J = 8.5, 6.0, and 0.5 Hz, C*H*CH_2O), 2.06 (dd, J = 9.5 and 7.5 Hz, NCH_2CH), 2.03 (ddd, J = 11.5, 5.0, and 3.0 Hz, CH_2N), 1.70 (ddd, J = 10.5, 8.5, and 2.5 Hz, NC*H*CH), 1.54 (ddd, J = 11.5, 4.0, and 3.0 Hz, CH_2), 1.6–1.9 (m, 3 H), and 1.2–1.3 (m, 2 H); ^{13}C NMR: δ 74.5 (t), 69.0 (t), 63.2 (d), 60.9 (t), 54.8 (d), 52.4 (t), 30.5 (t), 25.1 (t), 24.3 (t); MS m/e (EI) ($C_9H_{16}N_2O$) 168 (m, 87), 167 (M – 1, 23), 150 (M – H_2O, 7), 137 (M – CH_2OH, 100), 122 (69), and 110 (89).

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Formation and Electrophilic Reactions of Benzeneselenenyl *p*-Toluenesulfonate. Preparation and Properties of Addition Products with Acetylenes

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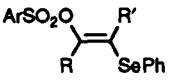
Benzeneselenenyl *p*-toluenesulfonate (**1**) was generated in situ by the reaction of silver *p*-toluenesulfonate with benzeneselenenyl chloride in acetonitrile. The reagent reacted with acetylenes by electrophilic 1,2-addition to afford the β-(phenylseleno)vinyl *p*-toluenesulfonates **2–12**, generally in high yield. The latter were formed preferentially by anti addition, but with poor regioselectivity, unless a strongly orienting group (e.g., phenyl) was present. Selenenyl sulfonate **1** was also unexpectedly produced via radical pathways by heating *p*-toluenesulfonic acid with AIBN in the presence of diphenyl diselenide, or from the pyrolysis of sulfinyl sulfone **15** with the diselenide. The regioisomeric adducts **3** and **4** were prepared from **1** and 1-decyne, and both underwent elimination with potassium *tert*-butoxide to afford the acetylenic selenide **19** initially, which isomerized to a 6:1 mixture of the propargylic and allenic selenides **20** and **21** upon further equilibration. A Fritsch–Buttenberg–Wiechell rearrangement is proposed for the elimination of **4**. The syn elimination of the selenoxide of **4** required forcing conditions and afforded only ca. 20% of the corresponding allenic sulfonate **22**. The electrophile **1** induced the efficient cyclization of 5-hexen-1-ol and 4-pentenoic acid to the corresponding pyran **24** and lactone **25**, respectively. It failed to cyclize alkynols, but afforded the lactones **28** and **29** from 4-pentynoic acid in low yield.

The reactions of electrophilic selenium compounds are both synthetically important and mechanistically interesting.[1] The majority of such species are selenenyl halides or pseudohalides (RSeX, where X = a leaving group) that are formally related to selenenic acids (RSeOH). For instance, selenenyl chlorides (RSeCl) and bromides (RSeBr) and diselenides (RSeSeR) are well-known, often commercially available compounds, with numerous applications. Examples of less frequently encountered selenenic electrophiles include benzeneselenenyl acetate (PhSeOAc)[2] and trifluoroacetate,[2j,3] selenocyanates (RSeCN),[4] benzeneselenenyl fluoride (PhSeF)[5] and iodide (PhSeI),[6] *N*-(phenylseleno)phthalimide[7] and -succinimide,[7a,8] sele-

Table I.[a] **Preparation, from RC≡CR′, of**



no.	R	R′	method[b]	yield,[c] %
2	H	H	A	51
3	n-C_8H_{17}	H	A	81 (3:4 = 57:43)
4	H	n-C_8H_{17}	B	85 (3:4 = 55:45)
			C	68 (3:4 = 53:47)
5	Ph	H	A	62
			B	40
			C	23
6	Ph	Me	A	75
7	Ph	n-Bu	A	65
8	Ph	Ph	A	60
9	n-Bu	n-Bu	A	84
			B	56
			C	52
10	$ClCH_2$	CH_2Cl	A	80
11	H	CO_2Me	A	42
12	MeO_2C	CO_2Me	A	25

[a] Ar = *p*-tolyl. [b] Method A: $AgOSO_2Ar$, PhSeCl, RC≡CR′; MeCN; room temperature. Method B: $ArSO_3H$, AIBN, PhSeSePh, RC≡CR′; C_6H_6; Δ. Method C: $ArS(O)SO_2Ar$, PhSeSePh, RC≡CR′; C_6H_6; Δ. [c] Isolated yields are reported except for **12** (see Experimental Section).

(1) For a review of electrophilic reactions of selenium compounds, see: (a) Back, T. G. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 1. For other recent reviews of organoselenium chemistry, see: (b) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1986 (Vol. 1), 1987 (Vol. 2). (c) Paulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986. (d) Nicolaou, K. C.; Petasis, N. A. In *Selenium in Natural Products Synthesis*; CIS: Philadelphia, 1984.

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(3) (a) Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1974**, 100. (b) Reich, H. J. *J. Org. Chem.* **1974**, *39*, 428. (c) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (d) Detty, M. R. *J. Org. Chem.* **1980**, *45*, 274. (e) Seebach, D.; Calderari, G.; Knochel, P. *Tetrahedron* **1985**, *41*, 4861.

(4) For a review, see: Toshimitsu, A.; Uemura, S. In ref 1b, Vol. 2, Chapter 14.

(5) Although this electrophile has not been characterized, it is a possible intermediate in several recent procedures: (a) Tomoda, S.; Usuki, Y. *Chem. Lett.* **1989**, 1235. (b) McCarthy, J. R.; Matthews, D. P.; Barney, C. L. *Tetrahedron Lett.* **1990**, *31*, 973. (c) Saluzzo, C.; Alvernhe, G.; Anker, D. *Tetrahedron Lett.* **1990**, *31*, 2127. (d) Uneyama, K.; Kanai, M. *Tetrahedron Lett.* **1990**, *31*, 3583.

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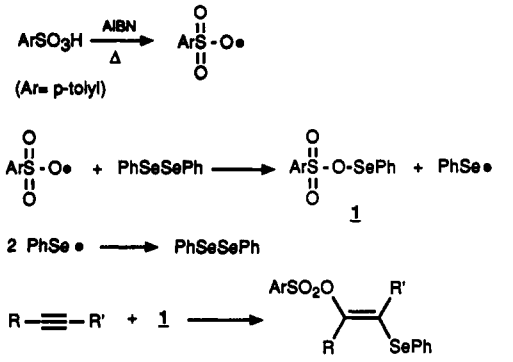
nosulfonates ($ArSO_2SePh$),[9] and others.[10] The unstable parent selenenic acids, or their anhydrides (RSeOSeR),[11] can themselves be generated in situ by a variety of methods, and these species are useful in oxyselenenylations and other applications.[12]

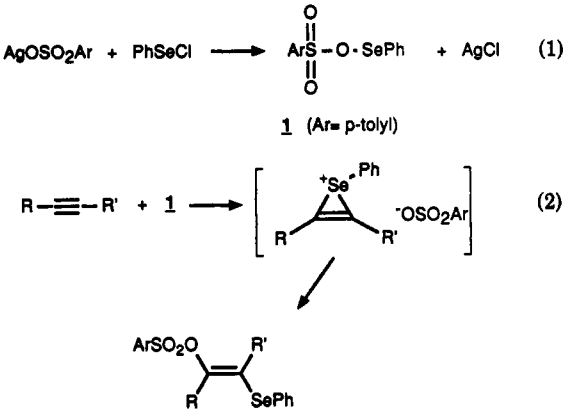
In view of the general interest in selenenic derivatives, we wished to explore the chemistry of selenenyl sulfonates (RSO_2OSeR'). The latter are formally mixed anhydrides of selenenic and sulfonic acids and are a virtually unknown class of compounds. Although benzeneselenenyl triflate (CF_3SO_2OSePh) was reported recently,[13] its properties are expected to be atypical of selenenyl sulfonates because of the extremely nonnucleophilic nature of the triflate anion. Also, while our work was in progress,[14] Yoshida and coworkers[15] postulated benzeneselenenyl *m*-nitrobenzenesulfonate (*m*-NO_2PhSO_2OSePh) as an intermediate in electrophilic selenenylations effected by diphenyl diselenide and *m*-nitrobenzenesulfonyl peroxide. We now report the facile preparation of benzeneselenenyl *p*-toluenesulfonate (1) from the substitution of benzeneselenenyl chloride with silver *p*-toluenesulfonate, and its reactions with acetylenes and olefins. We also report the unexpected formation of **1** from the reaction of *p*-toluenesulfonic acid with the radical initiator AIBN in the presence of diphenyl diselenide, and from the pyrolysis of a mixture of a sulfinyl sulfone ($ArS(O)SO_2Ar$) and the diselenide.

Scheme I



Formation of 1 by Direct Substitution and Its Electrophilic Addition to Acetylenes

Benzeneselenenyl *p*-toluenesulfonate (1) was prepared by the addition of benzeneselenenyl chloride to a solution of silver *p*-toluenesulfonate in acetonitrile, as shown in eq 1. Attempts to isolate the product **1** were unsuccessful, and so it was typically employed in situ. The subsequent introduction of acetylenes resulted in efficient electrophilic 1,2-additions to produce the corresponding β-(phenylseleno)vinyl *p*-toluenesulfonates **2–12**, according to eq 2. The results are summarized in Table I (method A).



The addition of **1** to acetylene produced the corresponding *E* and *Z* adducts **2a** and **2b** in the ratio of 90:10. The stereochemical assignments were based on their vinylic coupling constants of 12.3 and 5.1 Hz, respectively, and on the presence of an infrared absorption at 924 cm^{-1} in **2a**. These values are consistent with those of the *E* and *Z* adducts produced from other selenenic electrophiles and acetylene.[16] The strong preference for anti addition suggests the formation of the bridged selenirenium ion intermediate[10e,16a] shown in eq 2. The other adducts in Table I were also formed in a highly stereospecific manner, and we tentatively assign them the *E* configuration by analogy.

The similar treatment of 1-decyne with **1** afforded a mixture of the two regioisomers **3** and **4** in nearly equal amounts, whereas adducts **5**, **6**, **7**, and **11** were obtained as single regioisomers. Compound **5** produced 1-phenyl-

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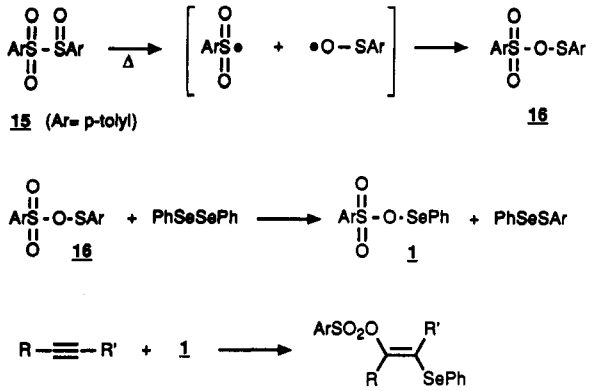
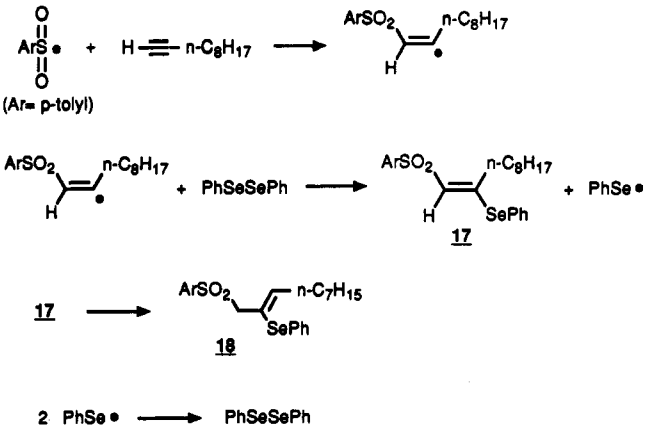
(16) For instance, these values for the adduct of PhSeCl and acetylene are J_{trans} = 13.6 Hz and J_{cis} = 6.3 Hz. See: (a) Schmid, G. H.; Garratt, D. G. *Chem. Scr.* **1976**, *10*, 76. For NMR and IR data on other, similar adducts, see: (b) Kataev, E. G.; Mannafov, T. G.; Samitov, Y. Y. *Zh. Org. Khim.* **1975**, *11*, 2324.

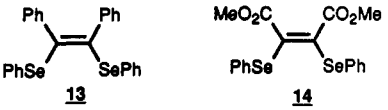
Scheme II



Scheme III



ethanol, but no 2-phenylethanol, upon reduction with excess lithium aluminum hydride. The assigned Markovnikov regiochemistry of **5** is thereby confirmed. These results indicate that the regioselectivity of the addition is poor, unless a strongly orienting group such as the phenyl group is present. The addition of the selenenyl sulfonate to acetylenes containing electron-withdrawing groups was also possible. Methyl propiolate and dimethyl acetylenedicarboxylate thus afforded **11** and **12**, respectively, as unique stereo- and regioisomers, albeit in relatively low yield because of competing polymerization and the persistence of unreacted starting material. The assignment of the indicated regiochemistry to **11** is based on the literature precedents of the additions of other selenenic electrophiles to propiolic acids and acetylenic ketones,[17] and on the ^{13}C NMR spectrum of **11** [δ 144.4 for $=CHOSO_2Ar$ and δ 110.9 for $=C(SePh)CO_2Me$]. The bis(selenides) **13** and **14** were unexpected minor byproducts of compounds **8** and **12**, respectively.[18]



Formation of Selenenyl Sulfonate 1 from Other Sources

The formation of the same adducts **3** and **4** was observed when *p*-toluenesulfonic acid, diphenyl diselenide, AIBN, and 1-decyne were refluxed overnight in benzene (method B). Moreover, these compounds were also formed when sulfinyl sulfone **15**,[19] diphenyl diselenide, and 1-decyne were heated in benzene (method C). Adducts **5** and **9** were similarly prepared from phenylacetylene and 5-decyne, respectively. These results are also included in Table I. Method A is recommended for preparative purposes because it generally provides higher yields.

A plausible mechanism for the formation of **3** and **4** under the conditions of method B is shown in Scheme I, where sulfonate radicals ($ArSO_3^{\bullet}$) are produced via hydrogen atom abstraction from the sulfonic acid by free radicals generated from the pyrolysis of AIBN.[20] The sulfonate radicals then react with the diselenide[21] to afford **1**, followed by its electrophilic addition to the acetylene as in method A. Failure to observe adducts **3** and **4** when AIBN was omitted in a control experiment is consistent with this hypothesis. The radicals produced from the pyrolysis of AIBN also reacted with the diselenide in a competing process, as confirmed by the formation of the same byproducts in a separate reaction containing only the diselenide and AIBN.

The mechanism that we propose to explain the results obtained via method C is described in Scheme II. Kice and Pawlowski[22] reported the isomerization of sulfinyl sulfone **15** to the sulfenyl sulfonate **16** via dissociation and recombination of $ArSO^{\bullet}$ and $ArSO_2^{\bullet}$ radicals under conditions similar to those employed here. The disproportionation of **16** with diphenyl diselenide would again produce the selenenyl sulfonate **1**, which could then add to acetylenes in the usual manner. The postulated disproportionation step was tested by preparing the sulfenyl sulfonate **16** from the direct substitution of benzenesulfenyl chloride with silver *p*-toluenesulfonate[23a] and permitting it to react with the diselenide in the presence of 1-decyne. The continued formation of **3** and **4** supports the proposed mechanism. It is interesting to note that no substantial amount of addition products of the sulfenyl sulfonate **16** to the acetylene were observed, suggesting that the selenium analogue **1** is considerably more reactive than **16**.[23] We also observed small amounts of **17**, the product of free-radical selenosulfonation[24] of 1-decyne, as well as its isomer **18**, via method C. This suggests that some of the sulfonyl radicals ($ArSO_2^{\bullet}$) produced during the decomposition of sulfinyl sulfone **15** escape from their solvent cage and attack the acetylene, as shown in Scheme III, instead of recombining with $ArSO^{\bullet}$ radicals to form **16** as in Scheme II. The isomerization of **17** to **18** accounts for the presence of the latter, as confirmed by the conversion of an authentic sample of **17** into **18**[25] by heating it with

(17) Kataev, E. G.; Mannafov, T. G.; Saidov, O. O. *Zh. Org. Khim.* **1971**, *7*, 2229.

(18) Compound **13** was obtained as a single isomer of unknown geometry, arbitrarily shown as the *Z* isomer. Compound **14** was predominantly the *Z* isomer, as determined by comparison with authentic samples of the *E* and *Z* forms (see Experimental Section). The mechanism for the formation of these byproducts is unclear at this time and warrants further investigation.

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(21) The diselenide is a good radical trapping agent: (a) Perkins, M. J.; Turner, E. S. *J. Chem. Soc., Chem. Commun.* **1981**, 139. (b) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398. (c) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533.

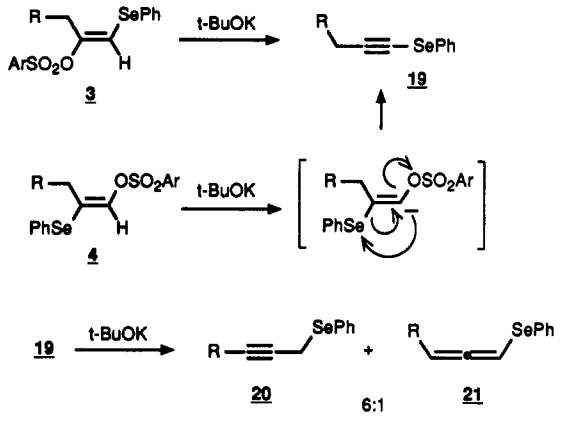
(22) Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898.

(23) For related work on the additions of sulfenyl sulfonates to acetylenes and further reactions of the products, see: (a) Capozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc. C* **1970**, 2617. (b) Capozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc. C* **1970**, 2621. (c) Capozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc. C* **1970**, 2625. (d) Modena, G.; Tonellato, U. *J. Chem. Soc. B* **1971**, 1569.

(24) (a) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. (b) Back, T. G.; Collins, S.; Gokhale, U.; Law, K.-W. *J. Org. Chem.* **1983**, *48*, 4776. (c) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.

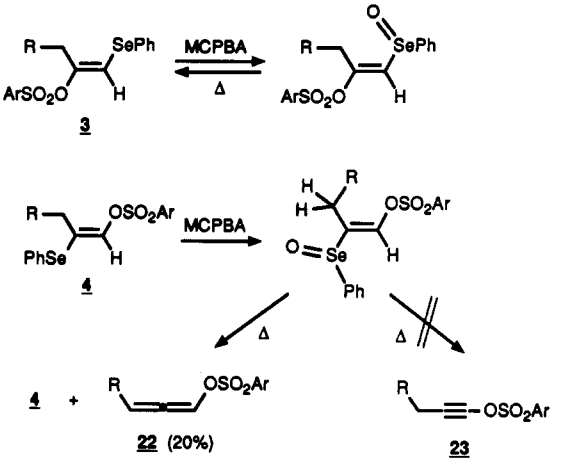
(25) Compound **18** has been previously prepared by the base-catalyzed isomerization of **17**: Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 4146.

Scheme IV[a]



[a] Ar = *p*-tolyl; R = n-C_7H_{15}.

Scheme V[a]



[a] Ar = *p*-tolyl; R = n-C_7H_{15}.

the sulfinyl sulfone **15** under similar conditions in a control experiment.

The postulated formation of **1** in all three methods, as well as its electrophilic addition to the acetylenes, is consistent with the observed regiochemistry of the addition step. Nearly identical ratios of the regioisomers **3** and **4** were obtained from 1-decyne in methods B and C as in the clearly electrophilic addition in method A. Furthermore, the same Markovnikov regioisomer **5** was produced from phenylacetylene by all three methods, albeit in lower yields via methods B and C. An alternative explanation for these results could be that the addition of **1** to the acetylene occurs by means of a free-radical mechanism, followed by equilibration of the initially formed anti-Markovnikov isomers. To rule out this possibility, we obtained a partially separated sample of the anti-Markovnikov isomer **4** (**4**:**3** = ca. 9:1) by careful chromatography of the usual mixture of **3** and **4**. Compound **4** did not isomerize to **3** when refluxed in benzene alone or in the presence of diphenyl diselenide and *p*-toluenesulfonic acid. These observations all support the mechanisms in Scheme I and II.

Elimination Reactions of β-(Phenylseleno)vinyl Sulfonates

The mixture of regioisomers **3** and **4** proved to be relatively stable toward solvolysis in both acidic and basic media, surviving 24 h in THF containing 5% aqueous KOH or 1 N HCl, or 19 h in refluxing aqueous dioxane containing a catalytic amount of perchloric acid.[23c,d] No substantial change in the ratio of the two isomers was observed under these conditions.

On the other hand, treatment of the same mixture of **3** and **4** with potassium *tert*-butoxide in THF at 0 °C resulted in the rapid consumption of both regioisomers and the formation of three isomeric selenides, **19**, **20**, and **21**, in the ratios of 59:35:6, 22:67:11, and 0:86:14 after 4 min, 15 min, and 1 h, respectively. Evidently, the acetylenic selenide **19** is the initial product of elimination and it then undergoes isomerization to the propargylic selenide **20** and the allenic selenide **21**, formed in the ratio of 6:1 at equilibrium.

The initial formation of the acetylenic selenide from regioisomer **3** presumably proceeds via a simple base-catalyzed syn elimination of *p*-toluenesulfonic acid. However, the elimination of **4** requires a more complex pathway, which we suggest involves the α-elimination of *p*-toluenesulfonic acid accompanied by 1,2-migration of the phenylseleno group. This is reminiscent of the Fritsch–Buttenberg–Wiechell rearrangement,[26] in which migration of an alkyl group accompanies the base-catalyzed elimination of a hydrogen halide from a vinyl halide. The eliminations of **3** and **4** are depicted in Scheme IV.

The syn elimination of the selenoxide[27] corresponding to **4** could, in principle, produce either the interesting allenic[28] or acetylenic[29] sulfonates **22** and **23**, respectively (Scheme V). Oxidation of the mixture of **3** and **4** with (*m*-CPBA) afforded the respective selenoxides. Pyrolysis of the latter mixture in benzene in the presence of DABCO[27] proceeded slowly, affording substantial amounts of the original selenides **3** and **4**,[30] as well as the allenic sulfonate **22**, which was formed in ca. 20% yield as determined by NMR integration. Similar attempts to effect selenoxide syn eliminations with adducts **6**, **7**, **9**, and **11** failed to produce any significant amounts of the corresponding allenic or acetylenic sulfonates. The forcing conditions required to effect these selenoxide eliminations presumably do not permit the survival of the desired products.

Cyclizations with Selenenyl Sulfonate 1

The reactions of simple olefins such as 5-decene with **1** did not produce stable adducts. However, the cyclizations of unsaturated alcohols, carboxylic acids, and related substrates with selenenic electrophiles have numerous synthetic applications.[31] Such cyclofunctionalizations[32]

(26) For a review, see: (a) Köbrich, G.; Buck, P. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Dekker: New York, 1969; Chapter 2, pp 117–134. (b) A referee has pointed out that an alternative mechanism involving elimination of benzeneselenol from **4**, followed by addition–elimination, could account for the formation of **19**. While we cannot completely rule out this possibility, we note the previously reported failure of Stang and co-workers to form the required alkynyl tosylate intermediate by elimination processes (see ref 29b). We therefore favor the well-precedented Fritsch–Buttenberg–Wiechell rearrangement.

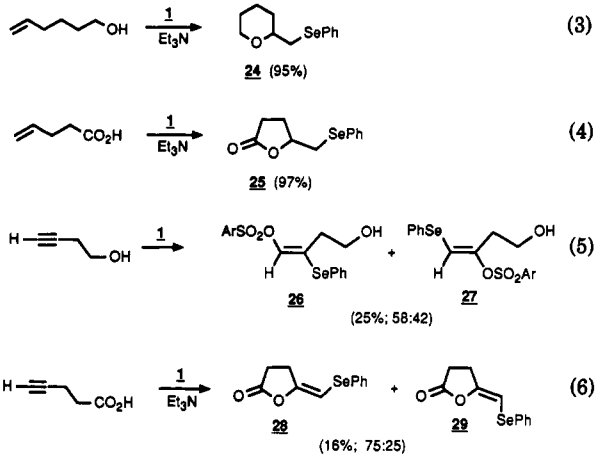
(27) For the formation of other acetylenes and allenes from the elimination of vinyl selenoxides, see: Reich, H. J.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5967. The use of DABCO was recommended by these authors. The known tendency of selenoxides to eliminate away from oxygen substituents (see ref 2c) leads to the expectation that the allenic sulfonate would be preferred over the acetylenic isomer in the case of the selenoxide of **4**.

(28) For another allenic sulfonate, see: Oelberg, D. G.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 1804.

(29) For other acetylenic sulfonates, see: (a) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452. (b) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.

(30) The reduction of selenoxides to selenides as a side reaction of selenoxide syn eliminations has been reported previously. For examples, see: (a) Walter, R.; Roy, J. *J. Org. Chem.* **1971**, *36*, 2561. (b) Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 1396.

can be effected with selenenyl halides, *N*-(phenylseleno)-phthalimide, and similar reagents. The illustrative examples in eqs 3 and 4 show that the selenenyl sulfonate **1** can be similarly employed when the unsaturated moiety is olefinic. The cyclofunctionalization of acetylenic substrates, however, gave unsatisfactory results. Thus, 3-butyn-1-ol afforded only the corresponding 1,2-addition products **26** and **27** in 25% yield (eq 5) and no products of cyclization.[33] The 4-pentyn-1-ol homologue produced only polymeric material, while 4-pentynoic acid afforded the corresponding lactones **28** and **29** in low yield (eq 6).



Experimental Section

All NMR spectra were obtained in $CDCl_3$ solution at 200 MHz. Chromatographic separations (flash, TLC, and preparative TLC) were performed with silica gel as the adsorbent. Sulfinyl sulfone **15** was prepared by the method of Bredereck et al.,[19] with an excess of the sulfinyl chloride as recommended by Kice and Pawlowski.[22] All other starting materials were purchased from commercial sources and purified as necessary by standard methods.

Addition of Benzeneselenenyl p-Toluenesulfonate (1) to Acetylenes via Method A. 2-(Phenylseleno)-1-ethenol p-Toluenesulfonate (2). Benzeneselenenyl chloride (191 mg, 1.00 mmol) was added in portions to silver *p*-toluenesulfonate (279 mg, 1.00 mmol) in 10 mL of dry acetonitrile. A white precipitate formed immediately, and the pale yellow mixture was stirred for 5 min. Acetylene was bubbled through it for 10 min, and stirring was continued for 4 h. The mixture was then filtered through Celite, evaporated in vacuo, and separated by flash chromatography (elution with 25% dichloromethane–hexane) to afford 179 mg (51%) of the *E* adduct **2a**: mp 49–50 °C (from chloroform–hexane); IR (Nujol) 1595, 1376, 1192, 1176, 1027, 924 cm^{-1}; ^1H NMR δ 7.80 (d, J = 8.4 Hz, 2 H), 7.40–7.22 (complex, 7 H), 6.79 (d, J = 12.3 Hz, 1 H), 6.31 (d, J = 12.3 Hz, satellites with $J_{gemSe-CH}$ = 12.1 Hz, 1 H), 2.48 (s, 3 H); mass spectrum, m/z (relative intensity, %) 354 (47, M^+), 199 (68, $M^+ - ArSO_2^{\bullet}$), 171 (40, $ArSO_3^+$), 91 (100, $C_7H_7^+$). Anal. Calcd for $C_{15}H_{14}O_3SSe$: C, 50.99; H, 3.99. Found: C, 51.09; H, 4.04.

NMR analysis of the crude reaction mixture also revealed the presence of signals at δ 6.87 (d, J = 5.1 Hz) and 6.04 (d, J = 5.1 Hz), attributed to the *Z* isomer **2b** and integrating in the ratio of 1:9 with those assigned to the *E* isomer.

The following compounds were prepared similarly, except that the acetylene (1.0–1.1 molar equiv) was added to the selenenyl sulfonate and stirring was continued for 12–24 h. Yields are given in Table I.

1-(Phenylseleno)-1-decen-2-ol p-Toluenesulfonate (3) and 2-(Phenylseleno)-1-decen-1-ol p-Toluenesulfonate (4). The unseparated mixture of regioisomers **3** and **4** was obtained in the ratio of 57:43 (NMR integration) by flash chromatography (elution with 15% ethyl acetate–hexane). It was a pale yellow oil: IR (film) 1626, 1598, 1377, 1192, 1179 cm^{-1}; ^1H NMR δ 7.83–7.20 (complex, 9 H, **3** and **4**), 6.82 (s, **4**) and 6.12 (s, **3**, total 1 H), 2.47 (s, **4**) and 2.44 (s, **3**, total 3 H), 2.37 (t, J = 7.4 Hz, **3**) and 2.11 (t, J = 7.3 Hz, **4**, total 2 H), 1.5–1.1 (complex, 12 H, **3** and **4**), 0.87 (t, J = 6.6 Hz, 3 H, **3** and **4**); mass spectrum, m/z (relative intensity, %) 466 (33, M^+), 311 (37, $M^+ - ArSO_2^{\bullet}$), 171 (75, $ArSO_3^+$), 157 (56, $PhSe^+$), 155 (59, $ArSO_2^+$), 135 (89), 91 (100, $C_7H_7^+$); exact mass calcd for $C_{23}H_{30}O_3SSe$ 466.1081, found 466.1082.

Partial separation of **3** and **4** was achieved by further flash chromatography to afford (elution with 5% dichloromethane–hexane) **4** containing ca. 10% of **3**, and **3** (elution with 20% dichloromethane–hexane) containing ca. 15% of **4**.

1-Phenyl-2-(phenylseleno)-1-ethenol p-Toluenesulfonate (5). The product was isolated by flash chromatography (elution with 10% ethyl acetate–hexane): mp 80–81 °C (from chloroform–hexane); IR (Nujol) 1596, 1367, 1190, 1175, 1003 cm^{-1}; ^1H NMR δ 7.68 (d, J = 8.4 Hz, 2 H), 7.46–7.17 (complex, 12 H), 6.59 (s, 1 H), 2.37 (s, 3 H); mass spectrum, m/z (relative intensity, %) 430 (12, M^+), 275 (20, $M^+ - ArSO_2^{\bullet}$), 247 (49), 167 (95), 105 (84, $PhC^+{=}O$), 91 (72, $C_7H_7^+$), 77 (100). Anal. Calcd for $C_{21}H_{18}O_3SSe$: C, 58.74; H, 4.22. Found: C, 58.63; H, 4.24.

1-Phenyl-2-(phenylseleno)-1-propen-1-ol p-Toluenesulfonate (6). The product was isolated by flash chromatography (elution with 10% ethyl acetate–hexane): mp 75–76 °C (from chloroform–hexane); IR (Nujol) 1596, 1365, 1189, 1174, 1021, 972 cm^{-1}; ^1H NMR δ 7.48–7.06 (complex, 14 H), 2.35 (s, 3 H), 2.11 (s, 3 H); mass spectrum, m/z (relative intensity, %), 444 (2, M^+), 289 (19, $M^+ - ArSO_2^{\bullet}$), 157 (23, $PhSe^+$), 115 (100), 105 (35, $Ph^+C{=}O$), 91 (45, $C_7H_7^+$), 77 (65). Anal. Calcd for $C_{22}H_{20}O_3SSe$: C, 59.59; H, 4.55. Found: C, 59.63; H, 4.39.

1-Phenyl-2-(phenylseleno)-1-hexen-1-ol p-Toluenesulfonate (7). The product was isolated by flash chromatography (elution with 15% ethyl acetate–hexane) as a pale yellow oil: IR (film) 1598, 1578, 1372, 1189, 1177, 967 cm^{-1}; ^1H NMR δ 7.43–7.04 (complex, 14 H), 2.46 (t, J = 7.8 Hz, 2 H), 2.34 (s, 3 H), 1.53 (m, 2 H), 1.24 (m, 2 H), 0.83 (t, J = 7.2 Hz, 3 H); mass spectrum, m/z (relative intensity, %) 486 (11, M^+), 331 (78, $M^+ - ArSO_2^{\bullet}$), 129 (100); exact mass calcd for $C_{25}H_{26}O_3SSe$ 486.0768, found 486.0792.

1,2-Diphenyl-2-(phenylseleno)-1-ethenol p-Toluenesulfonate (8). Flash chromatography of the crude product obtained from the reaction of 178 mg (1.00 mmol) of diphenylacetylene with 1.00 mmol of **1** afforded (elution with 20% dichloromethane–hexane) 68 mg (14%) of 1,2-diphenyl-1,2-bis(phenylseleno)ethene (**13**): mp 159–161 °C (from chloroform–hexane); IR (Nujol) 1574, 775, 744, 703, 690 cm^{-1}; ^1H NMR δ 7.26–7.00 (complex); mass spectrum, m/z (relative intensity, %) 492 (29, M^+), 335 (50, $M^+ - PhSe^{\bullet}$), 254 (35), 178 (100, $PhC{\equiv}CPh^{\bullet+}$). Anal. Calcd for $C_{26}H_{20}Se_2$: C, 63.68; H, 4.11. Found: C, 63.34; H, 3.87.

Elution with 50% dichloromethane–hexane afforded 305 mg (60%) of the title compound **8**: mp 120–121 °C; IR (Nujol) 1620, 1598, 1576, 1357, 1174, 932, 765 cm^{-1}; ^1H NMR δ 7.52–6.94 (complex, 19 H), 2.33 (s, 3 H); mass spectrum, m/z (relative intensity, %) 506 (38, M^+), 351 (48, $M^+ - ArSO_2^{\bullet}$), 323 (30), 194 (51), 178 (100, $PhC{\equiv}CPh^{\bullet+}$). Anal. Calcd for $C_{27}H_{22}O_3SSe$: C, 64.15; H, 4.39. Found: C, 64.01; H, 4.29.

6-(Phenylseleno)-5-decen-5-ol p-Toluenesulfonate (9). The product was isolated by flash chromatography (elution with 15% ethyl acetate–hexane) as a pale yellow oil: IR (film) 1639, 1598, 1579, 1372, 1191, 1180, 1089, 889 cm^{-1}; ^1H NMR δ 7.85 (d, J = 8.4 Hz, 2 H), 7.82–7.21 (complex, 7 H), 2.71 (t, J = 7.4 Hz, 2 H), 2.46 (s, 3 H), 2.14 (t, J = 7.6 Hz, 2 H), 1.44–1.07 (complex, 8 H), 0.82 and 0.77 (2 overlapping t, total 6 H); mass spectrum, m/z (relative intensity, %) 466 (2, M^+), 311 (24, $M^+ - ArSO_2^{\bullet}$), 157 (22, $PhSe^+$), 85 (100); exact mass calcd for $C_{23}H_{30}O_3SSe$ 466.1081, found 466.1080.

1,4-Dichloro-3-(phenylseleno)-2-buten-2-ol p-Toluenesulfonate (10). The product was isolated by flash chromatography (elution with 50% dichloromethane–hexane): mp 73–74 °C (from chloroform–hexane); IR (film) 1625, 1597, 1579, 1367, 1189, 1177, 974, 815, 710 cm^{-1}; ^1H NMR δ 7.89 (d, J = 8.4 Hz,

(31) For a review, see: Nicolaou, K. C.; Petasis, N. A.; Claremon, D. A. In *Organoselenium Chemistry*; Liotta, D., Eds.; Wiley: New York, 1987; Chapter 2.

(32) (a) Clive, D. L. J.; Chittattu, G.; Curtis, N. J.; Kiel, W. A.; Wong, C. K. *J. Chem. Soc., Chem. Commun.* **1977**, 725. (b) Clive, D. L. J.; Russell, C. G.; Chittattu, G.; Singh, A. *Tetrahedron* **1980**, *36*, 1399.

(33) For other reports of the failure of acetylenic alcohols to cyclize in the presence of selenenic electrophiles, see: (a) Filer, C. N.; Ahern, D.; Fazio, R.; Shelton, E. J. *J. Org. Chem.* **1980**, *45*, 1313. (b) Garratt, D. G.; Beaulieu, P. L.; Morisset, V. M. *Can. J. Chem.* **1981**, *59*, 927.

2 H), 7.54–7.39 (complex, 7 H), 4.66 (s, 2 H), 4.08 (s, 2 H), 2.47 (s, 3 H); mass spectrum, m/z (relative intensity, %) 450 (4, M^+), 295 (20, $M^+ - ArSO_2^\bullet$), 260 (22), 183 (29), 157 (53, $PhSe^+$), 91 (92, $C_7H_7^+$), 69 (100). Anal. Calcd for $C_{17}H_{16}Cl_2O_3SSe$: C, 45.35; H, 3.58. Found: C, 44.95; H, 3.51.

3-Hydroxy-2-(phenylseleno)propenoic Acid Methyl Ester *p*-Toluenesulfonate (11). The product was isolated by flash chromatography (elution with dichloromethane): mp 50–51 °C (from chloroform–hexane); IR (film) 1727, 1597, 1578, 1387, 1235, 1195, 1181, 1074, 736 cm^{-1}; ^1H NMR δ 7.78 (d, J = 8.3 Hz, 2 H), 7.39–7.23 (complex, 7 H), 7.21 (s, 1 H), 3.63 (s, 3 H), 2.46 (s, 3 H); ^{13}C NMR δ 163.6 (C=O), 146.0 (C), 144.4 (vinylic CH), 132.3 (CH), 132.0 (C), 130.0 (CH), 129.3 (CH), 128.7 (C), 128.0 (CH), 127.9 (CH), 110.9 (vinylic C), 52.5 (CH_3), 21.6 (CH_3); mass spectrum, m/z (relative intensity, %) 412 (45, M^+), 257 (28, $M^+ - ArSO_2^\bullet$), 197 (57), 157 (70, $PhSe^+$), 155 (80, $ArSO_2^+$), 91 (100, $C_7H_7^+$). Anal. Calcd for $C_{17}H_{16}O_5SSe$: C, 49.63; H, 3.92. Found: C, 49.40; H, 3.91.

2-Hydroxy-3-(phenylseleno)butenedioic Acid Dimethyl Ester *p*-Toluenesulfonate (12). The crude product obtained from the reaction of 142 mg (1.00 mmol) of dimethyl acetylenedicarboxylate with 1.00 mmol of 1 was partly separated by flash chromatography (elution with 50% dichloromethane–hexane) to afford 207 mg of a mixture containing **12**, (*E*)**14**,[21c] and (*Z*)**14**[21c] in the ratio of 57:2:41 (NMR integration), representing yields of 25%, 1%, and 18%, respectively. Repeated recrystallization of this mixture from chloroform–hexane afforded the pure title compound **12**: mp 148–149 °C; IR (film) 1738, 1709, 1597, 1308, 1251, 1193, 1179, 755 cm^{-1}; ^1H NMR δ 7.83–7.31 (complex, 9 H), 3.77 (s, 3 H), 2.99 (s, 3 H), 2.44 (s, 3 H); mass spectrum, m/z (relative intensity, %) 470 (25, M^+), 315 (32, $M^+ - ArSO_2^\bullet$), 255 (57), 157 (70, $PhSe^+$), 155 (70, $ArSO_2^+$), 91 (100, $C_7H_7^+$). Anal. Calcd for $C_{19}H_{18}O_7SSe$: C, 48.62; H, 3.87. Found: C, 48.70; H, 3.87.

The mother liquors from **12** were combined and partly separated by preparative TLC (50% ether–hexane) to afford crude (*Z*)-**14**, which was identical with an authentic sample[21c] after recrystallization.

Addition of Benzeneselenenyl *p*-Toluenesulfonate to Acetylenes via Method B. 1-(Phenylseleno)-1-decen-2-ol *p*-Toluenesulfonate (3) and 2-(Phenylseleno)-1-decen-1-ol *p*-Toluenesulfonate (4). *p*-Toluenesulfonic acid monohydride (190 mg, 1.00 mmol) and diphenyl diselenide (312 mg, 1.00 mmol) were dissolved in 20 mL of refluxing benzene. 1-Decyne (0.180 mL, 1.00 mmol) and AIBN (164 mg, 1.00 mmol) were added in succession, and the solution was refluxed for 15 h. The solvent was then evaporated, and the mixture was separated by flash chromatography as in method A to afford 398 mg (85%) of adducts **3** and **4** in the ratio of 55:45 (NMR integration). Byproducts with NMR signals at δ 1.69 (s) and 1.64 (s) were observed both in the crude reaction mixture and in a control experiment in which AIBN was pyrolyzed in benzene in the presence of diphenyl diselenide.

Adducts **5** and **9** were prepared similarly, and the yields are given in Table I.

Addition of Benzeneselenenyl *p*-Toluenesulfonate to Acetylenes via Method C. 1-(Phenylseleno)-1-decen-2-ol *p*-Toluenesulfonate (3) and 2-(Phenylseleno)-1-decen-1-ol *p*-Toluenesulfonate (4). *p*-Tolylsulfinyl *p*-tolyl sulfone (**15**) (353 mg, 1.20 mmol), diphenyl diselenide (312 mg, 1.00 mmol), and 1-decyne (0.180 mL, 1.00 mmol) were refluxed for 27 h in 7 mL of benzene. The solvent was then evaporated, and the mixture was separated by flash chromatography as in Method A to afford 314 mg (68%) of adducts **3** and **4** in the ratio of 53:47 (NMR integration). A more polar component contained the selenosulfonation adduct **17** of 1-decyne and its allylic sulfone isomer **18** in the ratio of 62:38, as well as unidentified products, as determined by comparison of the NMR spectrum with those of authentic samples of **17**[24a] and **18**.[25]

Adducts **5** and **9** were prepared similarly, and the yields are given in Table I.

Reduction of Adduct 5 with Lithium Aluminum Hydride. The adduct (100 mg, 0.233 mmol) and $LiAlH_4$ (25 mg, 0.66 mmol) were stirred for 24 h in 2 mL of anhydrous THF. The reaction mixture was then quenched with a minimum of water. The mixture was filtered through anhydrous $MgSO_4$ and evaporated cautiously under reduced pressure at room temperature. NMR analysis of the resulting oil showed the nearly quantitative formation of 1-phenylethanol, which was not purified further.

Disproportionation of Sulfenyl Sulfonate 16 with Diphenyl Diselenide in the Presence of 1-Decyne. Benzenesulfenyl chloride (144 mg, 1.00 mmol) in 2 mL of chloroform was added to silver *p*-toluenesulfonate (279 mg, 1.00 mmol) in 5 mL of dry acetonitrile to generate the sulfenyl sulfonate.[23a] After 5 min, diphenyl diselenide (312 mg, 1.00 mmol) and 1-decyne (0.180 mL, 1.00 mmol) were added, and stirring was continued for 19 h. The mixture was filtered through Celite and evaporated in vacuo. The residue showed NMR signals of the selenenyl sulfonate adducts **3** and **4** in the ratio of 52:48 and no other vinyl signals could be attributed to the corresponding sulfenyl sulfonate adducts.

Elimination of Adducts 3 and 4: With Potassium *tert*-Butoxide. The mixture of adducts **3** and **4** (117 mg, 0.250 mmol) was stirred with potassium *tert*-butoxide (84 mg, 0.75 mmol) in 5 mL of dry THF at 0 °C for 15 min. The reaction mixture was quenched with water, diluted with ether, washed three times with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. Preparative TLC of the mixture in hexane afforded 36.5 mg (50%) of the propargylic selenide **20** as a pale yellow oil: R_f 0.23; IR (film) 2200, 1579 cm^{-1}; ^1H NMR δ 7.60–7.25 (complex, 5 H), 3.52 (t, J = 2.5 Hz, 2 H), 2.16 (m, 2 H), 1.47–1.26 (complex, 10 H), 0.88 (t, J = 6.7 Hz, 3 H); mass spectrum, m/z (relative intensity, %) 294 (28, M^+), 195 (27), 157 (26, $PhSe^+$), 115 (100); exact mass calcd for $C_{16}H_{22}Se$ 294.0887, found 294.0909. A less polar band afforded 29.5 mg (40%) of an unseparated mixture of selenides **19** and **21**. NMR signals of the acetylenic selenide **19** in the mixture matched those of an authentic sample.[34] The presence of the allenic selenide was inferred from an IR absorption at 1946 cm^{-1} and allenic hydrogen signals at δ 6.03 (dt, J = 5.9, 2.2 Hz) and δ 5.22 (dt, 5.9, 7.3 Hz) in the NMR spectrum.

The reaction was repeated, and aliquots were removed and quenched after 4 min, 15 min, and 1 h. The ratio of **19**:**20**:**21** was determined to be 59:35:6, 22:67:11, and 0:86:14, respectively, by NMR integration. No further change occurred after 5 h.

By Selenoxide Elimination. The mixture of selenides **3** and **4** (50 mg, 0.11 mmol) was oxidized with *m*-CPBA (32 mg, 0.19 mmol) in 10 mL of chloroform for 10 min. TLC showed the disappearance of the starting material. The reaction mixture was washed three times with aqueous K_2CO_3, dried ($MgSO_4$), and evaporated in vacuo. The resulting mixture of selenoxides was pyrolyzed in 0.5 mL of benzene containing DABCO (19 mg, 0.17 mmol) for 24 h in a sealed tube at 85–100 °C. The mixture was washed with dilute HCl solution and aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. The NMR spectrum of the product revealed the presence of the original selenides **3** and **4** and of 1,2-decadien-1-ol *p*-toluenesulfonate (**22**) with NMR signals at δ 6.65 (dt, J = 5.5, 2.0 Hz) and δ 5.75 (dt, J = 5.5, 6.8 Hz), as well as unidentified byproducts. The yield of **22** was estimated to be ca. 20% by NMR integration, and its identity was confirmed by an allenic absorption at 1980 cm^{-1} in the IR spectrum of the mixture. Attempts to isolate **22** by various chromatographic methods were unsuccessful.

Cyclizations with Selenenyl Sulfonate 1. 5-Hexen-1-ol. Selenenyl sulfonate **1** (1.00 mmol) was generated in situ in acetonitrile as in method A. 5-Hexen-1-ol (0.120 mL, 1.00 mmol) was added, followed by triethylamine (0.139 mL, 1.00 mmol). After 3 h, the mixture was filtered through Celite, evaporated under reduced pressure, and separated by flash chromatography (elution with dichloromethane) to afford 243 mg (95%) of pyran **24**.[10h,35]

4-Pentenoic Acid. The reaction of selenenyl sulfonate **1** (1.00 mmol) with 4-pentenoic acid (0.102 mL, 1.00 mmol) of triethylamine (0.139 mL, 1.00 mmol) was carried out as in the preceding procedure to afford 248 mg (97%) of lactone **25**.[32b]

3-Butyn-1-ol. Selenenyl sulfonate **1** (1.00 mmol) and 3-butyn-1-ol (0.076 mL, 1.00 mmol) were stirred for 20 h in 3 mL of acetonitrile. Workup as in the case of 5-hexen-1-ol afforded 101 mg (25%) of the unseparated 1,2-adducts **26** and **27** in the ratio of 58:42: IR (film) 3374, 1633, 1597, 1579, 1373, 1192, 1178 cm^{-1};

(34) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Chem. Lett.* **1982**, 1249.

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^{1}H NMR δ 7.82 (d, **26** and **27**, J = 8.4 Hz, 2 H), 7.40–7.23 (complex, **26** and **27**, 7 H), 6.93 (s, **26**) and 6.25 (s, **27**, total 1 H), 3.81 (t, **27**, J = 6.0 Hz) and 3.60 (t, **26**, J = 6.3 Hz, total 2 H), 2.68 (t, **27**, J = 6.0 Hz), 2.48 and 2.45 (2 s superimposed on t, **26** and **27**, total 5 H), δ 1.7 (br s, **26** and **27**, 1 H); mass spectrum, m/z (relative intensity, %) 398 (20 M^+), 243 (17, $M^+ - ArSO_2^{\bullet}$), 213 (38), 183 (48), 157 (63, $PhSe^+$), 155 (50, $ArSO_2^+$), 91 (100, $C_7H_7^+$); exact mass calcd for $C_{17}H_{18}O_4SSe$ 398.0091, found 398.0103. Inclusion of triethylamine did not improve the yield.

4-Pentynoic Acid. The reaction of selenenyl sulfonate **1** (1.00 mmol) with 4-pentynoic acid (98 mg, 1.00 mmol) and triethylamine (0.139 mL, 1.00 mmol) was carried out as in the case of 4-pentenoic acid. Preparative TLC of the crude product in 50% dichloromethane–hexane afforded 41 mg (16%) of the products **28** and **29** in the ratio of 3:1 (NMR integration), with NMR and IR spectra as reported in the literature.[36]

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Electrochemical Oxidation of Proline Derivatives: Total Syntheses of Bulgecinine and Bulgecin C

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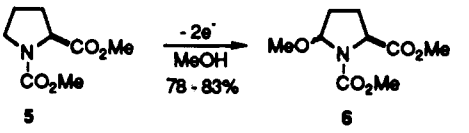
The influence of structure on the efficiency of the electrochemical C-5 oxidation of (2*S*,4*S*)-hydroxyproline carbamate esters is presented. Optimum methoxylation was observed with (2*S*,4*S*)-4-acetoxy-1,2-pyrrolidinedicarboxylic acid 2-methyl 1-(2-(trimethylsilyl)ethyl) ester (**19**). The corresponding C-5 methoxy derivative **20** was converted into bulgecinine (**4**) via a stereospecific radical homologation to incorporate the C-5 hydroxymethyl substituent. Bulgecin C (**1c**) was prepared via a β-stereoselective glycosidation reaction using a 2-azido-2-deoxy-α-D-glucopyranosyl trichloroacetimidate derivative, regiospecific C-4′ sulfation, and deprotection.

The bulgecins A (**1a**), B (**1b**), and C (**1c**), SQ-28504 (**2**), and SQ-28546 (**3**) are potent β-lactam synergists found in the culture broth of *Pseudomonas acidophila*, *Pseudomonas mesoacidophila*,[1] and *Chromobacterium violaceum*.[2] These natural products mediate, in concert with β-lactams, the development of bulges in the cell wall of Gram-negative bacteria. These curious morphological changes are accompanied by an increased sensitivity of the organism to inhibition and as a result, bacteria are killed at lower β-lactam concentrations. However, none of these glycopeptide sulfates exhibit antibacterial activities when administered alone. In consequence of these unusual biological effects and structural novelty, the bulgecins have been the subject of synthetic investigations. The bulgecin aglycon, bulgecinine (**4**), has been synthesized from D-glucose,[3] D-glucuronic acid,[4] pyroglutamic acid,[5] and an L-allylglycine derivative.[6] Additionally, Shiba and coworkers have reported the syntheses of bulgecin A (**1a**), 6-deoxybulgecin A, and 5-dehydroxymethylbulgecin A.[7]

Scheme I



5 **6**

Herein we report studies on the electrochemical oxidation of several proline derivatives, the use of radical chemistry to stereoselectively functionalize C-5 of proline, and experimental details on the first total synthesis of bulgecin C (**1c**).[8]

Electrochemical Oxidations of Proline Derivatives. Shono and co-workers have reported that carbamates including the proline derivative **5** may be regioselectively oxidized by electrolysis in methanol to provide the corresponding carbinolamine ether **6** (Scheme I).[9] This methodology should be applicable for the concise conversion of commercial (4*R*)-4-hydroxyproline (**7**) into bulgecinine (**4**) via anodic oxidation and subsequent homologation at C-5. The amino acid **7** was smoothly converted into the (4*S*)-ester **9** by protection[10] and esterification using the excellent Mitsunobu procedure[11] (Scheme II). However, much to our disappointment, the anodic oxidation of **9** proceeded to give a legion of products that may have contained the desired ether **10** (≤5%). This poor conversion stands in stark contrast to successful anodic oxidations of proline derivatives lacking a 4-substituent.[12]

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