the presence of a γ-sulfur atom in the side chain is essential to occurrence of the 5-exo cyclization encountered with radicals **2a** and **4a**. Stannylated alkenes (*E*)-**21b** and (*E*)-**24b** were exclusively obtained by reacting butynyl amine **19b** and butynyl ether **22b**, respectively (Scheme 4).

Scheme 4



19a,b (X = NH) **20a,b** (X = NH) **21a,b** (X = NH)
22a,b (X = O) **23a,b** (X = O) **24a,b** (X = O)
a: m = 1; **b**: m = 2.

Scheme 5



It is worth pointing out that all of the examined vinyl radicals **2a–c**, **4a**, **20b**, and **23b** abstract a hydrogen atom to give (*E*)-alkenes exclusively (or predominantly), whereas the cyclization of **2a** (and **4a**) on the phenyl ring occurred only with the (*Z*)-radical. The observed *cis*-stereospecific addition of tin hydride parallels the general behavior exhibited by β-stannylvinyl radicals[15] but contrasts with what has been observed in radical additions of thiols,[5b] chloroform,[16] silanes,[17] and selenides[6a] to terminal alkynes. These reactions give adducts arising from (*Z*)-vinyl radical intermediates through hydrogen atom transfer. In these cases, it is generally accepted that the stereochemistry is not governed by the relative abundance of the rapidly interconverting (*E*)- and (*Z*)-radicals but by the ease of approach of the scavenger. In contrast, β-stannylvinyl radicals seem to abstract a hydrogen atom only when in the (*E*)-configuration, which entails less steric repulsion between the substituent and the adjacent bulky stannyl group but is more hindered with respect to the approaching scavenger. The (*Z*)-adduct is obtained only when the vinyl radical bears a heteroatom in the β- or γ-position that is fit for complexation with tin.[18]

Thus, we suggest that the hydrogen abstraction products **7a–c**, **10**, **21**, and **24** might be thermodynamically controlled and predominantly arise from the prevalent equilibrium species, i.e., the (*E*)-radicals, whereas the cyclization products might be kinetically controlled and derive from the vinyl radicals that lead to less steric hindrance in the transition state, i.e., (*Z*)-**2a** and (*Z*)-**4a**.

The observed effect of the sulfur atom in the 5-exo cyclization is somewhat unclear. It could be due to either the longer C–S bond (relative to C–N and C–O), which may lead to a less strained transition state, or some overlap between the low-energy d-orbitals of sulfur and the unpaired electron orbital. This interaction might force the reaction centers to approach each other and achieve a configuration suitable for cyclization (Scheme 5). This effect was also observed in α-phenyl-β-(phenylthio)vinyl radicals,[5c] which undergo a facile 5-membered ring closure, as do radicals **2a** and **4a**.

The feasibility of an intramolecular attack of the vinyl radical on the sulfur atom was proven by the reaction of

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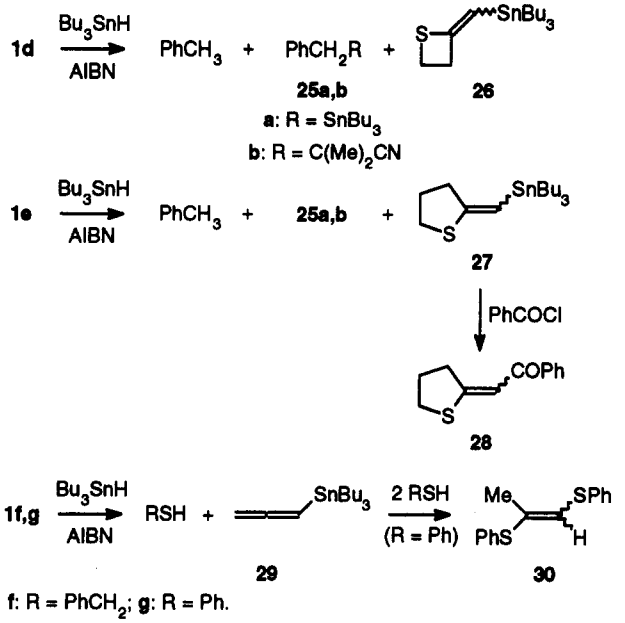
(18) Ensley, H. E.; Buescher, R. R.; Lee, K. *J. Org. Chem.* **1982**, *47*, 404.

Scheme 6



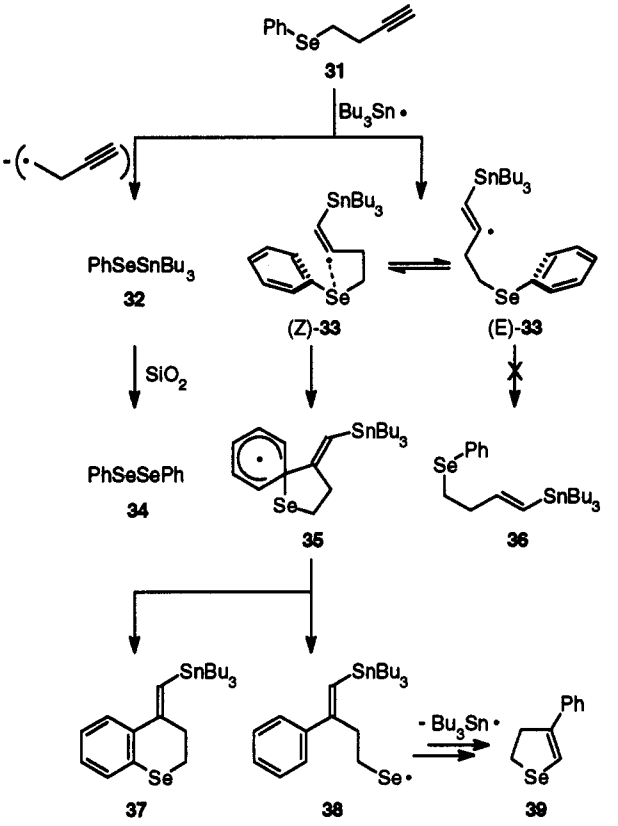
butynyl benzyl sulfide **1d** (Scheme 6). A GC–MS analysis showed the presence of significant amounts of the thietane **26**, which is the S_H2 product derived from a 4-membered radical intermediate by displacement of a stable benzyl radical. Toluene and compounds **25a,b** (the coupling products of benzyl radical with stannyl and cyanopropyl radicals) were also detected. Moreover, the pentynyl sulfide **1e** exclusively afforded a mixture of (*E*)- and (*Z*)-tetrahydrothiophenes **27**, which results from the corresponding radical **2e** through a more favorable 5-membered radical–sulfur interaction. Products **26** and **27** were not isolated because of complete destannylation that occurred during chromatographic workup. Compound **27** was fully characterized by destannylative palladium-catalyzed reaction with benzoyl chloride,[9] which gave a mixture of (*E*)- and (*Z*)-ketones **28**. The formation of both isomers (*E*)- and (*Z*)-**27** might suggest that both (*Z*)- and (*E*)-radicals **2e** are able to cyclize on the sulfur atom. This is probably a consequence of minor steric requirements in the transition state.

A similar S_H2 reaction, possibly leading to a methylenethiirane, was not observed with benzyl propargyl sulfide **1f**, which exclusively afforded the stannylallene **29** and toluenethiol, arising from radical **2f** by β-scission of the C–S bond. These fragmentations to allene **29** and thiyl radicals have been previously reported.[19]

Evidence that γ-heteroatoms, which have low-energy empty orbitals, are capable of promoting the 5-exo cyclization of stannylvinyl radicals came from the reaction of butynyl selenide **31**. Column chromatography isolated major amounts of compounds arising from S_H2 attack of the stannyl radical at the selenium atom and minor amounts of selenophene **39**, which is almost the only product derived from vinyl radical **33** (ony trace amounts of the possible selenopyran **37** were detected by GC–MS). Vinyl radical **33** would rearrange to selenyl radical **38** through the spirocyclohexadienyl **35**, in analogy to radical **2a** (and **4a**). Cyclization of selenyl radical **38** would eventually afford selenophene **39** (Scheme 7). The absence of the hydrogen abstraction product **36** might be due to

(19) Ueno, Y.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 1893.

Scheme 7



a strong interaction between the carbon radical and the selenium atom. This would greatly favor the competing reaction leading to the spirocyclohexadienyl radical **35**. In accordance with the above assumption that both 5- and 6-membered rings derive from an initial 5-exo cyclization, the virtual absence of selenopyran **37** suggests that radical **35** is not subject to a competing ring expansion, presumably owing to the fairly low energy of the C–Se bond.

The attempt to achieve 5-endo cyclization of β-stannylvinyl radicals failed. Under our reaction conditions, vinyl radical **2g** gave only β-scission to allene **29** and benzenethiol, as previously reported[19] (Scheme 6). Chromatographic workup of the reaction mixture of **1g** afforded benzenethiol, as well as significant amounts of (*E*)- and (*Z*)-bis-sulfides **30**. These compounds might arise from a double addition of the thiol to the allene **29**, followed by the removal of the tributylstannyl moiety. Finally, propargyl amine **19a** and propargyl ether **22a** only furnished the adducts (*E*)-**21a** and (*E*)-**24a**, respectively (Scheme 4).

Conclusions. The reactivity of the β-stannylvinyl radicals reported above strongly depends on the characteristics of the side chain. α-(Thioalkyl)vinyl radicals undergo a β-fragmentation reaction, giving allene **29**, when a thiyl radical can be eliminated. An intramolecular S_H2 reaction at the sulfur atom takes place when a stable benzyl radical can be displaced, viz. in radicals **2d** and **2e**. A stereospecific 5-exo cyclization of (Z)-radicals, followed by ring expansion or β-scission, is a feasible process when the alkylic chain contains a sulfur or selenium atom while 6-(or more)-membered ring closures (both endo and exo) on the adjacent aryl ring do not occur. On the contrary, nitrogen- and oxygen-containing vinyl radicals **19a,b** and **22a,b** give products arising only from hydrogen atom transfer. The effect of sulfur and selenium, in favoring

the 5-membered ring closure, might entail an interaction between their empty low-energy orbitals and the radical center. Finally, the hydrogen abstraction occurs on the (*E*)-radical almost exclusively. This distinguishes the reaction of tributyltin hydride with alkynes from the other radical additions of X–H molecules to carbon–carbon triple bonds.

Experimental Section

Structural assignments to the reaction products were generally made on the basis of ^{1}H NMR and MS spectral data. Elemental analyses of the hitherto unknown stannyl derivatives were not performed because their purification was somewhat difficult.

^{1}H NMR spectra were recorded in $CDCl_3$ solutions with Me_4Si as internal standard. Mass spectra and high-resolution mass spectra (HRMS) were determined by the electron impact method. GC–MS analyses were performed on an instrument equipped with a Quadrex 007-2-25-0.25F capillary column (gas flow = 1 mL/min). Column chromatography was carried out on Merck silica gel (0.040–0.063 particle size) by elution with light petroleum (bp 40–70 °C), unless otherwise stated.

Starting Materials. The phenyl (and *p*-tolyl) alkynyl sulfides **1a–c**, **1g**[20] (and **3a**) and the benzyl sulfides **1d,e** and **1f**[20] were prepared in ca. 80% yield by heating for 3–4 h a 0.2 M benzene solution of the appropriate alkynyl derivative (tosylate in the cases of **1a**, **1c**, **1d**, and **3a**, chloride in the cases of **1b** and **1e**, bromide in the case of **1f** and **1g**) and equimolar amounts of sodium benzenethiolate or sodium toluenethiolate, respectively. These new sulfides were obtained as oily products. But-1-yn-4-yl phenyl sulfide (**1a**): ^{1}H NMR δ = 2.05 (1H, t, J = 2.6 Hz), 2.5 (2H, dt, J_d = 2.6 Hz, J_t = 7.5 Hz), 3.07 (2H, t, J = 7.5 Hz), 7.1–7.5 (5H, m); MS m/z (rel inten) 162 (M^+, 45), 123 (100), 110 (10), 109 (10); HRMS calcd for $C_{10}H_{10}S$ 162.05032, found 162.05085.

Pent-1-yn-5-yl phenyl sulfide (**1b**): ^{1}H NMR δ = 1.85 (2H, tt, $J_1 = J_2$ = 8 Hz), 1.98 (1H, t, J = 2.6 Hz), 2.35 (2H, dt, J_d = 2.6 Hz, J_t = 8 Hz), 3.04 (2H, t, J = 8 Hz), 7.1–7.4 (5H, m); MS m/z (rel inten) 176 (M^+, 70), 148 (90), 147 (100), 135 (30) 123 (70), 110 (90), 109 (70), 77 (35), 65 (50); HRMS calcd for $C_{11}H_{12}S$ 176.06597, found 176.06623.

Hex-1-yn-6-yl phenyl sulfide (**1c**): ^{1}H NMR δ = 1.6–1.85 (4H, m), 1.94 (1H, t, J = 2.6 Hz), 2.2 (2H, dt, J_d = 2.6 Hz, J_t = 7 Hz), 2.94 (2H, t, J = 7 Hz), 7.1–7.4 (5H, m); MS m/z (rel inten) 190 (M^+, 30), 189 (40), 161 (45), 148 (40), 147 (80), 135 (40), 123 (100), 110 (95), 109 (40); HRMS calcd for $C_{12}H_{14}S$ 190.08162, found 190.08180.

Benzyl but-1-yn-4-yl sulfide (**1d**): ^{1}H NMR δ = 2.02 (1H, t, J = 2.6 Hz), 2.38–2.48 (2H, m), 2.56–2.66 (2H, m), 3.8 (2H, s), 7.30 (5H, m); MS m/z (rel inten) 176 (M^+, 75), 175 (30), 143 (40), 137 (90), 92 (50), 91 (100), 65 (70); HRMS calcd for $C_{11}H_{12}S$ 176.06597, found 176.06618.

Benzyl pent-1-yn-5-yl sulfide (**1e**): ^{1}H NMR δ = 1.71 (2H, tt, $J_1 = J_2$ = 7 Hz), 1.88 (1H, t, J = 2.6 Hz), 2.22 (2H, dt, J_d = 2.6, J_t = 7 Hz), 2.47 (2H, t, J = 7 Hz), 3.65 (2H, s), 7.1–7.3 (5H, m); MS m/z (rel inten) 190 (M^+, 10), 162 (20), 129 (45), 91 (100), 65 (40); HRMS calcd for $C_{12}H_{14}S$ 190.08162, found 190.08183.

But-1-yn-4-yl *p*-tolyl sulfide (**3a**): ^{1}H NMR δ = 2.0 (1H, t, J = 2.6 Hz), 2.30 (3H, s), 2.45 (2H, dt, J_d = 2.6 Hz, J_t = 7.5 Hz), 3.0 (2H, t, J = 7.5 Hz), 7.0 (2H, d, J = 8.5 Hz), 7.30 (2H, d, J = 8.5 Hz); MS m/z (rel inten) 176 (M^+, 90), 137 (100), 91 (40); HRMS calcd for $C_{11}H_{12}S$ 176.06597, found 176.06591.

N-Phenyl-*N*-prop-1-yn-3-ylamine (**19a**) and *N*-but-1-yn-4-yl-*N*-phenylamine (**19b**) were obtained as oily products in ca. 40–50% yield by refluxing a 0.1 M benzene solution of propargyl bromide or butynyl tosylate, respectively, for 60 h with a 3-fold excess of aniline. **19a**: ^{1}H NMR δ = 2.2–2.3 (1H, m), 3.8–4.0 (3H, m), 6.75 (2H, d, J = 8.5 Hz), 6.85 (1H, t, J = 8.5 Hz), 7.2–7.3 (2H, m); MS m/z (rel inten) 131 (M^+, 80), 130 (100), 103 (35), 102 (25), 77 (60), 65 (70); HRMS calcd for C_9H_9N 131.07350, found 131.07358. **19b**: ^{1}H NMR δ = 1.98 (1H, t, J = 2.6 Hz), 2.45 (2H, dt, J_d = 2.6 Hz, J_t = 6.5 Hz), 3.25 (2H, t, J = 6.5 Hz), 6.5–6.7 (3H, m), 7.05–7.15 (2H, m), 7.20 (NH, s); MS m/z (rel inten) 145 (M^+, 60), 107 (15), 106 (100), 77 (60); HRMS calcd for $C_{10}H_{11}N$ 145.08915, found 145.08922.

Reaction of sodium phenolate with propargyl bromide or butynyl tosylate gave the ethers **22a**[20] or **22b**, respectively, in ca. 70% yield. But-1-yn-1-yl phenyl ether (**22b**) was obtained as an oily product: ^{1}H NMR δ = 2.07 (1H, t, J = 2.6 Hz), 2.65 (2H, dt, J_d = 2.6 Hz, J_t = 7.1 Hz), 4.1 (2H, t, J = 7.1 Hz), 6.9–7.05 (3H, m), 7.25–7.4 (2H, m); MS m/z (rel inten) 146 (M^+, 40), 145 (20), 131 (20), 107 (35), 94 (100); HRMS calcd for $C_{10}H_{10}O$ 146.07316, found 146.07325.

Reaction of sodium benzeneselenolate with butynyl tosylate gave but-1-yn-1-yl phenyl selenide (**31**) in 75% yield: ^{1}H NMR δ = 2.05 (1H, t, J = 2.5 Hz), 2.55 (2H, dt, J_d = 2.5 Hz, J_t = 7.5 Hz), 3.0 (2H, t, J = 7.5 Hz), 7.2–7.3 (3H, m), 7.5–7.6 (2H, m); MS m/z (rel inten) 210 (M^+, 50), 171 (50), 158 (40), 91 (100), 78 (50); HRMS calcd for $C_{10}H_{10}Se$ 209.99477, found 209.99403. All other materials were commercially available and were used as received, except α,α'-azobisisobutyronitrile (AIBN), which was recrystallized from $CHCl_3$/methanol.

Reaction of Alkynes 1a–g, 3a, 19a,b, 22a,b, and 31 with Tributyltin Hydride. Procedure A. A benzene solution (10 mL) of tributyltin hydride (0.54 mL, 2 mmol) and AIBN (330 mg, 2 mmol) was added during 3 h by a syringe pump to a boiling solution of the appropriate alkyne (2 mmol) and AIBN (65 mg, 0.4 mmol) in benzene (20 mL, unless otherwise stated). The reaction mixture was allowed to reflux for a further 30 min and then was directly analyzed by GC–MS (temperature programming = 80–260 °C; rate = 15 °C/min). After removal of the solvent, the residue was analyzed by ^{1}H NMR and then chromatographed on silica gel column. All the reactions described below were performed according to this procedure, unless otherwise stated.

Procedure B. A benzene solution (20 mL) of the appropriate alkyne (2 mmol), tributyltin hydride (0.54 mL, 2 mmol), and AIBN (65 mg, 0.4 mmol) was refluxed for 2 h. The resulting reaction mixture was treated as described in procedure A.

From But-1-yn-4-yl Phenyl Sulfide (1a). Chromatography gave a ca. 20:1 mixture of (*E*)- and (*Z*)-4-(phenylthio)-1-(tributylstannyl)but-1-ene [(*E*)- and (*Z*)-**7a**] (500 mg, 55%) [^{1}H NMR $\delta_{(E)\text{-isomer}}$ = 0.8–0.95 (15H, m), 1.2–1.6 (12H, m), 2.4–2.52 (2H, m, collapsing to triplet, J = 7.5 Hz, upon irradiation at δ = 6.0), 2.98 (2H, t, J = 7.5 Hz, collapsing to singlet upon irradiation at δ = 2.45), 5.96–6.01 (2H, m, collapsing to a broad singlet upon irradiation at δ = 2.45; computer simulation gave an ABX_2 system, J_{AB} = 18 Hz, J_{AX} = 4.0 Hz, J_{BX} = 1.3 Hz, inner lines separation = 2 Hz), 7.1–7.4 (5H, m); $\delta_{(Z)\text{-isomer}}$ = 0.8–1.0 (15H, m), 1.2–1.6 (12H, m), 2.3–2.45 (2H, m), 2.95 (2H, t, J = 7 Hz), 5.93 (1H, dt, J_d = 12 Hz, J_t = 1 Hz), 6.55 (1H, dt, J_d = 12 Hz, J_t = 7 Hz), 7.2–7.4 (5H, m); MS m/z (rel inten) 397 (M^+ – 57, 60), 341 (50), 283 (30), 229 (75), 163 (100), 123 (90)], 4-methylenebenzo[*b*]thiopyran (**11**)[21] (30 mg, 10%), and 2,3-dihydro-4-phenylthiophene[11] (**6**) (60 mg, 20%).

GC–MS and ^{1}H NMR analyses of the reaction mixture showed the absence of **11** and the presence of the possible (*E*)-4-[(tributylstannyl)methylene]benzo[*b*]thiopyran (**5**) (t_R = 8.65 min): ^{1}H NMR δ = 6.50 (vinylic proton); GC–MS m/z (rel inten) 395 (M^+ – 57, 45), 339 (20), 281 (30), 162 (60), 147 (100). The reaction was repeated, according to a modified procedure A, by adding the tin hydride to a 0.02 M benzene solution (100 mL) of **1a**. The ^{1}H NMR spectrum of the reaction mixture showed the presence of products **5**, **6**, and **7a** in a 1:2:1 ratio. The crude was allowed to stand at room temperature in a 10:1 mixture of deuteriomethanol-d_1 and acetic acid-d_1 for 3 d. After this time the solution was neutralized with 1 M NaOH and extracted with ether, and the solvent removed. ^{1}H NMR and GC–MS analyses of the residue showed peaks due to thiophene **6**, (*E*)-4-(deuteriomethylene)benzo[*b*]thiopyran (**11**-d_1) [^{1}H NMR δ = 5.52 (br s, =CH); GC–MS m/z 163 (M^+)], unchanged (*E*)-**7a**, and (*E*)-1-deuterio-4-(phenylthio)but-1-ene [(*E*)-[1-D]-**12a**]. The reaction carried out according to procedure B led to the formation of (*E*)-**7a** as main product, in addition to small amounts of (*Z*)-**7a**, **5**, and **6**, as determined by ^{1}H NMR analysis. The crude was allowed to stand at room temperature for 6 days in a 10:1 mixture

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of methanol and acetic acid. After workup, the residue was chromatographed to give 4-(phenylthio)but-1-ene (**12a**)[22] (250 mg, 75%). Similar treatment with a 10:1 MeOD/AcOD mixture gave (*E*)-[1-D]-**12a**, detected by GC–MS and ^{1}H NMR analyses of the reaction mixture: ^{1}H NMR δ = 2.3–2.5 (2H, m), 3.0 (2H, t, J = 7 Hz), 5.05 (1H, br d, J_d = 17 Hz), 5.75–5.95 (1H, m), 7.1–7.4 (5H, m). GC–MS m/z 165 (M^+, 20), 123 (100).

From Pent-1-yn-5-yl Phenyl Sulfide (1b). Chromatography gave (*E*)-5-(phenylthio)-1-(tributylstannyl)pent-1-ene [(*E*)-**7b**] (800 mg, 85%) as an oil: ^{1}H NMR δ = 0.8–0.95 (15H, m), 1.2–1.6 (12H, m), 1.76 (2H, tt, $J_1 = J_2$ = 7.3 Hz), 2.2–2.35 (2H, m), 2.92 (2H, t, J = 7.3 Hz), 5.9–5.95 (2H, m, collapsing to singlet upon irradiation at δ = 2.3 Hz), 7.1–7.4 (5H, m); MS m/z (rel inten) 411 (M^+ – 57, 100), 229 (70), 177 (60), 149 (25), 123 (25), 110 (20). The same results were obtained when the reaction was carried out in 0.02 M solution. Reaction of **7b** (470 mg, 1 mmol) in a 10:1 methanol/acetic acid solution (10 mL) carried out as described above gave, after column chromatography, 5-(phenylthio)pent-1-ene (**12b**)[23] (160 mg, 90%). Compound **7b** (235 mg, 0.5 mmol) was allowed to react in a 10:1 mixture of MeOD and AcOD (5 mL) for 3 days. After usual workup the residue was directly analyzed by GC–MS and ^{1}H NMR. (*E*)-1-Deuterio-5-(phenylthio)pent-1-ene ([1-D]-**12b**) was detected as exclusive product (t_R = 7.95 min): ^{1}H NMR δ = 1.75 (2H, m), 2.1–2.3 (2H, m), 2.92 (2H, t, J = 7 Hz), 5.0 (1H, dt, J_d = 17 Hz, J_t = 2 Hz), 5.80 (1H, m), 7.1–7.4 (5H, m); MS m/z 179 (M^+).

From Hex-1-yn-6-yl Phenyl Sulfide (1c). ^{1}H NMR and GC–MS analyses of the reaction mixture evidenced the almost exclusive formation of 6-(phenylthio)-1-(tributylstannyl)hex-1-ene (**7c**) (t_R = 8.80 min): ^{1}H NMR showed, in addition to multiplets at δ = 0.8–1.7, signals at δ = 2.1–2.25 (=CCH$_2$–, m), 2.85–2.95 (SCH$_2$–, m), 5.9–5.95 (HC=CH, m, collapsing to a broad singlet upon irradiation at δ = 2.15), 7.1–7.4 (Ph, m); GC–MS m/z (rel inten) 425 (M^+ – 57, 75), 343 (70), 233 (30), 229 (100), 190 (15), 177 (35), 110 (25), 79 (70). Chromatography gave 6-(phenylthio)hex-1-ene (**12c**) (320 mg, 83%).[24]

From Benzyl But-1-yn-4-yl Sulfide (1d). GC–MS analysis showed major peaks ascribable to toluene, 2-cyano-2-methyl-1-phenylpropane (**25b**) (t_R = 6.45 min), benzyltributyltin (**25a**) (t_R = 12.95 min), (possible) 2-[(tributylstannyl)methylene]thietane (**26**) (t_R = 13.15 min) [m/z (rel inten) 376 (M^+, 5), 319 (M^+ – 57, 100), 263 (80), 205 (100)], and (possible) adduct **7d** (t_R = 20.70 min) [m/z 411 (M^+ – 57, 100), 365 (20), 177 (60), 91 (100)]. Column chromatography gave bis(tributyltin) (40 mg), benzyltributyltin (**25a**) (60 mg, 13%), a mixture of unseparable and unidentified stannylated products (300 mg), and starting **1d** (140 mg, 40%). Elution with light petroleum/ether 90:10 yielded compound **25b** (20 mg, 10%).

From Benzyl Pent-1-yn-3-yl Sulfide (1e). Attempts to separate the reaction products by column chromatography were unsuccessful. ^{1}H NMR and GC–MS analyses of the reaction mixture showed the presence of toluene, benzyltributyltin (**25a**), 2-cyano-2-methyl-1-phenylpropane (**25b**), and a 40:60 mixture of (*E*)- and (*Z*)-2-[(tributylstannyl)methylene]tetrahydrothiophene [(*E*)- and (*Z*)-**27**] (t_R = 9.05 min): ^{1}H NMR $\delta_{(E)\text{-isomer}}$ = 0.85–1.0 (15H, m), 1.2–1.6 (12H, m), 2.0–2.2 (2H, m), 2.50 (2H, dt, J_d = 2 Hz, J_t = 6.8 Hz), 3.14 (2H, t, J = 6.3 Hz), 5.72 (1H, t, J = 2 Hz); $\delta_{(Z)\text{-isomer}}$ = 0.85–1.0 (15H, m), 1.2–1.6 (12H, m), 2.0–2.2 (2H, m), 2.64 (2H, dt, J_d = 1.5, J_t = 6.8 Hz), 3.13 (2H, t, J = 6.3 Hz), 5.67 (1H, t, J = 1.5 Hz); MS m/z 291 (rel inten) (M^+ – 99, 5), 269 (100), 213 (45), 177 (35), 155 (50), 121 (20), 100 (5). The crude residue obtained from a repeated reaction was allowed to react with benzoyl chloride (270 mg, 2 mmol) and 1 mol % of BnCl(PPh$_3$)$_2$-Pd (16 mg) in refluxing chloroform (20 mL) for 18 h. The resulting mixture was worked up as described in the literature;[9] subsequent chromatography gave (*Z*)- and (*E*)-2-(benzoylmethylene)tetrahydrothiophene (**28**) (200 mg, 50%) in a 65:35 ratio: ^{1}H NMR δ = 1.85–2.15 (2H, m), 2.55 (1.3H, t, J = 7.5 Hz), 2.95 (0.7H, br t, J = 7.5 Hz), 3.05–3.15 (2H, m), 7.20 (0.35H, br s), 7.40–7.60 (ca. 3.5 H, m), 7.9–8.15 (2H, m); MS m/z (rel inten) 204 (M^+, 4), 105 (100), 100 (60), 77 (80); IR ν_{max} 1710 and 1660 cm^{-1}; HRMS calcd for $C_{12}H_{12}OS$ 204.06089, found 204.06102.

From Benzyl Prop-1-yn-3-yl Sulfide (1f). ^{1}H NMR analysis showed the exclusive formation of (tributylstannyl)allene (**29**) and toluenethiol. Chromatography gave toluenethiol (200 mg, 80%). No allene **29** was recovered.

From Prop-1-yn-3-yl Phenyl Sulfide (1g). ^{1}H NMR analysis showed the exclusive formation of (tributylstannyl)-allene (**29**) and benzenethiol. Chromatography gave benzenethiol (90 mg, 40%), diphenyl disulfide (35 mg, 15%), and (*E*)-1,2-bis(phenylthio)propene [(*E*)-**30**][25] (80 mg, 30%) and its (*Z*)-isomer [(*Z*)-**30**][25] (25 mg, 10%).

From But-1-yn-4-yl *p*-Tolyl Sulfide (3a). The reaction was performed, according to the modified procedure A, by using a 0.01 M benzene solution of the alkyne **3a**. Chromatography gave (*E*)-4-(*p*-tolylthio)-1-(tributylstannyl)but-1-ene (**10**) (150 mg, 15%) [^{1}H NMR δ = 0.8–1.0 (15H, m), 1.2–1.6 (12H, m), 2.30 (3H, s), 2.35–2.5 (2H, m), 2.9 (2H, t, J = 7 Hz), 5.95 (2H, m), 7.05–7.15 (2H, m), 7.20–7.35 (3H, m); MS m/z (rel inten) 411 (M^+ – 57, 100), 355 (15), 243 (30), 177 (100), 91 (20)], (*E*)-6-methyl-4-[(tributylstannyl)methylene]benzo[*b*]thiopyran (**13**) (70 mg, 20%) [^{1}H NMR δ = 2.28 (3H, s), 2.75–2.85 (2H, m), 3.0–3.1 (2H, m), 4.95 (1H, br s), 5.45 (1H, br s), 6.93 (1H, br d, A part of an AB system, J = 8 Hz), 7.0 (1H, B part of an AB system, J = 8 Hz), 7.34 (1H, br s); MS m/z (rel inten) 176 (M^+, 70), 175 (30), 161 (100). Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86; S, 18.19. Found: C, 75.15; H, 6.90; S, 18.05. Treatment with Raney-nickel in boiling ethanol for 30 min gave 2-(*m*-tolyl)butane as exclusive reaction product (GC–MS analysis)], and 2,3-dihydro-4-(*p*-tolyl)-thiophene (**9**) (115 mg, 33%): mp 96–98 °C; ^{1}H NMR δ = 2.30 (3H, s), 3.12 (2H, A part of an A_2B_2X system, J_{AB} = 7 Hz, J_{AX} = 1.5 Hz), 3.38 (2H, B part of an A_2B_2X system, J_{AB} = 7 Hz), 6.50 (1H, t, J = 1.5 Hz), 7.10 (2H, d, J = 8 Hz), 7.25 (2H, d, J = 8 Hz); MS m/z (rel inten) 176 (M^+, 100), 175 (50), 161 (30), 128 (20). Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86; S, 18.19. Found: C, 75.10; H, 6.80; S, 18.30. Treatment with Raney-nickel in boiling ethanol for ca. 30 min gave 2-(4-tolyl)butane as exclusive reaction product. ^{1}H NMR and GC–MS analyses of the reaction mixture showed the absence of **13** and the presence of the (possible) tributyltin derivative **8** [^{1}H NMR δ = 2.30 (CH$_3$), 6.45 (=CH)].

From *N*-Prop-1-yn-3-yl-*N*-phenylamine (19a). Chromatographic elution with light petroleum/ether 95:5 gave (*E*)-*N*-phenyl-*N*-1-(tributylstannyl)prop-1-en-3-ylamine [(*E*)-**21a**] (720 mg, 85%): ^{1}H NMR δ = 0.85–1.0 (15H, m), 1.2–1.6 (12H, m), 3.85 (3H, d, J = 4.0 Hz, superimposed to a broad singlet), 6.1 (1H, A part of an ABX_2 system, J_{AB} = 18 Hz, J_{AX} = 4 Hz), 6.25 (1H, B part of an AB system, J_{AB} = 18 Hz), 6.6–6.8 (3H, m), 7.1–7.3 (2H, m); MS m/z (rel inten) 423 (M^+, 10), 366 (75), 310 (30), 252 (55), 312 (25), 132 (100), 106 (90), 77 (70).

From *N*-But-1-yn-4-yl-*N*-phenylamine (19b). Chromatographic elution with light petroleum/ether 95:5 gave (*E*)-*N*-phenyl-*N*-1-(tributylstannyl)but-1-en-4-ylamine [(*E*)-**21b**] contaminated by trace amounts of an isomeric product, which might be its (*Z*)-isomer (GC–MS analysis) (740 mg, 85%): ^{1}H NMR δ = 0.9–1.0 (15H, m), 1.2–1.6 (12H, m), 2.55 (2H, m), 3.25 (2H, t, J = 7 Hz), 3.7 (1H, br s), 6.0 (1H, A part of an ABX_2 system, J_{AB} = 18.5 Hz, J_{AX} = 5.2 Hz), 6.12 (1H, B part of an AB system, J_{AB} = 18.5 Hz), 6.6–6.8 (3H, m), 7.15–7.30 (2H, m); MS m/z (rel inten) 437 (M^+, 1), 380 (60), 177 (20), 146 (20), 106 (100)].

From Prop-1-yn-3-yl Phenyl Ether (22a). Chromatographic elution with light petroleum/ether 95:5 gave (*E*)-phenyl 1-(tributylstannyl)prop-1-en-3-yl ether [(*E*)-**24a**] contaminated by trace amounts of its (possible) (*Z*)-isomer (GC–MS analysis) (590 mg, 70%): ^{1}H NMR δ = 0.8–1.0 (15H, m), 1.2–1.6 (12H, m), 4.57 (2H, dd, J_{d1} = 4.5 Hz, J_{d2} = 1.3 Hz), 6.2 (1H, A part of an ABX_2 system, J_{AB} = 19 Hz, J_{AX} = 4.5 Hz), 6.38 (1H, B part of an ABX_2 system, J_{AB} = 19 Hz, J_{BX} = 1.3 Hz), 6.85–7.0 (3H, m), 7.24–7.34 (2H, m); MS m/z (rel inten) 366 (M^+ – 57, 100), 311 (60), 255 (40), 213 (65), 133 (15), 120 (30).

From But-1-yn-4-yl Phenyl Ether (22b). Chromatographic elution with light petroleum/ether 95:5 gave (*E*)-phenyl-1-(tributylstannyl)but-1-en-4-yl ether [(*E*)-**24b**] contaminated by trace amounts of its (possible) (*Z*)-isomer (GC–MS analysis) (790

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mg, 90%): ^{1}H NMR δ = 0.8–1.0 (15H, m), 1.2–1.6 (12H, m), 2.4–2.5 (2H, m), 4.05 (2H, t, J = 6.8 Hz), 6.05 (2H, m; computer simulation gave: ABXY system, J_{AB} = 18 Hz, J_{AX} = 5.1 Hz, J_{AY} = 2.5 Hz, J_{BX} = 0.5 Hz, J_{BY} = 1.0 Hz; inner lines separation = 6 Hz), 6.85–7.0 (3H, m), 7.2–7.35 (2H, m); MS m/z (rel inten) 381 (M^+ – 57, 60), 325 (25), 313 (55), 148 (40), 94 (100), 77 (60). The reaction was repeated according to procedure B and gave the same results.

From But-1-yn-4-yl Phenyl Selenide (31). Chromatography gve a fraction (700 mg) containing mainly diphenyl diselenide[26] (**34**), and phenyl tributylstannyl selenide[27] (**32**). This mixture was allowed to react in a 10:1 solution of methanol/acetic acid to give, after workup (see below), the diselenide **34** as the only product detectable by GC–MS analysis (t_R = 13.35 min). Further elution gave a 3:1 mixture of starting alkyne **31** and 2,3-dihydro-4-phenylselenophene (**39**) (90 mg, 20% overall yield): ^{1}H NMR δ = 3.20 (2H, A part of an A_2B_2X system, J_{AB} = 7 Hz, J_{AX} = 1.5 Hz), 3.40 (2H, B part of an A_2B_2X system, J_{AB} = 7 Hz), 7.0 (1H, t, J = 1.5 Hz), 7.2–7.6 (5H, m); GC–MS m/z (rel inten) 210 (M^+, 85), 129 (80), 128 (100). GC–MS analysis of the reaction mixture showed products **31**, **32**, **34**, **39**, and trace amounts of the (possible) benzo[*b*]selenopyran **37** (t_R = 9.02 min): m/z (rel inten) 210 (M^+, 60), 209 (50), 195 (100), 193 (40), 128 (90).

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Supplementary Material Available: ^{1}H NMR spectra of compounds **1a–e**, **3**, (*E*)-**7a**, (*E* + *Z*)-**7a**, **7b–c**, **10**, **19a–b**, **21a–b**, **22b**, **24a–b**, **27**, **28**, **31**, **39**, [1-D]-**12a**, [1-D]-**12b**, and simulated (*E*)-**7a** and (*E*)-**24b** (25 pages). This material is available 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.