Cyclizations and Rearrangements of Samarium Diiodide-Generated Vinyl Radicals

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Vinyl bromides **1**, **5**, **15**, **20**, **23**, **27**, **33a,b**, **41a-c**, **44a-c**, **46a,b**, **52a,b**, **55a**, **56a,b**, and **60a,b** react with samarium diiodide in THF and/or acetonitrile to give the corresponding vinyl radicals. Radicals **3**, **7**, and **16** afforded products deriving from cyclization on the adjacent triple bond in a 5-(*π-exo*)-*exo*, 6-(*π-endo*)*exo*, and 6-(*π-exo*)*exo* mode, respectively. Radical **7** undergoes competitive 1,5-hydrogen translocation. Vinyl radicals **21** and **24** readily cyclize on the proximal double bond, leading to 5- and 6-membered rings, respectively. Thienyl-substituted radical **28** leads to a product deriving from 5-*exo* cyclization on the thiophene ring and subsequent *β*-fission of the C–S bond, whereas thienyl-substituted radicals **34a,b** undergo almost exclusively 1,5-hydrogen translocation. Aryl-substituted radicals obtained from vinyl bromides **41**, **44**, **46**, **52**, and **55** do not form any products deriving from *5-exo* or *6-exo* cyclization (or *ipso* cyclization). Finally, naphthyl-substituted radicals **57a** and **61a** give only direct reduction products, whereas the radical **61b** affords, in addition to the direct reduction product, a rearranged product deriving from a 1,3-radical migration of the naphthylthio group. Evidence is reported for the reduction of EWG-substituted benzene rings and thio-substituted naphthalene rings to radical anions, which can fragment on the side chain with the elimination of allyl radicals. α-Oxy(and α-thio)-substituted radicals deriving from 1,5-shift rearrange to alcohols (and thiols) through a Wittig rearrangement or a cyclization/fragmentation process.

Radical-induced cyclizations represent a good alternative method for building ali- or heterocyclic rings. Therefore, these reactions must be taken into account when planning synthetic strategies.[1] The initial step of a radical cyclization is the formation of a radical center on a molecule containing a radicophilic moiety. This is the most crucial step in the process, and in recent years organic chemists have aimed at discovering new methods of generating radical species. In the second step, the radical center adds intramolecularly to the radicophilic moiety, i.e., alkenic, aromatic, or heteroaromatic double bonds (trigonal cyclizations) or triple bonds (digonal cyclizations). The generated radical center can be either outside (*exo* cyclization) or inside (*endo* cyclization) the formed ring. Finally, quenching of the resulting cyclic radical generally occurs via hydrogen abstraction or loss of a radical species.

Among radical cyclizations, those involving vinyl radicals seem particularly attractive from both a speculative and a synthetic standpoint.[2] Vinyl radicals can be generated in three ways: i) by addition to the alkyne triple bond of silicon-,[3] tin-,[4] carbon-,[5] sulfur-,[6] or selenium-centered[7] radicals (the radicophilic moiety may (annulation reactions) or may not be contained on the attacking radical); (ii) from vinyl halides through halogen abstraction by stannyl[8] or silyl[9] radicals; and (iii) by electrochemical[10] or chemical reduction of vinyl bromides; this latter reaction can be achieved with samarium(II) iodide.[11] The reaction of organic halides with samarium iodide is depicted in Scheme 1. Electron transfer between

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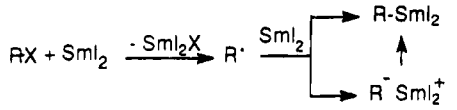
Scheme 1



samarium(II) and the organic halide leads to the corresponding "free radical" through loss of the halide ion. When the organic radical is a primary or a secondary alkyl one, subsequent reaction with another molecule of samarium iodide affords a samarium reagent which can react with electrophilic species as do Grignard reagents.[12] It is somewhat unclear if these alkyl radicals directly give samarium reagents through an inner sphere electron transfer or if carbanions are involved as transient intermediates (Scheme 1). Evidence has been reported for and against both mechanisms.[12,13] In contrast with the behavior exhibited by primary and secondary alkyl radicals, vinyl, phenyl, and tertiary alkyl radicals do not undergo further reduction to samarium reagents to an appreciable extent.[12a,b] Whatever the mechanism may be, this reaction has been developed into a method for generating radical species,[14] and several examples of cyclizations of SmI_2-promoted alkyl and phenyl radicals have been performed.[15]

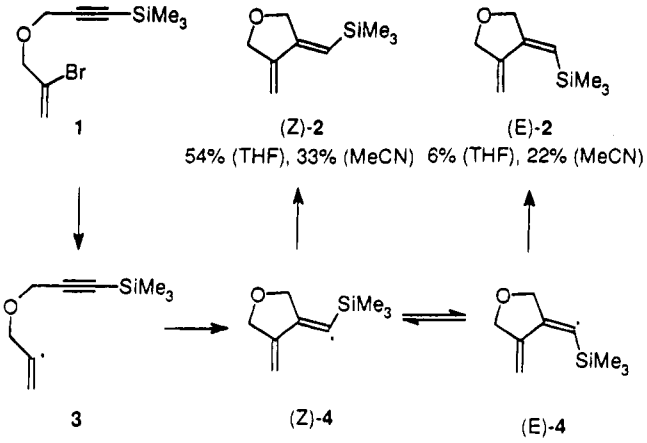
We now report results obtained from SmI_2-promoted reactions of vinyl bromides containing suitable radicophilic moieties. The aim was to explore the fate of the resulting vinyl radicals and, in particular, their capability to undergo 5- and/or 6-ring cyclizations onto carbon–carbon double and triple bonds and aromatic and heteroaromatic rings under the reductive conditions employed.[16]

Results and Discussion

Reactions of vinyl bromides **1**, **5**, **15**, **20**, **23**, **27**, **33a,b**, **41a-c**, **44a-c**, **46a,b**, **52a,b**, **55a**, **56a,b**, and **60a,b** with samarium iodide (3 mol equiv) were carried out at room temperature in anhydrous tetrahydrofuran (THF) and/or acetonitrile, in the absence of air under nitrogen atmosphere and in the presence of hexamethylphosphoramide (HMPA).[17] Reactions were quenched with brine after ca. 3 h and the mixtures analyzed by GC/MS and ^1H NMR; the reaction products were then isolated by column chromatography. Unreacted vinyl bromide was usually recovered in about 10–20% yield.

Cyclization on the Carbon–Carbon Triple Bond. Reaction of 2-bromopropenyl 3-(trimethylsilyl)propynyl ether **1** with samarium iodide gave the dihydrofuran derivative **2** in fairly good yield as the only isolable product. This product derived from the initially formed vinyl radical **3** through a 5-(*π-exo*)*exo*-dig cyclization on the adjacent triple bond and subsequent hydrogen abstraction reaction by the *exo* cyclic radical intermediate **4** (Scheme 2). No formation of any 6-*endo* cyclization product was detected. This finding was expected, since the 5-*exo* radical cyclization is highly favored over the 6-*endo* one, as predicted by the Baldwin–Beckwith rules.[18] The stereochemical behavior of the cyclization of radical **3** was quite interesting. When the reaction was carried out in acetonitrile, the product **2** was obtained as a 40:60 *E*/*Z*-isomeric mixture. It is generally accepted that the configuration of hydrogen abstraction products of vinyl radicals strongly depends on the ease of approach of the radical scavenger to the radical center.[6a,19] Thus, the observed lack of stereoselectivity should indicate that no structural features exist in radical **4** which favor the approach of the scavenger to either one or the other isomeric form. In spite of this, the reaction carried out in THF was highly *cis*-stereoselective, cyclization product **2** being obtained in a >90:10 *Z*/*E*-isomeric mixture. Configurational assignment of (*E*)- and (*Z*)-**2** isomers arose from NOE measurements. Irradiation of the Me_3Si signal of the pure *Z*- isomer caused an enhancement of signals at δ 4.46 (allylic methylene) and 6.0 (vinylic proton geminal to the Me_3Si group), whereas vinylic proton signals at δ 4.92 and 5.4 remained unchanged. Moreover, irradiation of the Me_3Si signals of a 40:60 *E*/*Z* mixture caused, in addition to the enhancement of signals at δ 4.46 and 6.0, enhancement of signals at δ 5.4 (*E*-isomer vinylic proton geminal to Me_3Si group) and 5.52 (*E*-isomer vinylic proton *cis* to Me_3Si group).

Scheme 2



The samarium iodide promoted reaction of 3-bromopropenyl 3-(trimethylsilyl)propynyl ether **5** (ca. 1:1 *Z*/*E*-isomeric ratio) gave a rather complex mixture mainly containing the allyl propynyl ether **9**, a *Z*/*E* mixture of the dihydropyran **6**, the allene **11**, and the hydroxy derivative **13** (Scheme 3). The dihydropyran **6** resulted from the 6-(*π-endo*)*exo*-dig cyclization of vinyl radical intermediate **7**. This cyclization mode is somewhat rare in vinyl radicals which, strictly following the Baldwin–

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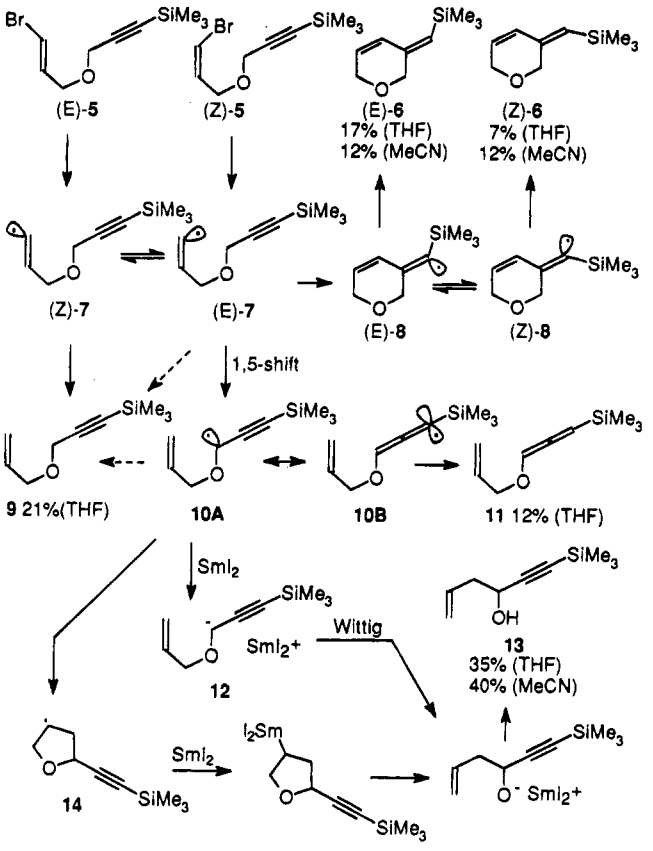
Scheme 3



Beckwith rules, generally show a very low tendency to undergo 6-ring closure. Although there are some examples of 6-*exo* cyclizations of vinyl radicals onto alkenes,[4c,8b,c] to our knowledge 6-member cyclization onto alkynes has been reported only once.[20] The stereochemistry of pyran **6** depended on the nature of the solvent employed. The ratio of *E*/*Z*-isomers observed was 50:50 and 70:30 in acetonitrile and THF, respectively. Thus, in acetonitrile both the 5-*exo* cyclization of **3** and the 6-*exo* cyclization of **7** were found to be nonstereoselective, whereas in THF the 6-ring closure of **7** occurred in a *trans*-stereoselective mode, in contrast with the behavior exhibited by radical **3**. Structural assignment of (*E*)- and (*Z*)-**6** isomers was made on the basis of NOE measurements. Irradiation of the Me_3Si signals of a 70:30 *E*/*Z*-isomeric mixture caused an enhancement of the signals of the exocyclic vinylic protons of both isomers as well as of the C(3)-H signal of the vinylic proton of the *E*-isomer.

Allene **11** and alcohol **13** are believed to have arisen from radical **7** via an initial 1,5-hydrogen shift. 1,5-Hydrogen translocations from "activated" methylene groups to vinylic carbon-centered radicals occur readily.[21] Thus, the resulting radical **10** could lead to the allene **11** through hydrogen abstraction from THF by the mesomeric form **10B** or might undergo further reduction to **12**, possibly furnishing the hydroxy derivative **13** through a 2,3-sigmatropic rearrangement (Scheme 3, path a). The route leading to **13** was the exclusive reaction exhibited by radical **10** in acetonitrile. 2,3-Sigmatropic Wittig rearrangements have been investigated in detail; they are generally believed to occur through intermediate transient carbanions and cyclic transition states involving six electrons.[22a] Analogous rearrangements in allyl (trimethylsilyl)propynyl ethers have already been reported.[22b,c] Unfortunately, our finding that transient carbanions can be involved in SmI_2 reduction of alkyl radicals is far from being conclusive, since an alternative route could be considered starting from radical **10** and leading to **13**. In fact, 5-*endo* cyclization on the adjacent double bond would lead to the alkyl radical **14**, which might afford **13** through reduction to the samarium reagent and subsequent ring opening by elimination of an alkoxide ion (samarium–Boord reaction) (Scheme 3, path b). Examples of the rather uncommon 5-*endo* cyclization mode have been recently reported.[6c,23]

The allyl ether **9** could possibly arise from both radicals **10** and **7** through hydrogen abstraction reaction. However, GC/MS and ^1H NMR analysis of the reaction mixture obtained by reacting pure isomer (*Z*)-**5** with samarium iodide in THF only revealed the formation of products **6**, **11**, and **13**. The absence of ether **9** in the latter reaction could indicate that this product was formed from the vinyl radical (*Z*)-**7** and not from the *E*-isomer (*E*)-**7** nor from the alkyl radical **10**. Thus, it would appear that for the vinyl radical (*E*)-**7**, both 1,5-hydrogen shift and cyclization on the triple bond prevail over *E*/*Z* interconversion. This finding is quite surprising because it is generally reported that (*E*)/(*Z*) interconversion of vinyl radicals is a fast process[24] and that the stereochemical outcome of a reaction does not depend on the configuration of the radical precursors.[19b,25] However, a few examples are reported of vinyl radicals abstracting a hydrogen atom before interconverting. The rate of interconversion appears to be particularly slow for vinyl radicals having α-heteroatoms.[26]

The reaction of 2-bromopropenyl 4-(trimethylsilyl)-butynyl ether **15** in THF led mainly to the reduction product **17** plus a small amount of the pyran derivative **19**. The yield of **19** slightly increased when the reaction was carried out in acetonitrile. Pyran **19** arose from vinyl radical **16** through an unprecedented 6-(π-*exo*)*exo*-dig cyclization (Scheme 4). Previous attempts to perform such a stereoelectronically unfavored cyclization failed.[20] In both THF and acetonitrile we obtained the product **19** in a 50:50 *E*/*Z*-isomeric mixture. This finding indicates that the alkadienyl radical **18**, unlike its analogues **4** and **8**, undergoes a hydrogen abstraction reaction in a nonstereoselective fashion regardless of the solvent employed. We have no definite explanation to account for the different stereochemical behaviors exhibited by radicals **4**, **8**, and **18**. Although evidences have been reported that α-silylalkenyl radicals are sp-hybridized,[27] our findings suggest that α-silylalkadienyl radicals **4**, **8**, and **18** could be sp^2-hybridized. Thus, the *E*- and *Z*-isomeric forms could exist in equilibrium in a *Z*/*E* ratio depending

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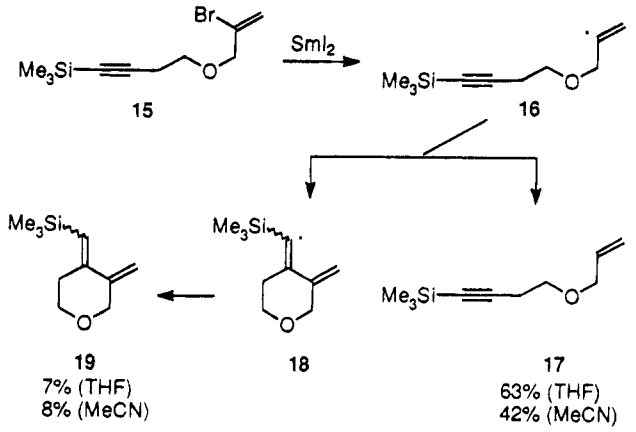
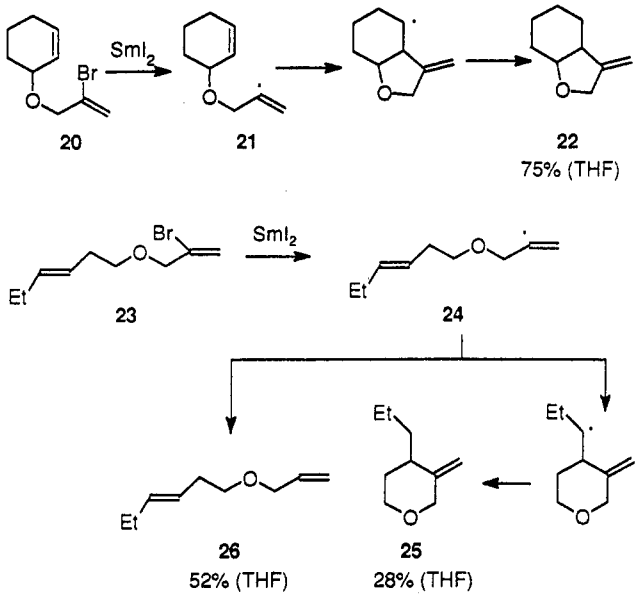
Scheme 4



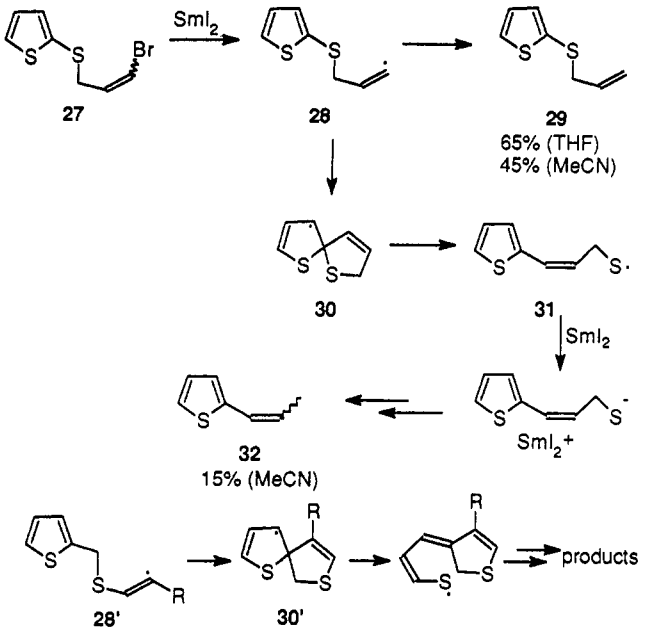
Scheme 5



on both their configuration (*exo–exo* or *exo–endo*) and the nature of the solvent. In the absence of steric effects, the *Z/E* ratio of the hydrogen abstraction products **2**, **6**, and **19** would be determined by the *Z/E* ratio of the corresponding alkadienyl radicals **4**, **8**, and **18.**

Cyclization on the Carbon–Carbon Double Bond. 2-Bromoallyl cyclohexenyl ether **20** upon reaction with samarium iodide in THF exclusively gave compound **22**, which was derived from vinyl radical **21** through a facile 5-(*π-exo*)*exo*-trig cyclization on the adjacent double bond. Similar cyclizations have been reported [4c,18,20] (Scheme 5). No 6-*endo* cyclization product was obtained which might in principle be derived from the initially formed *exo* radical through a ring-expansion process. Vinyl radical cyclizations usually give *exo*/*endo* mixtures due to a rearrangement of the initially formed *exo*-closed radical.[8d,i] Presumably, in the present case, the *exo* mode radical was reduced to its organosamarium derivative before it could rearrange. On the other hand, 2-bromopropenyl hexenyl ether **23** gave a ca. 40:60 mixture of the pyran **25** and the propenyl ether **26**. These products were derived from radical **24** via a 6-(*π-exo*)*exo*-trig cyclization on the double bond and hydrogen abstraction, respectively (Scheme 5). In this case the hydrogen abstraction competes favorably with the cyclization reaction, the 6-ring closure being more slower than the 5-ring one.

Scheme 6



Cyclization on the Thiophene Ring. The thienylthio-substituted vinyl radical **28** provided an example of a 5-(*π-endo*)*exo*-trig cyclization on a heteroaromatic ring, although the hydrogen abstraction reaction was largely favored. In fact, the reaction of 3-bromopropenyl thienyl sulfide **27** with samarium iodide in THF gave exclusively the reduction product **29,** while in acetonitrile we obtained minor amounts of a 1:1 *Z/E* mixture of the propenylthiophene **32** in addition to the major product **29**. The thiophene **32** is believed to arise from the intermediate *spiro* radical **30** through *β*-scission of the carbon–sulfur bond and subsequent desulfuration of the resulting thiyl radical **31** (Scheme 6). Samarium iodide-promoted fission of a C–S bond has been reported to occur in sulfones and dithioacetals,[28] whereas reduction of thiols seems to be unprecedented. Independent experiments showed that both alkanethiols and arenethiols (except naphthenethiol) can be quantitatively reduced under our reaction conditions. The entire process leading to **32** represents an example of a 1,4-sulfur-to-carbon radical migration of a thienyl group toward a vinylic radical. A similar 1,4-migration of a phenyl group has been recently reported.[4a] The behavior exhibited by the spiro radical **30** is especially interesting when compared with that exhibited by the similar spiro radical **30′**. The latter did not give a 1,4-thienyl migration but did yield products deriving from thiophene ring opening.[29]

Attempts to achieve a 6-(*π-endo*)*exo*-trig cyclization on the thiophene ring failed. The ether **33a** reacted in THF to give mainly the alcohol **40**, whereas the sulfide **33b** mainly gave the butenylthiophene **37**. In both cases, the reduced compound **35** was also found as a minor product. Products **37** and **40** were formed from vinyl radicals **34a,b** through a 1,5-hydrogen translocation leading to alkyl radicals **36a,b** and, finally, to the rearranged salts **39a,b**. Thus, the alcoholate **39a** gave **40** upon aqueous workup, and the thiolate **39b** afforded **37** by subsequent reductive desulfuration (Scheme 7). In principle, the

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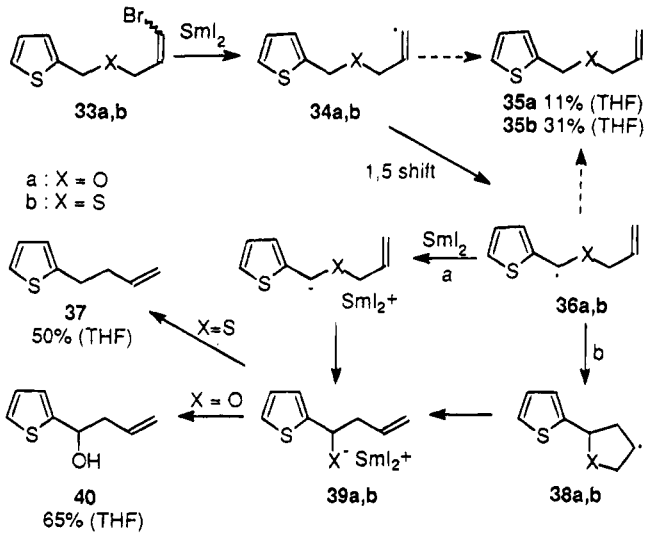
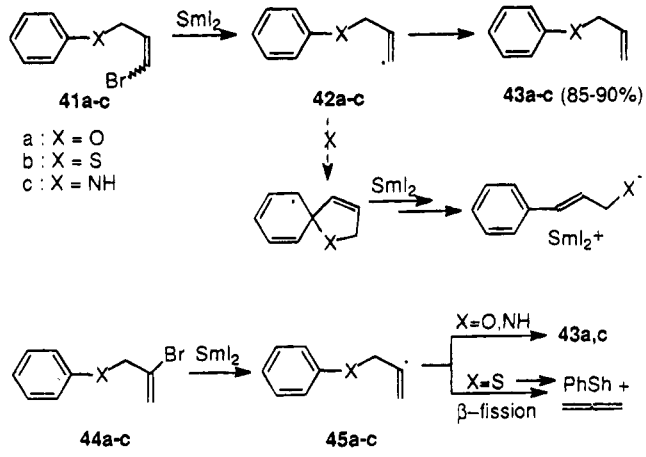
(29) These results will be published elsewhere.

Scheme 7



Scheme 8

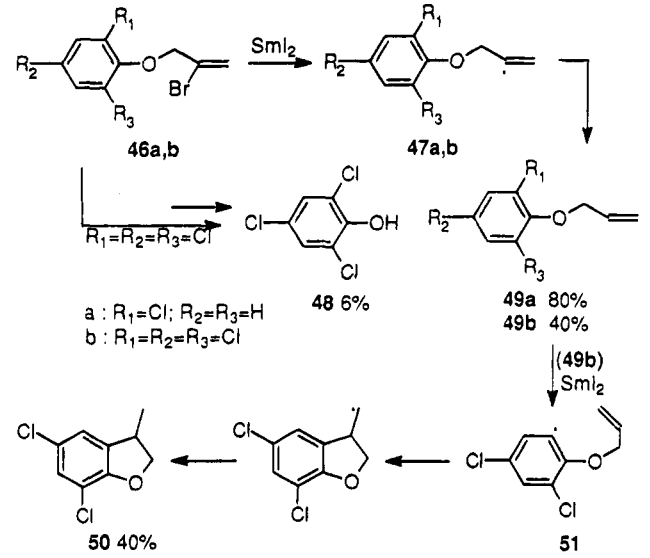


alkyl radicals **36a,b** may lead to **39a,b** through two kinds of reactions, in a similar fashion to that suggested for the related radical **14**: reduction to transient carbanions followed by Wittig rearrangement (Scheme 7, path a) or cyclization to *endo* radicals **38a,b** and subsequent samarium-promoted β-scission of the C–X bond (X = O, S) (Scheme 7, path b).

Cyclization on Aromatic Rings. Bromopropenyl phenyl derivatives **41a–c** reacted with samarium iodide in both THF and acetonitrile to yield only reduction products **43a–c**. No evidence of products deriving from a 5-(π-*endo*)*exo* cyclization of intermediate vinyl radicals **42a–c** on the adjacent benzene ring was found (Scheme 8). Similarly, no 5-membered *ortho* cyclization products were formed from radicals **45a–c**. Reaction of phenyl ether **44a** and phenylamine **44c** gave only the corresponding reduction products **43a,c**, whereas the sulfide **44b** provided, after workup and removal of the solvent, a few milligrams of a residue essentially constituted of thiophenol, as evidenced by GC/MS analysis. We believe that the vinyl radical **45b** exclusively underwent β-scission to lead to allene (not detected) and the benzenethiyl radical (to yield benzenethiol) (Scheme 8). Subsequent reductive desulfuration should lead to benzene (not detected). β-Scission of β-thiovinyl radicals has been previously reported.[4a,30]

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

Scheme 9

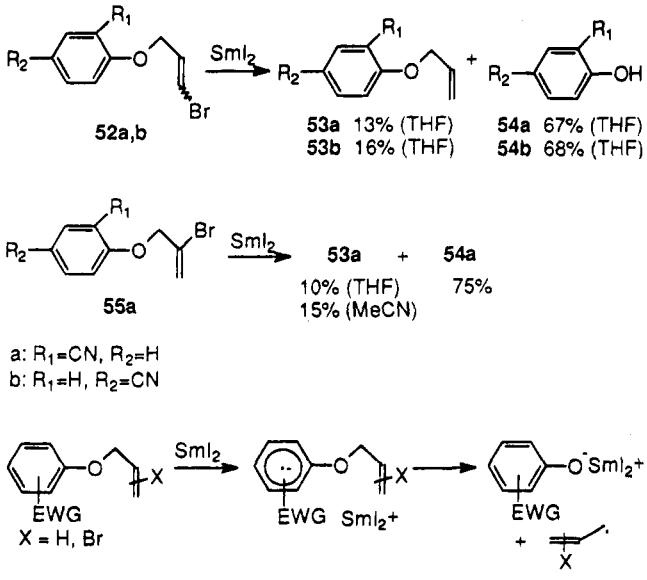


The lack of any *ortho* cyclization product is not surprising. The 5-*endo* cyclization mode is unfavored,[31] and the *ortho* 5-ring closure of vinyl radicals occurs only under severe conditions.[6b] Conversely, the lack of 5-*exo* cyclization products is somewhat unexpected. We have recently reported that the 5-*exo* vinyl radical cyclization on benzene rings occurs easily even in the presence of a strong hydrogen donor such as benzenethiol.[16c] Nevertheless, under reductive conditions, homolytic aromatic substitutions rarely occur because intermediate cyclohexadienyl radicals can not easily rearomatize.[32] However, in our cases the 5-*exo* ring closure of radicals **42a–c** should have led to spiro radical intermediates. If they had been formed, they would be expected to readily collapse to 1,4-phenyl migration products by C–X (X = O, S) bond scission (Scheme 8).

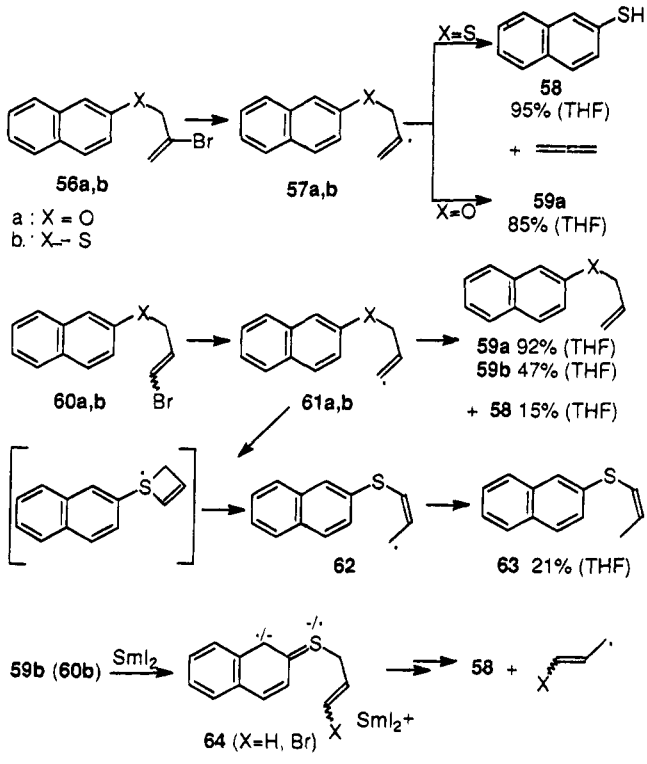
Attempts to achieve a 5-*endo* cyclization by ipso substitution of a chlorine atom were not successful, although cyclization of sp^2-carbon radicals on the ipso-position of halobenzenes has been reported (albeit at high temperature).[33] In fact, the 2-chlorophenyl ether **46a** reacted with samarium iodide to give only the reduced product **49a**, whereas the 2,4,6-trichlorophenyl analogue **46b** gave the reduced product **49b** in addition to minor amounts of 2,4,6-trichlorophenol (**48**) and variable amounts of the dihydrobenzofuran **50** (Scheme 9). The yield of **50** increased with the reaction time at the expense of **49b**. This finding suggested that **50** probably was a secondary product deriving from the initially formed allyl ether **49b**. Supporting evidence was provided by reaction of **49b** with samarium iodide, which afforded the benzofuran **50** in good yield. Compound **50** could very likely result from intermediate phenyl radical **51** through 5-ring closure on the adjacent double bond (Scheme 9). As far as the formation of trichlorophenol **48** is concerned, we found that EWG-substituted aryl bromoallyl ethers generally react with samarium iodide to give the corresponding phenol derivative as the main product. Thus, cyanophenyl ethers **52a,b** and **55a** gave mainly the corresponding phenols **54a,b** plus minor amounts of the

(31) Baldwin, J. E.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. C. *J. Chem. Soc., Chem. Commun.* **1976**, 736.
(32) See ref 1c, Chapter 4.2, pp 809–811. Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561.
(33) Benati, L.; Montevecchi, P. C.; Tundo, A. *J. Chem. Soc., Chem. Commun.* **1978**, 530.

Scheme 10



Scheme 11



reduced products **53a,b** (Scheme 10). However, control experiments showed that allyl ether **53b** also gave the phenol **54b** by reaction with samarium iodide. On this basis, vinyl radical intermediates can be confidently ruled out. We believe that the presence of EWGs renders electron transfer to the phenyl ring possible. The resulting radical anion might lead to a phenate ion (and then phenol) by loss of an allyl radical (Scheme 10).

Analogous to benzene derivatives, β-naphthyl bromoallyl ether **56a** and sulfide **56b** did not give any cyclization product. Ether **56a** gave only the reduction product **59a**, while sulfide **56b** gave β-naphthalenethiol (**58**), deriving from intermediate vinyl radical **57b** through β-elimination of allene (Scheme 11). Unlike the other thiols examined, the thiol **58** was found to be stable under our reaction conditions. Furthermore, β-naphthyl ether **60a** gave only the reduction product **59a**. In contrast, the sulfide **60b** showed a peculiar behavior affording the reduction product **59b**, the thiol **58**, and the rearranged sulfide **63**. The thiol **58** could be formed from allyl (and/or bromoallyl) sulfide **59b** (and/or **60b**) through the intermediate radical anion **64** (X = H, Br) by loss of an allyl (or bromoallyl) radical, similarly to what was suggested above for the reduction of EWG-substituted phenyl allyl ethers (Scheme 11). An independent experiment actually showed that the samarium iodide-promoted reaction of naphthyl allyl sulfide **59b** affords the thiol **58**, while, under the same reaction conditions, the ether **59a** did not give any naphthol. The rearranged sulfide **63** could result from vinyl radical **61b** through an intramolecular S_H2 reaction at the sulfur atom with displacement of a stable allyl radical. This process would represent a rare example of a 1,3-radical rearrangement. A similar S_H2 substitution by a vinyl radical, leading to a thietane derivative, has been recently reported.[4a]

Conclusions

SmI_2-Promoted reaction of vinyl bromides can represent a good method for the generation of vinyl radicals. These radicals gave 5- or 6-member cyclizations on both double and triple carbon–carbon bonds, whereas cyclization on the C(2)-position of the thiophene ring only occurred in a 5-*exo* fashion. When δ-activated methylenes were present, a 1,5-hydrogen shift could favorably occur. Resulting alkyl radicals rearranged by reduction to transient carbanions followed by 2,3-sigmatropic Wittig (or thio-Wittig) rearrangement or by cyclization on the adjacent double bond followed by samarium-promoted ring opening. Cyclization on aromatic rings did not occur, neither in a 5-*endo* nor in a 5-*exo* fashion. This latter finding indicates a low reactivity of these SmI_2-promoted vinyl radicals, which also showed some disinclination toward *E/Z* interconversion. EWG-Substituted benzene rings and thio-substituted naphthalene rings were reduced under the reaction conditions employed. Resulting radical anions could thus evolve by β-scission on the side chain leading to a stable allyl radical. Evidence was also provided for a 1,3-carbon-to-carbon radical migration of a naphthylthio group. Finally, reductive desulfuration of thiols (or thiolate ions) was observed.

Experimental Section

Thiophene derivatives **29**,[34] **32**,[35] **35b**,[36] and **37**,[37] ethers **17**,[20] **43a**,[38] **53b**,[39] **49a,b**,[40] and **59a**,[41] and sulfides **43b**[42] and **59b**[43] were identified by ^1H NMR and/or GC/MS spectral comparison with authentic specimens. Trimethylsilyl derivatives **2**, **6**, **9**, **11**, and **13** have been previously reported.[16]

(34) Mortensen, J. Z.; Hedegaard, B.; Lawesson, S. O. *Tetrahedron* **1971**, *27*, 3831.
(35) (a) Singaram, B.; Rangaishenvi, M. V.; Brown, H. C.; Goralski, C. T.; Hasha, L. *J. Org. Chem.* **1991**, *56*, 1543; (b) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U.; Bhat, N. G.; Prasad, J. V. N. V. *J. Org. Chem.* **1988**, *53*, 239.
(36) Anisimov, A. V.; Mozhaeva, L. V.; Kazennova, N. B.; Kuznetsova, S. V.; Viktorova, E. A. *Khim. Geterotsikl. Soedin.* **1987**, *7*, 883.
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(39) Lasek, W.; Makosza, M. *Synthesis* **1993**, *8*, 780.
(40) Sonnenberg, F. M. *J. Org. Chem.* **1970**, *35*, 3166.
(41) Bradshow, J. S.; Nielsen, N. B.; Rees, D. P. *J. Org. Chem.* **1968**, *33*, 259.
(42) Pollak, I. E.; Tritunac, A. D.; Grillot, G. F. *J. Org. Chem.* **1967**, *32*, 272.
(43) Makisumi, Y.; Takada, S.; Matsukura, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 850.

Structural assignment of hitherto unknown reaction products was generally made on the basis of ^{1}H NMR, MS, and HRMS analyses; their homogeneity was confirmed by GC/MS analysis. Compound **19** was not obtained pure; similarly, compounds **25** and **26** were obtained as inseparable mixture. Their identification arose by careful GC/MS and ^{1}H NMR spectral analyses.

Materials. Samarium diiodide is commercially available; it can be prepared from samarium and diiodoethane.[10] Hexamethylphosphoramide (HMPA), tetrahydrofuran (THF), and acetonitrile were freshly distilled.

Bromoallyl ethers **1**,[16] **5**,[16] **15**,[20] **20**, **23**, **33a**, **41a**, **44a**,[44] **46a,b**, **52a,b**, **55a**, **56a**, and **60a** and bromoallyl sulfides **27**, **33b**, **41b**, **44b**,[21] **56b**, and **60b** were prepared by heating in a sealed tube at 100 °C for ca. 3 h a THF solution of equimolar amounts of the corresponding sodium alcoholate (or sodium thiolate) and the appropriate 1,3-dibromo(or 1,2-dibromo)-propene. The reaction mixtures were poured in water and extracted with diethyl ether. Removal of the solvent followed by flash cromatography gave the crude product in ca. 70−90% yield. Bromoallylamines **41c** and **44c**[45] were similarly prepared in ca. 95% yield from the corresponding anilines. The following new products were obtained as oily products, unless otherwise stated.

2-Bromoprop-2-enyl 4-(trimethylsilyl)but-3-ynyl ether (15): ^{1}H NMR δ 0.15 (9H, s), 2.55 (2H, t, J = 7 Hz), 3.60 (2H, t, J = 7 Hz), 4.17 (2H, br s), 5.62 (1H, br s), 5.98 (1H, br s); MS *m/e* (rel intensity) 247, 245 (M^+ − 15, 1), 139, 137 (100), 73 (100).

2-Bromoprop-2-enyl cyclohex-2-enyl ether (20): ^{1}H NMR δ 1.5−2.2 (6H, m), 3.9−4.0 (1H, m), 4.15 (2H, s), 5.6 (1H, br s), 5.7−5.96 (2H, m, collapsing to δ 5.78, A part of an ABX_2 system, J_{AB} = 10 Hz, J_{AX} = 2 Hz, and 5.9, B part of an ABX_2 system, J_{AB} = 10 Hz, J_{BX} = 3.5 Hz, upon irradiation at δ 2.0), 5.96 (1H, br s); MS *m/e* (rel intensity) 188, 186 (M^+ − 28, 5), 137 (100), 81 (60), 79 (100), 69 (60).

(*E*)-2-Bromoprop-2-enyl hex-3-enyl ether [(*E*)-23]: ^{1}H NMR δ 0.95 (3H, t, J = 7 Hz), 2.0 (2H, m), 2.30 (2H, m), 3.5 (2H, t, J = 7 Hz), 4.10 (2H, s), 5.42 (1H, dt, J_d = 15 Hz, J_t = 5.5 Hz, collapsing to doublet upon irradiation at δ 2.3), 5.56 (1H, dt, J_d = 15 Hz, J_t = 4.5 Hz, collapsing to doublet upon irradiation at δ 2.0), 5.6 (1H, s), 5.92 (1H, s); MS *m/e* (rel intensity) 151, 149 (M^+ − 69, 5), 139 (40), 121, 119 (70), 69 (100).

3-Bromoprop-2-enyl 2-thienyl sulfide (27): 40:60 *E/Z* mixture; ^{1}H NMR δ 3.30 (0.8H, br d, J = 8 Hz), 3.5 (1.2H, br d, J = 7 Hz), 5.92 (0.4H A part of an AB system, J = 14 Hz), 6.10−6.30 (1.6H, m), 6.9−7.0 (1H, m), 7.10 (1H, m), 7.35 (1H, m); MS *m/e* (rel intensity) 236, 234 (M^+, 20), 155 (80), 121 (70), 115 (70), 71 (100); HRMS calcd for $C_7H_7BrS_2$ 233.91725, found 233.91717.

3-Bromoprop-2-enyl 2-thienylmethyl ether (33a): 70:30 *E/Z* mixture; ^{1}H NMR δ 4.0 (1.4H, d, J = 4.8 Hz), 4.25 (0.6H, d, J = 4.5 Hz), 4.69 (1.4H, br s), 4.71 (0.6H, br s), 6.2−6.5 (2H, m), 7.0 (2H, m), 7.3 (1H, m); MS *m/e* (rel intensity) 234, 232 (M^+, 5), 153 (25), 97 (100), 85 (20); HRMS calcd for C_8H_9Br0S 231.95574, found 231.95562.

3-Bromoprop-2-enyl 2-thienylmethyl sulfide (33b): 1:1 *E/Z* mixture; ^{1}H NMR δ 3.08 (2H, m), 3.32 (2H, dd, J_1 = 7.2 Hz, J_2 = 1 Hz), 3.88 (2H, br s), 3.95 (2H, br s), 6.12−6.25 (3H, m), 6.31 (1H, A part of an ABX_2 system, J_{AB} = 7.5 Hz, J_{AX} = 1 Hz), 6.9−7.0 (4H, m), 7.2−7.3 (2H, m); MS *m/e* (rel intensity) 250, 248 (M^+, 10), 169 (60), 97 (100), 45 (70); HMRS calcd for $C_8H_9BrS_2$ 247.93290, found 247.93281.

3-Bromoprop-2-enyl phenyl ether (41a): 1:1 *E/Z* mixture; ^{1}H NMR δ 4.5 (2H, d, J = 4 Hz), 4.73 (2H, d, J = 4 Hz), 6.35−6.55 (4H, m), 6.85−7.0 (6H, m), 7.2−7.4 (4H, m); MS *m/e* (rel intensity) 214, 212 (M^+, 20), 133 (100), 121, 119 (70), 105 (60); HRMS calcd for C_9H_9BrO 211.98367, found 211.98353.

3-Bromoprop-2-enyl phenyl sulfide (41b): 1:1 *E/Z* mixture; ^{1}H NMR δ 3.45 (2H, d, J = 6 Hz), 3.70 (2H, d, J = 6 Hz), 6.0−6.3 (4H, m, collapsing to 6.06, 1H, A part of an ABX_2 system, J_{AB} = 13.3 Hz, J_{AX} ~ 0 Hz, 6.20, 1H, B part of an ABX_2 system, J_{AB} = 13.3 Hz, J_{BX} = 6 Hz, 6.17, 1H, A′ part of an A′B′ system, $J_{A'B'}$ = 7.5 Hz, and 6.23, 1H, B′ part of A′B′ system, $J_{A'B'}$ = 7.5 Hz, upon irradiation at δ = 3.70), 7.2−7.4 (10H, m); MS *m/e* (rel intensity) 230, 228 (M^+, 100), 149, 147 (90), 121, 119 (80), 116 (80), 115 (80), 109 (80); HRMS calcd for C_9H_9BrS 227.96083, found 227.96071.

(3-Bromoprop-2-enyl)phenylamine (41c): 1:1 *E/Z* mixture; ^{1}H NMR δ 3.78 (2H, dd, J_1 = 1 Hz, J_2 = 3 Hz), 3.97 (2H, d, J = 4 Hz), 6.2−6.4 (4H, m), 6.6−6.8 (6H, m), 7.20 (4H, m); MS *m/e* (rel intensity) 213, 211 (M^+, 30), 132 (100), 130 (70), 117 (40), 106 (80); HRMS calcd for $C_9H_{10}BrN$ 210.99966, found 210.99954.

2-Bromoprop-2-enyl 2-chlorophenyl ether (46a): ^{1}H NMR δ 4.70 (2H, br s), 5.65 (1H, br s), 6.05 (1H, br s), 6.8−7.0 (2H, m), 7.1−7.2 (1H, m), 7.3−7.4 (1H, m); MS *m/e* (rel intensity) 248, 246 (M^+, 20), 169 (30), 167 (100), 130 (30), 128 (100); HRMS calcd for C_9H_8ClO 245.94470, found 245.94463.

2-Bromoprop-2-enyl 2,4,6-trichlorophenyl ether (46b): mp = 38−40 °C; ^{1}H NMR δ 4.60 (2H, d, J = 1 Hz), 5.75 (1H, m, collapsing to doublet, J = 2 Hz, upon irradiation at δ = 4.6), 6.20 (1H, m; collapsing to doublet, J = 2 Hz, upon irradiation at δ = 4.6), 7.30 (2H, s); MS *m/e* (rel intensity) 318 (25), 316 (40), 314 (M^+, 20); HRMS calcd for $C_9H_6BrCl_3O$ 313.86676, found 313.8663.

(*Z*)-3-Bromoprop-2-enyl 2-cyanophenyl ether [(*Z*)-52a]: ^{1}H NMR δ 4.83 (2H, m), 6.45 (2H, m), 6.9−7.1 (2H, m), 7.5−7.6 (2H, m); MS *m/e* (rel intensity) 239, 237 (M^+, 10), 158 (60), 121, 119 (100); HRMS calcd for $C_{10}H_8Br$ 236.97892, found 236.97885.

(*E*)-3-Bromoprop-2-enyl 2-cyanophenyl ether [(*E*)-52a]: mp = 72−74°C ^{1}H NMR δ 4.62 (2H, dd, J_1 = 5.4 Hz, J_2 = 1.5 Hz), 6.45 (1H, A part of an ABX_2 system, J_{AB} = 14 Hz, J_{AX} = 5.4 Hz), 6.60 (1H, B part of an ABX_2 system, J_{AB}= 14 Hz, J_{BX}= 1.5 Hz), 6.95 (1H, d, J = 8.5 Hz), 7.05 (1H, t, J = 8.5 Hz), 7.5−7.6 (2H, m); MS *m/e* (rel intensity) 239, 237 (M^+, 10), 158 (60), 121, 119 (100); HRMS calcd for $C_{10}H_8BrNO$ 236.97892, found 236.97885.

(*E*)-3-Bromoprop-2-enyl 4-cyanophenyl ether [(*E*)-52b]: ^{1}H NMR δ 4.5 (2H, dd, J_1 = 5 Hz, J_2 = 1 Hz), 6.4 (1H, A part of an ABX_2 system, J_{AB} = 13 Hz, J_{AX} = 5 Hz), 6.52 (1H, B part of an ABX_2 system, J_{AB} = 13 Hz, J_{BX} = 1 Hz), 6.90 (2H, d, J = 8.5 Hz), 7.60 (2H, d, J = 8.5 Hz); MS *m/e* (rel intensity) 239, 237 (M^+, 5), 158 (70), 121, 119 (100).

(*Z*)-3-Bromoprop-2-enyl 4-cyanophenyl ether [(*Z*)-52b]: ^{1}H NMR δ 4.75 (2H, d, J = 5 Hz), 6.35−6.50 (2H, m), 6.95 (2H, d, J = 8.5 Hz), 7.60 (2H, d, J = 8.5 Hz); MS *m/e* (rel intensity) 239, 237, (M^+, 10), 158 (60), 121, 119 (100); HRMS calcd for $C_{10}H_8BrNO$ 236.97892, found 236.97885.

2-Bromoprop-2-enyl 2-cyanophenyl ether (55a): mp = 47−49 °C; ^{1}H NMR δ 4.70 (2H, s), 5.70 (1H, br s), 6.10 (1H, br s), 6.90 (1H, d, J = 8.5 Hz), 7.05 (1H, t, J = 8.5 Hz), 7.4−7.6 (2H, m); MS *m/e* (rel intensity) 239, 237 (M^+, 20), 158 (80), 119 (100), 91 (60); HRMS calcd for $C_{10}H_8BrNO$ 236.97892, found 236.97885.

2-Bromoprop-2-enyl β-naphthyl ether (56a): ^{1}H NMR δ 4.78 (2H, t, J = 1.4 Hz), 5.72 (1H, dd, $J_1 = J_2$ ~ 1.5 Hz), 6.06 (1H, dd, $J_1 = J_2$ ~ 1.5 Hz), 7.1−7.25 (2H, m), 7.3−7.5 (2H, m), 7.7−7.8 (3H, m); MS *m/e* (rel intensity) 264, 262 (M^+, 15), 183 (100), 115 (100); HRMS calcd for $C_{13}H_{11}BrO$ 261.99932, found 261.99945.

2-Bromoprop-2-enyl β-naphthyl sulfide (56b): ^{1}H NMR δ 3.90 (2H, br s), 5.48 (1H, br d, J = 1 Hz), 5.76 (1H, br d, J = 1 Hz), 7.40−7.55 (3H, m), 7.70−7.90 (4H, m); MS *m/e* (rel intensity) 280, 278 (M^+, 30), 199 (100), 184 (90), 166 (80), 159 (100), 115 (100); HRMS calcd for $C_{13}H_{11}BrS$ 277.97648, found 277.97656.

3-Bromoprop-2-enyl β-naphthyl ether (60a): 1:1 *E/Z* mixture; ^{1}H NMR δ 4.6 (2H, d, J = 4 Hz), 4.85 (2H, dd, J_1 = 4.7 Hz, J_2 = 1 Hz), 6.4−6.6 (4H, m), 7.1−7.2 (4H, m), 7.3−7.5 (4H, m), 7.7−7.8 (6H, m); MS *m/e* (rel intensity) 264, 262 (M^+, 20), 183 (90), 115 (100); HRMS calcd for $C_{13}H_{11}BrO$ 261.99932, found 261.99945.

3-Bromoprop-2-enyl β-naphthyl sulfide (60b): 1:1 *E/Z* mixture; ^{1}H NMR δ 3.58 (2H, br d, J = 7 Hz), 3.82 (2H, br d,

(44) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 2049.

(45) Barluenga, J.; Foubelo, F.; Fananas, F. J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, *3*, 553.

J = 5.7 Hz), 6.1–6.4 (4H, m), 7.4-7.5 (6H, m), 7.7–7.9 (8H, m); MS *m/e* (rel intensity) 280, 278 (M^+, 15), 199 (40), 166 (70), 115 (100); HRMS calcd for $C_{13}H_{11}BrS$ 277.97648, found 277.97656].

Reaction of Vinyl Bromides with Samarium Diiodide. General Procedure. In THF. A solution of the appropriate vinyl bromide (1 mmol), HMPA (1.5 mL), and samarium iodide (3 mmol) in anhydrous THF (30 mL) was stirred under nitrogen atmosphere for ca. 3 h at room temperature. [The presence of air causes a rapid oxidation of samarium(II) as evidenced by the disappearance of the violet color (deep green in acetonitrile).] The reaction mixture was then hydrolyzed with brine and extracted with diethyl ether. Removal of the solvent gave an oily residue, which was analyzed by ^1H NMR and GC/MS and then chromatographed on a silica gel column by gradual elution with light petroleum (bp 40–70 °C)/diethyl ether, unless otherwise stated.

In Acetonitrile. THF solvent was distilled off under vacuum from the commercially available 0.1 M THF solution of SmI_2 (30 mL), and then a solution of the appropriate vinyl bromide (1 mmol) and HMPA (1.5 mL) in anhydrous acetonitrile (30 mL) was added under nitrogen atmosphere. The resulting mixture was stirred for ca. 3 h at room temperature and then worked-up as described above.

From (Trimethylsilyl)propynyl Ether 1. In THF. Column chromatography gave the furan derivative **2** as a 9:1 *Z/E* mixture (100 mg, 60%).

In Acetonitrile. Column chromatography gave the compound **2** as a 60:40 *Z/E* mixture (90 mg, 55%).

From (Trimethylsilyl)propynyl Ether 5 (1:1 *E/Z* Mixture). In THF. Column chromatography gave the allene **11** (20 mg, 12%), starting ether **5** (10 mg), the allyl ether **9** (35 mg, 21%), the pyran **6** (70:30 *E/Z* mixture; 40 mg, 24%), and the hexenol **13** (58 mg, 35%).

In Acetonitrile. Column chromatography gave starting product (30 mg, 12%), the pyran **6** (50:50 *E/Z* mixture; 30 mg, 25%), and the hexenol **13** (50 mg, 40%).

From (*Z*)-(Trimethylsilyl)propynyl Ether (*Z*)-5. In THF. GC/MS and ^1H NMR analysis of the reaction mixture showed the presence of allene **11**, pyran **6**, and hexenol **13** in a 17:33:50 ratio.

From (Trimethylsilyl)butynyl Ether 15. In THF. Elution with *n*-pentane gave a 90:10 inseparable mixture of ether **17** and 2-methylene-3-[(trimethylsilyl)methylene]pyran (**19**) (125 mg, 70%; 50:50 *E/Z* mixture): ^1H NMR δ 0.15 (9H, s), 2.5 (2H, m), 3.70 (2H, m), 4.10 (2H, br s), 4.72 (0.5H, br s), 4.92 (0.5H, br s), 5.02 (0.5H, br s), 5.12 (0.5H, br s), 5.30 (0.5H, br s), 5.68 (0.5H, br s); both *E*- and *Z*-isomers showed identical GC/MS spectra with peaks at *m/e* (rel intensity) 182 (M^+, 10), 167 (60), 75 (100), 73 (60), 59 (40).

In Acetonitrile. Column chromatography gave starting product (80 mg, 15%) and a 85:15 mixture of ether **17** and pyran **19** (50:50 *E/Z* mixture; 220 mg, 50%).

From Cyclohexenyl Ether 20. In THF. Elution with *n*-pentane gave starting ether **20** (45 mg, 20%) and 9-methylene-7-oxobicyclo[4.3.0]nonane (**22**) (85 mg, 75%): ^1H NMR δ 1.20–2.0 (8H, m), 2.50 (1H, m), 3.95 (1H, m), 4.30 (1H, A part of an AB system, J = 10 Hz), 4.46 (1H, B part of an AB system, J = 10 Hz), 4.84 (1H, d, J = 1.2 Hz), 4.90 (1H, d, J = 1.2 Hz); MS *m/e* (rel inten) 138 (M^+, 10), 120 (10), 109 (20), 95 (40), 81 (50), 79 (50), 67 (100); HRMS calcd for $C_9H_{16}O$ 140.12011, found 140.12020].

From Hexenyl Ether 23. In THF. Elution with *n*-pentane gave starting **23** (45 mg, 20%) and an inseparable 65:35 mixture of allyl ether **26** and pyran **25** (90 mg, 80%): ^1H NMR signals at δ 0.9 (t, J = 7 Hz), 1.6–1.7 (m), 1.9–2.4 (m), 3.3–3.5 (m), and 4.0–4.1 (m), ascribable to methyl and methylene groups of both allyl ether **26** and pyran **25**, and signals at δ 5.17 (br d, J = 10 Hz), 5.27 (br d, J = 17 Hz), 5.40 (A part of an ABX_2 system, J_{AB} = 15 Hz, J_{AX} = 5.5 Hz), 5.57 (B part of an ABX_2 system, J_{AB} = 15 Hz, J_{BX} = 5.5 Hz), and 5.92 (ddt, J_1 = 10 Hz, J_2 = 17 Hz, J_t = 5.5 Hz) (vinylic protons of ether **26**), and 4.77 (br s) and 4.86 (br s) (vinylic protons of pyran **25**); GC/MS *m/e* (rel intensity) (**25**) 140 (M^+, 5), 111 (10), 97 (100), 125 (M^+ − 15, 10), 112 (15), 69 (20), 41 (100).

From Thienyl Sulfide 27. In THF. Elution with *n*-pentane gave allyl thienyl sulfide **29** (100 mg, 65%).

In Acetonitrile. Elution with *n*-pentane gave a 75:25 mixture of the sulfide **29** and 1-(2-thienyl)propene (**32**) (50:50 *E/Z* mixture; 90 mg, 60%)

From Thienylmethyl Ether 33a (1:1 *E/Z* Mixture). In THF. Column chromatography gave allyl 2-thienylmethyl ether (**35a**): 15 mg, 11%; ^1H NMR δ 4.10 (2H, dt, J_d = 5.2 Hz, J_t = 1.5 Hz), 4.7 (2H, s), 5.23 (1H, ddt, J_1 = 10 Hz, $J_2 = J_t$ = 1.5 Hz), 5.30 (1H, ddt, J_1 = 17.5 Hz, $J_2 = J_t$ = 1.5 Hz), 5.95 (1H, ddt, J_1 = 17.5 Hz, J_2 = 10 Hz, J_t = 5.2 Hz), 6.9–7.1 (2H, m), 7.3 (1H, m); MS *m/e* (rel intensity) 154 (M^+, 30), 124 (30), 112 (40), 98 (60), 97 (100), 85 (60); HRMS calcd for $C_8H_{10}OS$ 154.04524, found 154.04530.

Also eluted was 1-(2-thienyl)but-3-enol (**40**): 85 mg, 65%; ^1H NMR δ 2.20 (br d, J = 3.5 Hz, OH), 2.65 (2H, dddd, $J_1 = J_2$ = 6.5 Hz, $J_3 = J_4$ = 1.5 Hz), 5.0 (1H, br dt, J_t = 6.5 Hz, J_d = 3.5 Hz), 5.18 (1H, ddt, J_1 = 10 Hz, $J_2 = J_t \sim$ 1.5 Hz), 5.20 (1H, ddt, J_1 = 17 Hz, $J_2 = J_t \sim$ 1.5 Hz), 5.85 (1H, ddt, J_1 = 17 Hz, J_2 = 10 Hz, J_t = 6.5 Hz), 7.0 (2H, m), 7.3 (1H, m); GC/MS *m/e* (rel intensity) 154 (M^+, 5), 135 (10), 113 (100), 85 (90); IR ν_{max} = 3640 (sh), 3345; HRMS calculated for $C_8H_{10}OS$ 154.04524, found 154.04535. Starting ether **33a** (25 mg, 15%) was also obtained.

From Thienylmethyl Sulfide 33b (1:1 *E/Z* mixture). In THF. Column chromatography gave butenylthiophene **37** (48 mg, 50%), allyl thienylmethyl sulfide **35b** (36 mg, 31%), and starting sulfide (24%).

From Phenyl Ether 41a, Phenyl Sulfide 41b, and Phenylamine 41c. In THF. Column chromatography gave the corresponding allyl phenyl derivatives **43a–c** (ca. 85–90%).

In Acetonitrile. GC/MS and ^1H NMR analyses of reaction mixtures showed exclusive formation of the products **43a–c**. **43c**: ^1H NMR δ 3.78 (2H, dt, J_d = 5 Hz, J_t = 1 Hz, superimposed to 1H, br s , NH), 5.16 (1H, ddt, J_1 = 10 Hz, $J_2 = J_t$ = 1 Hz), 5.28 (1H, ddt, J_1 = 17 Hz, $J_2 = J_t$ = 1 Hz), 5.95 (1H, J_1 = 17 Hz, J_2 = 10 Hz, J_t = 5 Hz), 6.60–6.75 (3H, m), 7.1–7.2 (2H, m); MS *m/e* (rel intensity) 133 (M^+, 90), 132 (80), 106 (100), 77 (80); HRMS calculated for $C_9H_{11}N$ 133.08915, found 133.08921.

From Phenyl Ether 44a and Phenylamine 44c. Reactions were carried out in both THF and acetonitrile. GC/MS and ^1H NMR analyses of reaction mixtures showed exclusive formation of allyl ether **43a** and allylamine **43c**.

From Phenyl Sulfide 44b. In THF. Workup and removal of the solvent afforded a few milligrams of thiophenol (GC/MS analysis).

From 2-Chlorophenyl Ether 46a. In THF and Acetonitrile. Chromatography gave 2-chlorophenyl ether **49a** (140 mg, 80%).

From 2,4,6-Trichlorophenyl Ether 46b. In THF. After 2 h trichlorophenyl ether **49b** and trichlorophenol **48** were the only products detectable by GC/MS. At this time further samarium iodide (2 mmol) was added, and the mixture was allowed to react for 3 h. Workup and column chromatography gave ether **49b** (95 mg, 40%) and 3-methyl-5,7-dichloro-2,3-dihydrobenzo[*b*]furan (**50**): 80 mg, 40%; ^1H NMR δ 1.32 (3H, d, J = 7.2 Hz, collapsing to singlet upon irradiation at δ 3.6), 3.5–3.7 (1H, m), 4.20 (1H, dd, J_1 = 7.2 Hz, J_2 = 7.5 Hz, collapsing to doublet, J = 7.2 Hz, upon irradiation at δ 3.6), 4.8 (1H, dd, $J_1 = J_2$ = 7.2 Hz), 7.0 (1H, s) 7.12 (1H, s); MS *m/e* (rel intensity) 202 (M^+, 80), 187 (100), 159 (60); HRMS calcd for $C_9H_8Cl_2O$ 201.99522, found 201.99535. Also eluted was trichlorophenol **48** (12 mg, 6%).

From 2-Cyanophenyl Ether 52a (1:1 *E/Z* Mixture). In THF. Chromatography gave allyl 2-cyanophenyl ether (**53a**): 20 mg, 13%; ^1H NMR δ 4.65 (2H, dt, J_d = 5 Hz, J_t = 1.5 Hz), 5.32 (1H, ddt, J_1 = 11 Hz, $J_2 = J_t$ = 1.5 Hz), 5.46 (1H, ddt, J_1 = 17 Hz, $J_2 = J_t$ = 1.5 Hz), 6.03 (1H, ddt, J_1 = 17 Hz, J_2 = 11 Hz, J_t = 5 Hz), 6.9–7.1 (2H, m), 7.4–7.6 (2H, m); MS *m/e* (rel intensity) 159 (M^+, 60), 119 (30), 41 (100); HRMS calcd for $C_{10}H_9NO$ 159.06841, found 159.06853. Also eluted was 2-cyanophenol (**54a**) (80 mg, 67%).

From (*Z*)-4-Cyanophenyl Ether (*Z*)-52b. In THF. Chromatography gave allyl 4-cyanophenyl ether (**53b**) (20 mg, 16%),

starting ether **52b** (50 mg, 20%), and 4-cyanophenol (**54b**) (65 mg, 68%). The same results were obtained by reacting the *E*-isomer (*E*)-**52b**.

From 2-Cyanophenyl Ether 55a. In THF. Chromatography gave 2-cyanophenyl ether **53a** (16 mg, 10%) and 2-cyanophenol (**54a**) (90 mg, 75%).

In Acetonitrile. Chromatography gave ether **53a** (20 mg, 15%), starting **55a** (35 mg, 15%), and phenol **54a** (75 mg, 75%).

From β-Naphthyl Ethers 56a and 60a. In THF. In both cases chromatography gave allyl naphthyl ether **59a** as the only isolable product in 85% and 92% yields, respectively. Starting ether **56a** was recovered in 25% yield.

In Acetonitrile. TLC and GC/MS showed formation of ether **59a** as the only reaction product.

From β-Naphthyl Sulfide 56b. In THF. Chromatography gave naphthalenethiol **58** (115mg, 95%) and starting ether **56b** (25%).

From β-Naphthyl Sulfide 60b. In THF. Chromatography gave naphthalenethiol **58** (20 mg, 15%), starting sulfide **60b** (40 mg, 15%), allyl β-naphthyl sulfide (**59b**) (80 mg, 47%), and β-naphthyl prop-1-en-1-yl sulfide (**63**): 1:1 *E/Z* mixture; 35 mg, 21%; ^{1}H NMR δ 1.9 (3H, br d, J = 6.7 Hz), 5.98 (0.5H, A part of an ABX_3 system J_{AB} = 10 Hz, J_{AX} = 6.7 Hz, collapsing to A part of an AB system upon irradiation at δ 1.9), 6.07 (0.5H, A′ part of an $A'B'X_3$ system, $J_{A'B'}$ = 15 Hz, $J_{A'X}$ = 6.7 Hz; collapsing to A′ part of an A′B′ system upon irradiation at δ 1.9), 6.25 (0.5H, B′ part of an $A'B'X_3$ system, $J_{A'B'}$ = 15 Hz, $J_{A'X}$ ~ 1 Hz), 6.33 (0.5H, B part of an ABX_3 system, J_{AB} = 10 Hz, J_{AX} ~ 1 Hz), 7.35–7.5 (3H, m), 7.7–7.85 (4H, m); Ms *m/e* (rel intensity) 200 (M^+, 100), 199 (20), 185 (70), 128 (40), 115 (65); HRMS calcd for $C_{13}H_{12}S$ 200.06597, found 200.06625.

Control Experiments. The appropriate substrate (1 mmol) was allowed to react with samarium diiodide (3 mmol) in THF/HMPA solution as described above in General Procedure. The reaction mixture was then analyzed by TLC, ^{1}H NMR, and/or GC/MS. α-Toluenethiol and 4-methylbenzenethiol gave toluole as the only product detectable by GC/MS besides trace amounts of starting thiol. β-Naphthalenethiol (**58**) was found to be unchanged. 4-Cyanophenyl allyl ether (**53b**) gave a 20:80 mixture of starting **53b** and 4-cyanophenol (**54b**). β-Naphthyl sulfide **59b** gave a ca. 30:70 mixture of β-naphthalenethiol (**58**) and starting **59b**. β-Naphthyl ether **59a** remained unchanged. Trichlorophenyl ether **49b** gave a 50:50 mixture of starting **49b** and dihydrofuran **50**.

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Supporting Information Available: ^{1}H NMR spectra of compounds **15**, **20**, **22**, **23**, **27**, **33a,b**, **35a**, **40**, **41a,c**, **46a,b**, **50**, (*E*)-**52a,b**, (*Z*)-**52a,b**, **53a**, **55a**, **56a,b**, **60a,b**, and **63** (26 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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