Se-Phenyl Areneselenosulfonates: Their Facile Formation and Striking Chemistry[1]

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Benzeneseleninic acid reacts rapidly at 0 °C with aromatic sulfinic acids according to the stoichiometry of eq 3 to form *Se*-phenyl areneselenosulfonates, $PhSeSO_2Ar$ (**2**), in high yield. In contrast to thiosulfonates, $PhSSO_2Ar$, areneselenosulfonates are extremely photosensitive and undergo quite rapid photodecomposition. The principal products of this photodecomposition are the sulfonic anhydride, $ArSO_2OSO_2Ar$, and diphenyl diselenide. In the presence of added alkenes the facile photodissociation of **2** can be used to initiate a free-radical chain reaction that results in the addition of **2** to the alkene to form β-phenylseleno sulfones in good yield. The β-phenylseleno sulfones can be converted to synthetically useful α,β-unsaturated sulfones by oxidation of the β-phenylseleno group to the corresponding selenoxide and subsequent elimination of PhSeOH. Photoaddition of **2** to 2,5-norbornadiene gives a 5-(phenylseleno)-*exo*-3-nortricyclyl aryl sulfone as the almost exclusive product, while photoaddition to 1,5-cyclooctadiene gives a mixture of approximately equal amounts of the 1,2-adduct, 5-(phenylseleno)-6-arenesulfonyl-1-cyclooctene, and the product of transannular addition, 6-(phenylseleno)-*exo*-2-arenesulfonyl-*cis*-bicyclo[3.3.0]octane. Besides their extraordinary ease of photodissociation, compounds **2** also react extremely readily with nucleophiles: $Nu^- + PhSeSO_2Ar \rightarrow PhSeNu + ArSO_2^-$. Kinetic studies show that the reactivity of $PhSeSO_2Ar$ with cyanide ion in such a reaction is 70 000 times larger than the reactivity of the corresponding thiosulfonate, $PhSSO_2Ar$.

Se-Aryl areneselenosulfonates, $ArSeSO_2Ar'$, were first reported by Foss[2] in 1947, and then were almost totally ignored during the next 30 years.[3] In the present paper we show (a) that they are very readily formed by the reaction of a seleninic acid with a sulfinic acid and (b) that they exhibit chemistry that is strikingly different from that of the structurally analogous thiosulfonates, $ArSSO_2Ar'$. Our results and related studies reported recently by Back and Collins[4,5] indicate that selenosulfonates clearly merit much more attention than they have previously received and that certain of their reactions, such as their facile addition to carbon–carbon double bonds, may make them reagents of significant utility in organic synthesis.

Results and Discussion

Reaction of Benzeneseleninic Acid with Sulfinic Acids. When dilute acetonitrile solutions of equimolar amounts of benzeneseleninic acid ($PhSeO_2H$) and an aromatic sulfinic acid ($ArSO_2H$) are mixed at 0 °C, a rapid reaction occurs, as evidenced by the crystallization from the solution after less than 5 min of one of the reaction products, a strongly acidic salt that can be shown to have structure **1**; the yield of **1** is 0.5 mol/mol $ArSO_2H$. The other principal product is an *Se*-phenyl areneselenosulfonate (**2**). The stoichiometry of the reaction under these conditions is shown in eq 1.

$$2PhSeO_2H + 2ArSO_2H \rightarrow PhSeO_2H_2^+ArSO_3^- + PhSeS(O)_2Ar + H_2O \quad (1)$$

1a, Ar = *p*-tolyl; b, Ar = C_6H_5; c, Ar = *p*-ClC_6H_4

2a, Ar = *p*-tolyl; b, Ar = C_6H_5; c, Ar = *p*-ClC_6H_4

The overall course of the reaction can be most simply explained as follows. First, $ArSO_2H$ is oxidized to $ArSO_3H$ by the seleninic acid, the latter being reduced to the selenenic acid PhSeOH (eq 2a). The sulfonic acid then

$$PhSeO_2H + ArSO_2H \rightarrow PhSeOH + ArSO_3H \quad (2a)$$

$$PhSeO_2H + ArSO_3H \rightleftharpoons PhSeO_2H_2^+ArSO_3^-\downarrow \quad (2b)$$

$$PhSeOH + ArSO_2H \rightarrow PhSeS(O)_2Ar + H_2O \quad (2c)$$

protonates a second molecule of $PhSeO_2H$ (seleninic acids are known[6] to be weakly basic) to form **1** (eq 2b). Most of the selenenic acid PhSeOH is trapped by reaction with $ArSO_2H$, giving **2** (eq 2c). Some escapes capture, however, as evidenced by the fact that some diphenyl diselenide, arising from the disproportionation[7] of PhSeOH ($3PhSeOH \rightarrow PhSeSePh + PhSeO_2H + H_2O$), is also found in the reaction products. If a 2:1 (rather than a 1:1) molar ratio of $PhSeO_2H$ to $ArSO_2H$ is used, the yield of **1** is ~70% and that of **2** about 25% of the respective amounts formed when a 1:1 molar ratio of reactants is employed. This shows that the rate of eq 2c must be competitive with that of eq 2a (otherwise all the $ArSO_2H$ would be used up by eq 2a before any could be consumed by eq 2c to form **2**) but, at the same time, that the rate of eq 2c cannot be much faster than that of eq 2a (otherwise the yields of *both* **1** and **2** would be reduced to the *same* extent).

Since 1 mol of seleninic acid is, in effect, wasted in forming the **1** that precipitates, acetonitrile is not the solvent of choice for the most efficient synthesis of areneselenosulfonates via the seleninic acid–sulfinic acid reaction. When ethanol is used as the solvent, salt **1** does not precipitate, and *all* of the seleninic acid is consumed in reaction with the sulfinic acid. Yields of *Se*-phenyl areneselenosulfonates ranging from 61% to 90% (based on the stoichiometry of eq 3) are obtained, and isolation of compounds **2** is very easy, since they are rather insoluble

(1) (a) This research supported by the National Science Foundation, Grant CHE-79-18877. (b) Portions of this work have appeared as preliminary communications: Gancarz, R. A.; Kice, J. L *Tetrahedron Lett.* **1980**, 1697, 4155.

(2) Foss, O. *J. Am. Chem. Soc.* **1947**, *69*, 2236.

(3) Austad, T. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 479.

(4) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, 2213.

(5) (a) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, 2215. (b) Back, T. G.; Collins, S. *J. Org. Chem.*, **1981**, *46*, 3249.

(6) Paetzold, R.; Schumann, H.-D.; Simon, A. *Z. Anorg. Allg. Chem.* **1960**, *305*, 98. Backer, H. J.; van Dam, W. *Recl. Trav. Chim. Pays-Bas* **1935**, *54*, 531.

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in cold ethanol and crystallize out in a quite pure state on cooling the final solution to −20 °C.

$$PhSeO_2H + 2ArSO_2H \rightarrow \underset{\mathbf{2}}{PhSeS(O)_2Ar} + ArSO_3H + H_2O \quad (3)$$

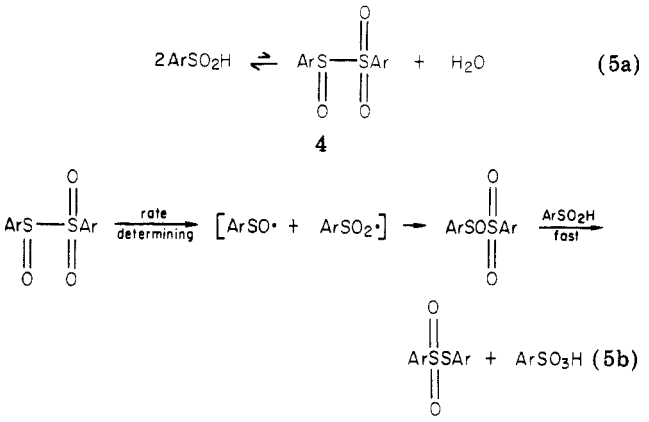
The very facile oxidation of sulfinic acids by $PhSeO_2H$ is yet another example of the ability of seleninic acids to act as oxidizing agents. Other species that have recently been shown to be easily oxidized by seleninic acids are hydrazines,[8a] phosphites,[8b] acyl hydrazides,[8c] phosphines,[8d] alkyl sulfides,[8d] and sulfonohydrazides.[4] The present reaction and the oxidations of acyl and sulfonohydrazides are the only ones in which the benzeneselenenic acid formed is trapped, either by the substrate or by an oxidation product derived from the substrate. In the other oxidations the PhSeOH produced undergoes disproportionation to PhSeSePh and $PhSeO_2H$.

One of the well-known reactions of aromatic sulfinic acids is their disproportionation[9] (eq 4). There is an

$$3ArSO_2H \rightarrow ArSO_3H + \underset{\mathbf{3}}{ArSS(O)_2Ar} + H_2O \quad (4)$$

obvious formal relationship between the disproportionation of sulfinic acids and the seleninic acid–sulfinic acid reaction in eq 3. In eq 3 the seleninic acid molecule plays the role of the sulfinic acid molecule in eq 4 that gets reduced to an ArS group.

The mechanism of eq 4 is well-established[10] and is shown in eq 5. Given the formal relationship between eq 3 and



4, one may wonder whether the actual mechanism for eq 3 should be written not as shown in eq 2a and 2c but rather with the formation from $ArSO_2H$ and $PhSeO_2H$ of a mixed sulfinic–seleninic "anhydride", $PhSe(O)SO_2Ar$, its isomerization to $PhSeOSO_2Ar$, and rapid reaction of the latter with the second $ArSO_2H$ molecule. However, one should keep in mind that, despite their formal similarity, reactions 3 and 4 are quite different in character. The disproportionation of $ArSO_2H$, because of 4 being the key intermediate, occurs readily only in media where the activity of water (and other nucleophilic protic solvents that rapidly solvolyze 4) is low. It also requires elevated temperatures (~70 °C) to proceed at a reasonable rate. The seleninic acid–sulfinic acid reaction, on the other hand, occurs rapidly at 0 °C and seems to proceed about as fast in ethanol as it does in acetonitrile. This last observation makes a mechanism where $PhSe(O)SO_2Ar$ is an intermediate seem less plausible than eq 2a and 2c, although, pending a detailed investigation of the mechanism of eq 3 planned for the future, one cannot absolutely rule it out.

The straightforward structural relationship between areneselenosulfonates (2) and arenethiolsulfonates (3) naturally suggests that their chemistry may be very similar. However, as the remainder of the paper will show, there are, in actuality, striking differences.

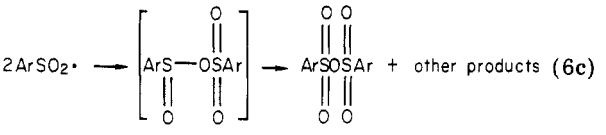
Photosensitivity and Photodecomposition of Areneselenosulfonates. Solutions of aryl arenethiosulfonates (3) in organic solvents show no evidence of decompsition upon exposure to room light even after long periods of time. In dramatic contrast, exposure of solutions of *Se*-phenyl areneselenosulfonates (2) to room light for 24 h results in significant decomposition of 2.

To investigate this facile photodecomposition of 2 in more detail a degassed solution of **2a** (0.3 M) in carbon tetrachloride was irradiated under nitrogen. After 7 h photodecomposition of **2a** was complete. The products that could be isolated and identified were: *p*-toluenesulfonic anhydride (**5a**, 0.35 mol/mol of **2a**) and diphenyl diselenide (0.42 mol/mol of **2a**). While most of the diphenyl diselenide (isolated by chromatography of the material remaining after the removal of the sulfonic anhydride) undoubtedly arises directly from the photodecomposition of **2a**, a small portion may come from the decomposition during the chromatographic workup of an unstable compound produced during the photodecomposition that we were not able to isolate and identify.

The scheme shown in eq 6a–d is suggested for the mechanism of the photodecomposition of 2. Combination of $ArSO_2\cdot$ radicals (eq 6c) gives the mixed anhydride 6.

$$\underset{\mathbf{2}}{PhSeSO_2Ar} \xrightarrow{h\nu} PhSe\cdot + ArSO_2\cdot \quad (6a)$$

$$PhSe\cdot + PhSeSO_2Ar \rightarrow PhSeSePh + ArSO_2\cdot \quad (6b)$$



$$2PhSe\cdot \rightarrow PhSeSePh \quad (6d)$$

Both the work of da Silva Correa and Waters[11] and studies in this laboratory[12] have indicated that compounds 6 are thermally quite unstable and on decomposing give large amounts of sulfonic anhydride 5. The nature of the other products besides 5 formed upon decomposition of 6 in the present system is not known, but obviously the sulfur must be in a reduced oxidation state. Examination of the crude diphenyl diselenide fraction showed that only a small amount of either ArSSePh or ArSSAr was present. As noted earlier, there is a compound produced that could not be isolated and identified due to its instability.

Photoaddition of Areneselenosulfonates to Alkenes. If the photodissociation of areneselenosulfonate **2a** is carried out in the presence of a 1-alkene, one observes

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(9) (a) Otto, R. *Chem. Ber.* **1876**, *9*, 1640. Pauly, C.; Otto, R. *Ibid.* **1877**, *10*, 2182. (b) Bere, C. M.; Smiles, S. *J. Chem. Soc.* **1924**, *125*, 2359. (c) Kice, J. L.; Bowers, K. W. *J. Am. Chem. Soc.* **1962**, *84*, 602.

(10) (a) Kice, J. L.; Guaraldi, G.; Venier, C. G. *J. Org. Chem.* **1966**, *31*, 3561. (b) Kice, J. L.; Hampton, D. C.; Fitzgerald, A. *Ibid.* **1965**, *30*, 882.

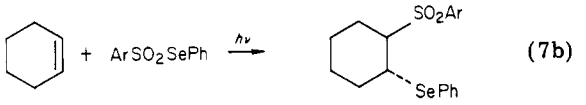
(11) da Silva Correa, C. M. M.; Waters, W. A. *J. Chem. Soc. D* **1968**, 1874.

(12) Wu, S.-M., unpublished results. Attempts to prepare 6 by reaction of $ArSO_3Ag$ with ArS(O)Cl in acetonitrile at low temperature led to a very unstable species (thought to be 6) which decomposed upon all attempts at isolation, giving principally 5 plus some ArSSAr and $ArSSO_2Ar$.

addition of the selenosulfonate across the alkene double bond in an anti-Markovnikov fashion to give a β-phenylseleno sulfone **7** (eq 7a) in 65–75% yield. Photoaddition

$$CH_2{=}CHR + ArSO_2SePh \xrightarrow{h\nu} ArSO_2CH_2CH(R)SePh \quad (7a)$$

7a, R = *n*-Bu; Ar = *p*-tolyl
b, R = Ph; Ar = *p*-tolyl

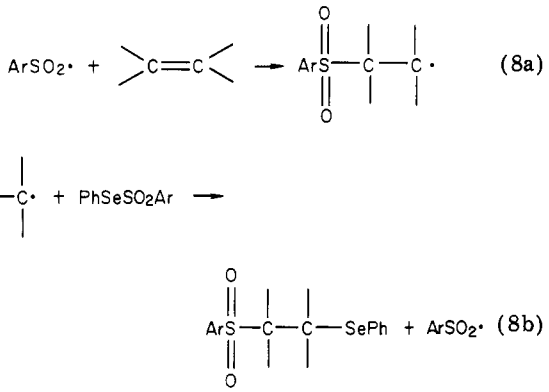


(7b)

trans-**7c**, Ar = *p*-tolyl

of **2a** to cyclohexene is also successful, the trans isomer of **7c** being isolated in 80% yield (eq 7b). However, photoaddition of **2** to 2,3-dimethyl-2-butene, a tetrasubstituted alkene, is not observed.

Experimental evidence indicates that the photoaddition of **2** to alkenes takes place by a free-radical chain reaction in the manner shown in eq 8. The fact that the reaction



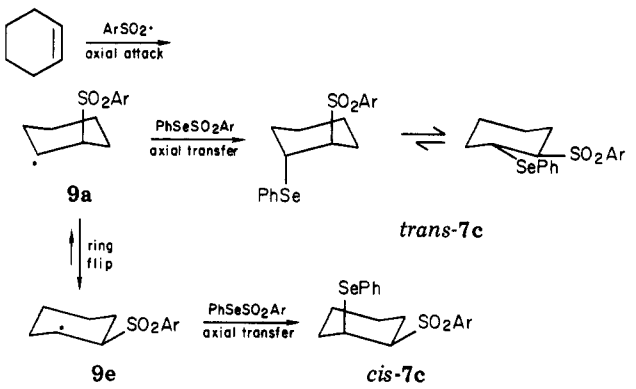
(8a)

(8b)

time required for the photoaddition of **2** to alkenes is much shorter than the time required for the photodecomposition of **2** in the absence of the alkene shows that the process must be a chain reaction. The fact that 2,3-dimethyl-2-butene does not undergo photoaddition of **2**, while styrene does, is incompatible with the reaction being an electrophilic addition, since 2,3-dimethyl-2-butene is known to be much more reactive than styrene toward electrophilic addition of such reagents as arenesulfenyl[13a] or benzeneselenenyl[13b] chlorides. It is, however, compatible with the free-radical mechanism in eq 8, since 2,3-dimethyl-2-butene is much less reactive than styrene toward free radicals.[14]

With the mechanism in eq 8 one would also expect to find that when the carbon free radical that is the product in eq 8a becomes sufficiently resonance stabilized, it will no longer be reactive enough to attack **2** readily, and rapid photoaddition of **2** to the alkene will no longer occur. The behavior of 1,1-diphenylethylene bears out this expectation. With this alkene (where the adduct from eq 8a will be the highly resonance-stabilized $ArSO_2CH_2\dot{C}Ph_2$) one does not observe rapid photoaddition of **2**. Instead photodecomposition of **2a** in the presence of 1,1-diphenylethylene is quite slow (15 h required for complete disappearance of **2a**). The major products formed are 1,1-diphenyl-2-(*p*-toluenesulfonyl)ethene,[15] **8**, (0.38 mol/mol of

Scheme I



2a), and diphenyl diselenide (0.47 mol/mol of **2a**). The unsaturated sulfone is thought to arise as shown in eq 9.

$$ArSO_2\cdot + CH_2{=}CPh_2 \rightarrow ArSO_2CH_2\dot{C}Ph_2 \quad (9a)$$

$$ArSO_2CH_2\dot{C}Ph_2 + [R\cdot] \rightarrow ArSO_2CH{=}CPh_2 + [RH]$$

8, Ar = *p*-tolyl

(9b)

When a large molar excess of a 1-alkene over **2a** is used, addition of the carbon free radical from eq 8a to another molecule of the 1-alkene can be competitive with eq 8b. Thus, when a molar ratio of hexene to **2a** of 10:1, rather than 1:1, is used, adducts of the structure $ArSO_2(CH_2CH(n\text{-Bu}))_nSePh$, where $n > 1$, are formed along with the 1:1 adduct **7a**.

The photoaddition of **2a** to cyclohexene is obviously highly stereoselective, since the trans adduct (*trans*-**7c**) is isolated in 80% yield and there is no indication of the formation of any significant amount of the cis adduct. In free-radical additions to cyclohexenes there is generally a strong preference for both axial attack of a radical on the cycloalkene[16] and also axial transfer of the second portion of the addend to the resulting cyclohexyl radical.[16,17] The high degree of trans stereoselectivity exhibited by the present system means that radical **9a**, formed by axial attack of $ArSO_2\cdot$ on cyclohexene (Scheme I), must undergo chain transfer with **2a** rapidly compared with the rate at which it equilibrates via a ring flip with the presumably conformationally more stable **9e**; otherwise, a significant amount of *cis*-**7c** should be found in the product. The stereochemistry of the reaction of **2** with cyclohexene is similar to that of the Cu(II)-catalyzed, free-radical addition of arenesulfonyl iodides to cyclohexene[18] (trans/cis ratio of ~20). It contrasts with the photoinitiated addition of bromotrichloromethane;[16a] there the ratio of trans to cis adduct is only 1.2, presumably because the initially formed axial 2-(trichloromethyl)cyclohexyl radical has time before reacting with $BrCCl_3$ to undergo substantial equilibration (via ring flipping) with the conformationally more stable form where the CCl_3 group is equatorial.

Back and Collins[5b] have shown that the free-radical addition of **2** to alkenes can also be induced thermally. Temperatures of 60–80 °C and reaction times of 20–96 h are required. The reaction is initiated by the thermal homolysis of the selenosulfonate ($2 \rightarrow ArSO_2\cdot + PhSe\cdot$); the subsequent steps are eq 8a and 8b. Back and Collins[5b]

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(15) Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898.
(16) (a) Traynham, J. G.; Lane, A. G.; Bhacca, N. *J. Org.* Chem. **1969**, *34*, 1302. (b) LeBel, N.; DeBoer, A. *J. Am. Chem. Soc.* **1967**, *89*, 2784. (c) Bordwell, F. G.; Landis, P. S.; Whitney, G. S. *J. Org. Chem.* **1965**, *30*, 3764. (d) Bohm, B. A.; Abell, P. I. *Chem. Rev.* **1962**, *62*, 599.
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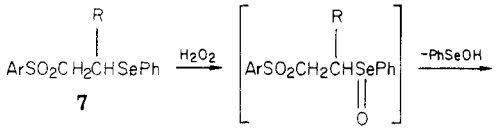
(18) Liu, L. K.; Chi, Y.; Jen, K.-W. *J. Org. Chem.* **1980**, *45*, 406.

have found that the thermal addition of **2** to an acyclic alkene is *not* significantly stereoselective, addition of **2a** to either (*E*)- or (*Z*)-5-decene giving the same mixture of erythro and threo stereoisomers. This shows that the high stereoselectivity observed in the photoaddition to cyclohexene must be due to the considerations outlined in the preceding paragraph and cannot be attributed to a bridged intermediate free radical, since bridging would be expected to result in the reaction being stereoselective for *both* cyclic and acyclic alkenes.

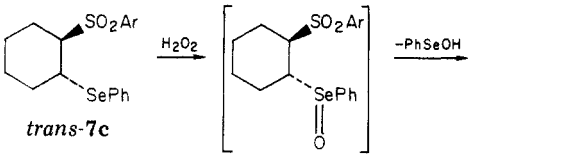
Conversion of β-Phenylseleno Sulfones to α,β-Unsaturated Sulfones. Treatment of β-phenylseleno sulfones (**7**) with excess hydrogen peroxide at −20 °C, followed by addition of triethylamine and warming of the solution to room temperature, converts **7** in good yield to the corresponding α,β-unsaturated sulfones **10** (eq 10). The



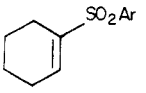
7

(10a)

(*E*)-**10a**, R = *n*-Bu; Ar = *p*-tolyl
(*E*)-**10b**, R = Ph; Ar = *p*-tolyl



trans-**7c**



(10b)

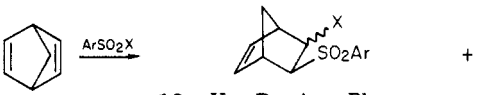
10c, Ar = *p*-tolyl

reaction involves oxidation of **7** to the selenoxide, followed by the facile fragmentation of the latter.[19] Formation of **10** is not accompanied by formation of any significant amount of the isomeric allylic (β,γ-unsaturated) sulfone. The coupling constant (J = 15 Hz) for the vicinal olefinic protons in **10a** (or **10b**) shows that it is the *E* isomer that is formed. Back and Collins,[5b] who carried out the conversion of β-phenylseleno sulfones to α,β-unsaturated sulfones using *m*-chloroperbenzoic acid rather than hydrogen peroxide, have explained the reasons for the exclusive formation of the *E* isomer in systems such as **7a** and **7b**. They have also pointed out that the addition of **2** to alkenes, followed by the oxidation–elimination of **7**, provides a versatile new route to α,β-unsaturated sulfones, compounds of proven synthetic value.

Photoaddition of Areneselenosulfonates to Norbornadiene and 1,5-Cyclooctadiene. The interconversion of norbornenyl (**11**) and nortricyclyl (**12**) radicals (eq 11) is known[20] to be very rapid, with the nortricyclyl radical

11 **12** (11)

being favored at equilibrium.[20ab] Because of this the majority of free-radical additions to 2,5-norbornadiene, for example, that of arenesulfonyl bromides (eq 12, X = Br),[21]



13a, X = Br; Ar = Ph
b, X = I; Ar = Ph
c, X = SePh; Ar = *p*-tolyl

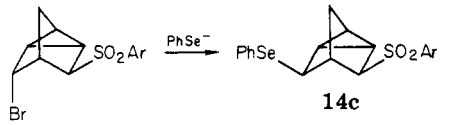
(12)

14a, X = Br; Ar = Ph
b, X = I; Ar = Ph
c, X = SePh; Ar = *p*-tolyl

15a, X = Br; Ar = Ph
b, X = I; Ar = Ph
c, X = SePh; Ar = *p*-tolyl

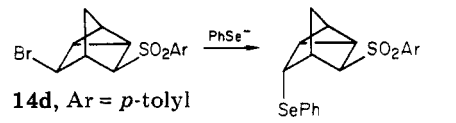
give mainly tricyclic products (**14a** and **15a**) and only limited amounts of the 1,2-adduct **13a**. Only when the addend is an extremely reactive chain-transfer agent such as, for example, an arenesulfonyl iodide (eq 12, X = I)[21a] is the 1,2-adduct (in this case **13b**) the major product.

Photoaddition of **2a** to norbornadiene (eq 12, X = SePh) in carbon tetrachloride solution gives a 75% yield of a mixture of 1:1 adducts, consisting almost entirely (90 ± 5%) of **14c** and **15c**, with only a small amount (10 ± 5%) of **13c**.[22] While **13c** can be separated from the two nortricyclyl sulfones by preparative TLC, we were unable to separate **14c** from **15c**. The two nortricyclyl sulfones are, however, easily distinguished by ^{1}H NMR, due to differences in the chemical shifts of their CHSO$_2$Ar (**14c**, δ 3.05; **15c**, 3.87) and CHSePh (**14c**, δ 3.19, **15c** 3.34) protons, and the ratio of **14c** to **15c** in the products (59:41) could be determined from the ^{1}H NMR spectrum of the product mixture after removal of **13c** by preparative TLC. The pure samples of **14c** and **15c** needed for the unequivocal assignment of the chemical shifts of the CHSO$_2$Ar and CHSePh protons in each of the two isomers were synthesized as shown in eq 13 by the S$_N$2 reaction of PhSe$^-$



(13a)

15d, Ar = *p*-tolyl



(13b)

14d, Ar = *p*-tolyl

15c

with the 5-bromo-3-nortricyclyl sulfones **15d** and **14d**, respectively. Sulfones **14d** and **15d** were prepared by photoaddition[21b] of *p*-toluenesulfonyl bromide to norbornadiene and separated by fractional crystallization; their stereochemistry was easily assigned, since the chemical shifts of the CHBr and CHSO$_2$Ar protons in each stereoisomer are virtually identical with those[21b] for the equivalent stereoisomer (**14a** or **15a**) of the corresponding nortricyclyl phenyl sulfone.

The ratio (90:10) of nortricyclyl (**14c** plus **15c**) to norbornenyl (**13c**) products in the photoaddition of **2a** to

(19) For reviews of the oxidation of selenides and elimination of the resulting selenoxides see: Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.

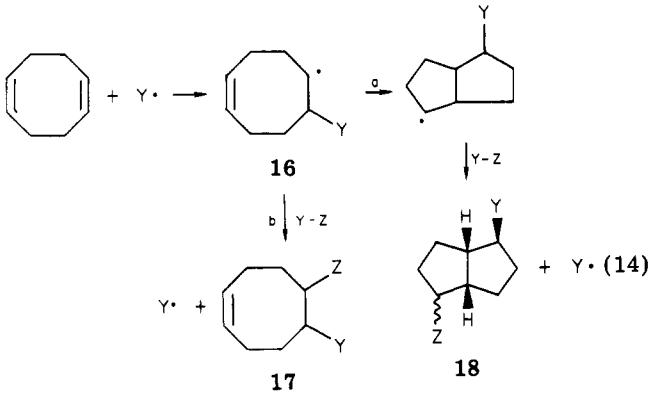
(20) (a) Alnajjar, M. S.; Kuivila, H. G. *J. Org. Chem.* **1981**, *46*, 1053. (b) Cristol, S. J.; Gleason, R. W. *Ibid.* **1969**, *34*, 1762. (c) Warner, C. R.; Strunk, R. J.; Kuivila, H. G. *Ibid.* **1966**, *31*, 3381. (c) Wilt, J. W. "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 466 ff.

(21) (a) Cristol, S. J.; Davies, D. I. *J. Org. Chem.* **1964**, *29*, 1282. (b) Cristol, S. J.; Harrington, J. K.; Singer, H. S. *J. Am. Chem. Soc.* **1966**, *88*, 1529.

(22) The amount of **13c** in the adduct mixture was determined from the integrated intensity of the ^{1}H NMR signal (δ 6.10–6.25) due to the olefinic protons in **13c**.

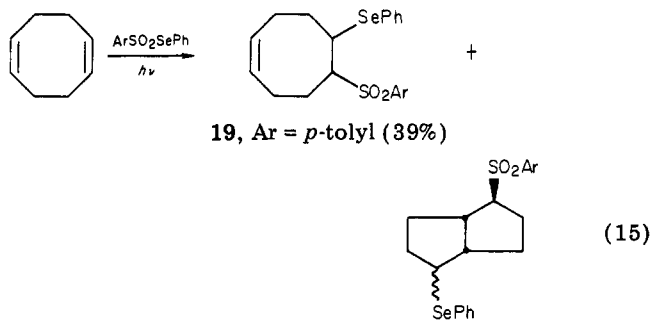
norbornadiene is virtually the same as that (87:13) found[21a] for the photoaddition of $PhSO_2Br$ to norbornadiene at similar dilution and is quite different from the ratio (27:73) found[21a] for the corresponding addition of $PhSO_2I$. This shows that, despite the fact that eq 8b occurs readily, the reactivity of selenosulfonates as chain-transfer agents does not equal that of sulfonyl iodides. Note also that the ratio of **14c** to **15c** formed (6:4) is not significantly different from the ratio of **14a** to **15a** (4:3) produced[21b] in the photoaddition of $PhSO_2Br$. Apparently a change from Br to PhSe as the group being transferred to the nortricyclyl radical has little effect on the preference for exo vs. endo transfer.

In free-radical additions to 1,5-cyclooctadiene very reactive chain-transfer agents like HBr[23c] and thioacetic acid,[23d] where the rate constant for step b in eq 14 is very

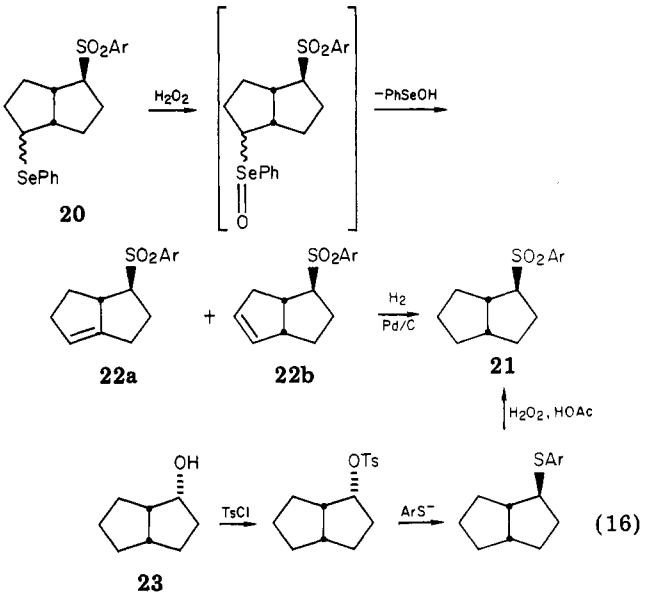


large, give only 1,2-adducts **17** as products. However, when the chain-transfer reactivity of the addend is lower, one gets a transannular ring closure of radical **16** prior to chain transfer, and the formation of bicyclo[3.3.0]octanes (**18**).[23a,b] The high ratio of nortricyclyl to norbornenyl products in the photoaddition of **2a** to norbornadiene suggests that the reactivity of **2a** as a transfer agent might be such as to allow considerable transannular reaction in its addition to 1,5-cyclooctadiene. This indeed turns out to be the case.

When **2a** is irradiated in carbon tetrachloride solution in the presence of 1,5-cyclooctadiene, two 1:1 adducts (which can be separated by chromatography) are formed in approximately equal amounts (eq 15). The ^1H NMR



spectrum of the first of these, which shows the presence of the olefinic CH=CH group, indicates it to be 5-(phenyseleno)-6-(*p*-toluenesulfonyl)-1-cyclooctene (**19**), the 1,2-adduct. The ^1H NMR of the second adduct shows no olefinic proton resonance and is consistent with this adduct being a mixture of the exo and endo isomers of 6-(phenylseleno)-*exo*-2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]octane (**20**). A proof of structure for the second adduct was provided by subjecting it to the series of transformations shown in eq 16. These converted it to *exo*-2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]octane (**21**), identical in all respects with a sample of the same sulfone prepared, as shown in eq 16, from *endo*-2-hydroxy-*cis*-bicyclo[3.3.0]octane[24] (**23**) by a straightforward route. The elimination of the selenoxide from **20** gives roughly equal amounts of bicyclo[3.3.0]octenes **22a** and **22b**. Given the syn stereochemistry for selenoxide elimination,[19] **22a** can only arise from the selenoxide of the *exo*-6-phenylseleno isomer of **20**. That **22a** constitutes about half the product indicates that a large part of the product formed in the photoaddition has the 6-phenylseleno group exo.[25]



The formation of **19** and **20** in approximately equal amounts in the photoaddition of **2a** to 1,5-cyclooctadiene shows that, while **2a** is less reactive as a chain-transfer agent than such reagents as HBr,[23c] it is more reactive than reagents like carbon tetrachloride,[23ab] whose free-radical additions to 1,5-cyclooctadiene give only **18** and no 1,2-adduct **17**. This is consistent with the results discussed earlier for the stereochemistry of the photoaddition of **2a** and cyclohexene. Those, it will be remembered, required that chain transfer of **2a** with an axial 2-(*p*-toluenesulfonyl)cyclohexyl radical be faster than inversion of the cyclohexane ring, while earlier work[16a] had shown that chain transfer of $BrCCl_3$ with an axial 2-(trichloromethyl)cyclohexyl radical has a rate comparable to the rate of ring inversion.

Reactivity toward Nucleophiles of Selenosulfonates vs. Thiosulfonates. Arenethiosulfonates (**3**) react readily with nucleophiles in the manner shown in eq 17, and reactions of this type dominate the chemistry of

$$Nu^- + PhSS(O)_2Ar \xrightarrow{k_S^{Nu}} PhSNu + ArSO_2^- \quad (17)$$

3.[26] One would expect that reactions of a similar type (eq 18) would also be observed with areneselenosulfonates.

$$Nu^- + PhSeS(O)_2Ar \xrightarrow{k_{Se}^{Nu}} PhSeNu + ArSO_2^- \quad (18)$$

(23) (a) Dowbenko, R. *Tetrahedron* **1964**, *20*, 1843; *J. Am. Chem. Soc.* **1964**, *86*, 946. (b) Friedman, L. *J. Am. Chem. Soc.* **1964**, *86*, 1885. (c) Gale, L. H. *J. Org. Chem.* **1968**, *33*, 3643. (d) Locke, J. M.; Duck, E. W. *Chem. Commun.* **1965**, 151.

(24) Whitesell, J. K.; White, P. D. *Synthesis* **1975**, 602.

(25) Since syn elimination of the selenoxide from *exo*-6-(phenylseleno)-*exo*-2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]octane may also give **22b**, the fraction of **20** having the 6-phenylseleno group exo may well be considerably larger than half.

(26) For a review of such reactions see: Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 137–147.

Table I. Kinetics of Reaction of Cyanide Ion with Selenosulfonates and Thiolsulfonates[a]

compd (concn, M)	$10^3[C_{CN}]$, M	10^2[Tris], M	10^2[Tris-H$^+$], M	k_1, s^{-1}	k_1[Tris-H$^+$]/[C_{CN}][Tris]
$PhSSO_2Ph$ (2×10^{-4})	1.0	1.1	0.90	2.5×10^{-4} [b]	0.22
	2.0	1.2	0.80	6.8×10^{-4} [b]	0.24
$PhSeSO_2Ph$ (2×10^{-5})	1.0	0.60	0.40	22.1	1.47×10^4
$PhSeSO_2C_6H_4Cl$-p (2×10^{-5})	1.0	0.60	0.40	30.9	2.06×10^4
$PhSeSO_2C_6H_4CH_3$-p (2×10^{-5})	1.0	0.60	0.40	17.3	1.15×10^4
	0.50	0.55	0.45	6.8 [b]	1.11×10^4

[a] All runs in 90% MeCN–10% H_2O at 25 °C. [b] Average of several runs. Rates reproducible to ±5%.

The question of interest is how the reactivity of **2** in such reactions will compare with that of **3**; i.e., what is a typical value of k_{Se}^{Nu}/k_S^{Nu}?

To obtain such information, we have measured the rate of reaction of both **2** and **3** with cyanide ($Nu^- = CN^-$) in a Tris buffer in 90% acetonitrile at 25 °C. All runs were carried out with cyanide present in large stoichiometric excess over **2** or **3**, so that the disappearnce of **2** or **3** followed first-order kinetics. The experimental first-order rate constants, k_1, for the different runs are shown in Table I. The constancy of k_1[Tris-H$^+$][C_{CN}][Tris] for a given substrate with variation in cyanide concentration shows that the reactions are, as expected, first-order in cyanide.

The ratio of k_1[Tris-H$^+$]/[C_{CN}][Tris] for $PhSeSO_2Ph$ to that for $PhSSO_2Ph$ gives k_{Se}^{CN}/k_S^{CN}. Its value (7×10^4) shows that the selenosulfonate is almost *five powers of ten* more reactive than the corresponding thiosulfonate toward cyanide ion. Comparable values of k_{Se}/k_S may be expected with other nucleophiles. Since the reactivity of arenethiosulfonates toward nucleophiles is generally quite high,[27] this indicates that another striking characterisitic of the chemistry of areneselenosulfonates is going to be extraordinarily high reactivity toward nucleophiles, with second-order rate constants for the reaction of highly reactive nucleophiles with **2** approaching the diffusion-controlled limit.

Table I indicates that a variation in the nature of the para substituent in the Ar ring in **2** from p-CH_3 to p-Cl leads to only a modest increase in rate, a plot of log k_1 for the three selenosulfonates vs. σ for the para substituents in Ar giving $\rho = +0.6$ for the reaction. Given the very large value of k_{Se}^{CN}, it is perhaps a bit surprising that eq 18 is even this sensitive to changes in the nature of the substituents in Ar.

Experimental Section

Synthesis of *Se*-Phenyl Areneselenosulfonates (2). Benzeneseleninic acid (1.89 g, 10.0 mmol) was dissolved in 20 mL of ethanol, and the solution was cooled to 0 °C. To this was then added 3.12 g (20 mmol) of p-toluenesulfinic acid, and the reaction mixture was stirred vigorously for 2 h at 0 °C in the dark. The precipitate of **2a** that formed was filtered off. Cooling the filtrate to −20 °C for several hours afforded a second crop of **2a**: total yield 2.80 g (90%); mp 76–78 °C (lit.[28] mp 77–79 °C); ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (complex, 9 H), 2.42 (s, 3 H); IR (KBr) 1325 (s), 1140 cm^{-1} (s, SO_2); mass spectrum, m/e 312 (M^+, ^{80}Se); UV (MeCN) λ_{max} 245 nm (ϵ 1.4×10^4).

Reaction of benzenesulfinic acid with $PhSeO_2H$ by using the same procedure gave **2b** [1.66 g (61%); mp 54–55 °C (lit.[3] mp 51 °C)], and reaction of p-chlorobenzenesulfinic acid with $PhSeO_2H$ gave **2c**: 2.2 g (72%); mp 99–100 °C; IR (KBr) 1325 (s), 1135 cm^{-1} (s, SO_2). Anal. Calcd for $C_{12}H_9ClO_2SSe$: C, 39.03; H, 2.95. Found: C, 39.21; H, 2.90.

Reaction of Benzeneseleninic Acid with *p*-Toluenesulfinic Acid in Acetonitrile. Benzeneseleninic acid (0.378 g, 2.0 mmol) was dissolved in 100 mL of acetonitrile, and the solution was cooled to 0 °C. To this was added a cold solution of 0.312 g (2 mmol) of p-toluenesulfinic acid dissolved in 30 mL of acetonitrile. After about 3 min a white precipitate began to appear. After 1 h the insoluble material was filtered off and dried over phosphorus pentoxide at room temperature, giving 0.360 g (100%) of salt **1a**: mp 174–175 °C; IR (KBr) 1605, 1450, 1320, 1240 (s), 1145 (s), 1110 (s), 1030, 1000 (s), 815 cm^{-1}; ^{1}H NMR (D_2O) δ 8.12–7.47 (complex, 9 H), 2.57 (s, 3 H). Anal. Calcd for $C_{13}H_{14}O_5SSe$: C, 43.21; H, 3.91. Found: C, 43.19; H, 4.01; equivalent molecular weight by titration with standard sodium hydroxide, 360.

The acetonitrile filtrate was treated with anhydrous, solid sodium carbonate to neutralize traces of **1a** still present in the solution, filtered, and evaporated to dryness under reduced pressure. Spectral examination of the residue indicated that it consisted primarily of **2a** (~0.7 mmol), admixed with some diphenyl diselenide. Pure **2a** (mp 77–79 °C) was isolated by preparative TLC of the residue on silica gel, followed by crystallization of **2a** from hexane.

Photodecomposition of 2a. Selenosulfonate **2a** (0.312 g, 1 mmol) was dissolved in 3 mL of degassed carbon tetrachloride, and the stirred solution was irradiated under nitrogen in a closed Pyrex flask in a Rayonet reactor (RPR-2537 lamp). After 7 h thin-layer chromatography indicated that photodecomposition of **2a** was complete. The solid which had precipitated was filtered off. Treatment of the solid with a small amount of chloroform separated it into chloroform-soluble and chloroform-insoluble fractions. The chloroform-soluble fraction (0.100 g, mp 126–131 °C) was shown to be p-toluenesulfonic anhydride[29] by comparison with an authentic sample. The chloroform-insoluble fraction (0.012 g mp 171–173 °C) was **1a**.

The carbon tetrachloride was removed from the filtrate under reduced pressure, and the residue was treated with a small amount of hexane. A small portion (0.015 g) of the residue was insoluble in hexane. This was shown to be additional p-toluenesulfonic anhydride. Removal of the hexane and chromatography of the residue on silica gel with benzene as eluant gave 0.130 g (0.42 mmol) of diphenyl diselenide. There was also present in the hexane-soluble material a relatively unstable compound that could not be successfully isolated or identified since it underwent decomposition upon attempts to separate it from diphenyl diselenide by TLC or other procedures.

Photoaddition of 2a to Alkenes. In the additions to cyclohexene, 1-hexene, or styrene, the alkene (1–2 mmol) and **2a** (0.312 g, 1 mmol) were dissolved in 1 mL of degassed carbon tetrachloride, and the solution was irradiated in a closed Pyrex vessel under nitrogen until TLC showed no **2a** remained (≤1.5 h). The solvent and excess alkene were then removed under reduced pressure, and the residue was worked up as described below for each specific case.

Cyclohexene. The residue was recrystallized from hexane, giving 0.33 g (80%) of *trans*-1-(phenylseleno)-2-(p-toluenesulfonyl)cyclohexane: mp 57–59 °C (lit.[5b] mp 58–59 °C); IR (KBr) 1320–1300 (s), 1150 cm^{-1} (s, SO_2); ^{1}H NMR ($CDCl_3$) δ 7.6 (d, J = 8 Hz, 2 H), 7.4–7.0 (complex, 7 H), 3.89 (dt as a quintet, J_1 = J_2 = 3.5 Hz, 1 H, $CHSO_2Ar$), 3.13 (dt as a quintet, J_1 = J_2 = 3.5 Hz, 1 H, CHSePh), 2.45 (s, 3 H, $CH_3C_6H_4$), 2.20–1.30 (complex, 8 H); mass spectrum, m/e 394 (M^+, ^{80}Se) 392 (M^+, ^{78}Se). Anal. Calcd for $C_{19}H_{22}O_2Se$: C, 58.01; H, 5.64. Found: C, 58.55; H, 5.78.

(27) Kice, J. L.; Rogers, T. E.; Warheit, A. C. *J. Am. Chem. Soc.* **1974**, *96*, 8020.

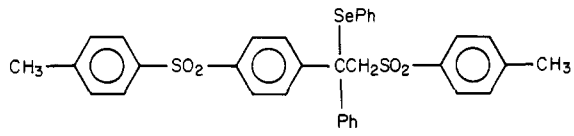
(28) Barton D. H. R.; Britten-Kelly, M. R.; Ferreira, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1682.

(29) Christensen, N. H. *Acta Chem. Scand.* **1966**, *20*, 1955; **1967**, *21*, 899.

1-Hexene. The residue was chromatographed on silica gel with benzene as the eluant, giving 0.260 g (66%) of 1-(*p*-toluenesulfonyl)-2-(phenylseleno)hexane (**7a**) as an oil that solidified on standing in the refrigerator for several weeks: mp 53–56 °C; IR (KBr) 1330 (s), 1150 cm^{-1} (s, SO_2); ^1H NMR ($CDCl_3$) δ 7.63 (d, J = 8 Hz, 2 H), 7.42–7.10 (complex, 7 H), 3.43 (complex, 3 H, CH_2SO_2Ar and CHSePh), 2.44 (s, 3 H, $CH_3C_6H_4$), 2.0–1.05 (m, 6 H), 0.90 (t, J = 6 Hz, 3 H); mass spectrum, m/e 396 (M^+, ^{80}Se) 394 (M^+, ^{78}Se). Anal. Calcd for $C_{19}H_{24}O_2SSe$: C, 57.56; H, 6.10. Found: C, 57.59; H, 6.29.

Styrene. The residue was recrystallized from carbon tetrachloride, giving 0.304 g (73%) of 1-phenyl-1-(phenylseleno)-2-(*p*-toluenesulfonyl)ethane (**7b**): mp 153–155 °C (lit.[5] mp 157–158 °C); IR (KBr) 1285 (s), 1120 cm^{-1} (s, SO_2); ^1H NMR ($CDCl_3$) δ 7.60–7.00 (complex, 14 H), 4.9–4.7 (m, 1 H), 4.30–3.60 (m, 2 H), 2.42 (s, 3 H).

1,1-Diphenylethylene. (10 mmol) and **2a** (1.56 g, 5 mmol) were dissolved in 15 mL of carbon tetrachloride, and the solution was irradiated in the same manner as with the other 1-alkenes; complete disappearance of **2a** required 15 h. A small amount of insoluble material (57 mg) that separated from the solution was filtered off and identified as *p*-toluenesulfonic acid monohydrate, mp 101–103 °C. Addition of 35 mL of hexane to the carbon tetrachloride filtrate caused the precipitation of 0.120 g of a substance: mp 139–139.5 °C (after two recrystallizations from ethanol); ^1H NMR ($CDCl_3$) δ 7.8–7.0 (complex, 22 H), 4.70 (s, 2 H), 2.16 (s, 3 H), 2.13 (s, 3 H); IR (KBr) 1610, 1505, 1455, 1305 (s), 1140 (s), 1085 cm^{-1}. The structure for the substance that seems in best accord with these data is **24**.



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The filtrate was evaporated, and the residue was dissolved in 150 mL of hot hexane. The hexane solution was allowed to stand at room temperature for 12 h, and the hexane was then decanted from the oil that had separated. The oil was treated with 35 mL of benzene, whereupon part dissolved, leaving behind 0.19 g of slightly violet crystals: IR (KBr) 1190 (s), 1130, 1045, 1005 cm^{-1}. To the benzene solution was then added 17 mL of hexane; this caused the separation of ~40 mg of oily material that was not identified. The benzene–hexane solution was decanted, the solvents were removed under reduced pressure, and the residue was chromatographed (SiO_2/benzene), giving 24 mg of diphenyl diselenide, small amounts of several unidentified compounds, and 0.22 g (0.67 mmol) of 1,1-diphenyl-2-(*p*-toluenesulfonyl)ethene (**8**): mp 102–103 °C (after recrystallization from ethanol) (lit.[15] mp 102–103 °C); ^1H NMR ($CDCl_3$) δ 7.6–6.9 (complex, 15 H), 7.0 (s, 1 H, $=CHSO_2$), 2.38 (s, 3 H).

When the decanted hexane solution was cooled to −20 °C for 2 days, 0.41 g (1.23 mmol) of additional **8** (mp 102–103 °C) separated. Concentration of the filtrate and cooling led to the separation of 0.2 g of material that was not identified, although ^1H NMR showed that it contained very few *p*-tolyl groups. Removal of the remaining hexane and chromatography of the residue on silica gel gave 0.41 g of unreacted 1,1-diphenylethylene, 0.74 g (2.37 mmol) of diphenyl diselenide, and 0.07 g of a compound that was not identified.

Norbornadiene. Freshly distilled 2,5-norbornadiene (0.22 mL, 2 mmol) and **2a** (0.312 g, 1.0 mmol) were dissolved in 3 mL of carbon tetrachloride and irradiated in same manner as in the additions of **2a** to other olefins. All **2a** was consumed after only 20 min. Removal of the solvent and excess norbornadiene gave 0.31 g of an oily residue that ^1H NMR indicated was a mixture of 1:1 adducts of **2a** and norbornadiene. Comparison of the integrated intensity of the weak signal for olefinic protons at δ 6.10–6.25 with that for the aromatic protons in the various adducts (δ 8.0–7.0) showed that only 10% of the mixture was 3-(phenylseleno)-5-norbornen-2-yl *p*-tolyl sulfone (**13c**). Preparative thin-layer chromatography of the residue on silica gel (CCl_4/Et_2O, 2:1) separated **13c** from the other adducts. The other adducts (0.280 g) have a strong absorption in the infrared at 807 cm^{-1} that is considered[21] characteristic of the nortricyclyl group. Comparison of their ^1H NMR spectra with those of known samples of *exo*-(**14c**) and *endo*-5-(phenylseleno)-*exo*-3-nortricyclyl *p*-tolyl sulfone (**15c**; whose preparation is described in the following paragraphs) showed that what one had in hand was a mixture of 59% of **14c** and 41% of **15c**; **14c** and **15c** are easily distinguished by the difference in the chemical shifts associated with the $CHSO_2Ar$ (**14c**, δ 3.05; **15c**, 3.87) and CHSePh (**14c**, δ 3.19; **15c**, 3.34) protons in the two isomers, and the ratio of **14c** to **15c** in the adduct mixture was determined from careful integration of these peaks. Attempts to separate the mixture of **14c** and **15c** by preparative TLC or other chromatographic procedures were unsuccessful.

Separate samples of **14c** and **15c** were synthesized in the following manner. *p*-Toluenesulfonyl bromide (4.0 g, 17 mmol) and 2.2 mL (20 mmol) of freshly distilled 2,5-norbornadiene were irradiated in benzene (10 mL) for 0.5 h. The mixture was then cooled, and the precipitate (2.1 g) that had separated was filtered off. Several recrystallizations from carbon tetrachloride gave pure *exo*-5-bromo-*exo*-3-nortricyclyl *p*-tolyl sulfone (**14d**): mp 157–158 °C; ^1H NMR ($CDCl_3$) δ 7.9–7.3 (AA'BB' pattern, 4 H), 3.79 (m appearing as a br s, 1 H, CHBr), 3.04 (m as a br s, 1 H, $CHSO_2$), 2.47 (s, 3 H $CH_3C_6H_4$), 2.66–1.5 (complex, 6 H). Anal. Calcd for $C_{14}H_{15}BrO_2S$: C, 51.39; H, 4.62. Found: C, 51.10; H, 4.52. The assignment of exo stereochemistry at C-5 is based on the correspondence between the chemical shifts for the CHBr and $CHSO_2$ protons and those for the same protons in the corresponding phenyl sulfone **14a**.[21b]

For isolation of the pure *endo*-5-bromo compound **15d**, the benzene filtrate was diluted with an equal volume of hexane. The material which precipitated (1.4 g) was fractionally crystallized from 20 mL of carbon tetrachloride in order to remove the remaining **14d**. Evaporation of the filtrate gave **15d** as an oil: ^1H NMR ($CDCl_3$) δ 7.9–7.2 (AA'BB' pattern, 4 H), 3.90, (m as a br s, 1 H, CHBr), 3.71 (m as a br s, 1 H, $CHSO_2$), 2.45 (s, 3 H, $CH_3C_6H_4$), 2.9–1.5 (complex, 6 H). Anal. ($C_{14}H_{15}BrO_2S$) C, H. The chemical shifts for the CHBr and $CHSO_2$ protons in **15d** correspond with those reported[21b] for the same protons in **15a**.

The *endo*-5-phenylseleno compound **15c** was prepared from **14d** in the following manner. Diphenyl diselenide (0.312 g, 1 mmol) was dissolved in 15 mL of ethylene glycol monomethyl ether, and, with the solution kept under nitrogen, sodium borohydride was gradually added during 0.5 h until the solution became colorless (~2.5 mmol of $NaBH_4$). Then **14d** (0.65 g, 2 mmol) was added, and the solution was refluxed under nitrogen for 5 h. After addition of 30 mL of water the mixture was extracted twice with 40-mL portions of carbon tetrachloride; the extracts were combined, washed with water, and dried ($MgSO_4$), and the solvent was removed under reduced pressure to give 0.58 g (71%) of **15c** as an oil, which was further purified by preparative TLC: ^1H NMR ($CDCl_3$) δ 7.9–7.1 (complex, 9 H), 3.87 (m, 1 H, $CHSO_2$), 3.34 (m, 1 H, CHSe), 2.50 (s, 3 H) 2.60–1.30 (complex, 6 H). Anal. ($C_{21}H_{20}O_2SSe$) C, H.

The *exo*-5-phenylseleno compound **14c** was prepared and purified in an exactly analogous fashion by starting from **15d**. There was obtained 0.54 g (67%) of **14c** as an oil: ^1H NMR ($CDCl_3$) δ 7.9–7.1 (complex, 9 H), 3.19 (m, 1 H, CHSe), 3.05 (m, 1 H, $CHSO_2$), 2.50 (s, 3 H), 2.60–1.30 (complex, 6 H). Anal. ($C_{21}H_{20}O_2SSe$) C, H.

1,5-Cyclooctadiene. A solution of **2a** (0.312 g, 1.0 mmol) and 1,5-cyclooctadiene (0.22 g, 2.0 mmol) in 3 mL of carbon tetrachloride was irradiated until all the **2a** had been consumed. Removal of the solvent and excess diene left an oily residue which could be separated by preparative TLC (silica gel, benzene) into five fractions (listed in order of decreasing R_f value): (a) diphenyl diselenide, 0.027 g; (b) an unidentified oil, 0.012 g; (c) an oil, (0.164 g) which is 5-(phenylseleno)-6-(*p*-toluenesulfonyl)-1-cyclooctene [**19**: IR (KBr) 3080, 3050, 2960, 1615, 1595, 1490, 1480, 1310 (s, SO_2), 1270, 1240, 1200, 1185, 1145 (s, SO_2), 1090, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.1 (complex, 9 H), 6.1–5.3 (m, 2 H, CH=CH), 4.3–4.1 (m, 1 H, $CHSO_2$) 3.7–3.2 (m, 1 H, CHSe), 2.43 (s, 3 H), 3.0–1.8 (complex, 8 H). Anal. ($C_{21}H_{24}O_2SSe$) C, H]; (d) an oil (0.144 g) shown by further conversions outlined below to be a mixture of *exo*- and *endo*-6-(phenylseleno)-*exo*-2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]octane [**20**: IR (KBr) 3080, 3055, 2970, 2890, 1615, 1595, 1490, 1460, 1450, 1300 (s, SO_2), 1150 (s, SO_2), 1095, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (complex, 9 H), 3.4–2.8

(complex, 2 H), 2.8–2.3 (complex, 2 H), 2.4 (s, 3 H), 2.2–1.1 (complex, 8 H). Anal. ($C_{21}H_{24}O_2SSe$) C, H]; (e) an unidentified oil, 0.03 g.

As a proof of structure for **20**, a 0.210-g (0.50 mmol) sample was dissolved in 2 mL of tetrahydrofuran, the solution was cooled to −20 °C, 1 mL of cold 30% hydrogen peroxide was added, and the solution was allowed to stand at −20 °C for 2 h. Triethylamine (0.5 mL) was then added, and the mixture was allowed to warm to room temperature and stand overnight. Carbon tetrachloride (10–15 mL) was added, the organic layer was washed several times with water and dried ($MgSO_4$), and the solvent was evaporated. Preparative TLC of the residue permitted the separation of 0.084 g (0.32 mmol, 64%) of what ^1H NMR indicated was a mixture of approximately equal parts (i.e., ~1.5 olefinic protons in the NMR) of 2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]-6-octene (**22b**) and 2-(*p*-toluenesulfonyl)bicyclo[3.3.0]-5-octene (**22a**). When dissolved in 20 mL of methanol and hydrogenated at room temperature at atmospheric pressure with 5% Pd/C as catalyst this mixture absorbed the calculated amount of hydrogen for one C=C per molecule. Removal of the catalyst and evaporation of the methanol gave a residue which was purified by preparative TLC on silica gel (toluene–ether, 10:2), giving 0.074 g (0.28 mmol) of *exo*-2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]octane (**21**) whose infrared, ^1H NMR, and mass spectrum were identical in all respects with those of a sample of **21** prepared by an unambiguous route (vide infra) from *endo*-2-hydroxy-*cis*-bicyclo[3.3.0]octane.[24]

Synthesis of 21 from *endo*-2-Hydroxy-*cis*-bicyclo[3.3.0]-octane (23). To 0.35 g (2.8 mmol) of **23**[24,30] dissolved in 3.5 mL of dry pyridine was added 1.0 g (5.2 mmol) of *p*-toluenesulfonyl chloride, and the solution was allowed to stand at room temperature for 7 days. Water (25 mL) was then added, and the mixture was extracted with 30 mL of hexane. The hexane extract was washed several times with water and dried ($MgSO_4$), and the hexane was removed under reduced pressure. Thin-layer chromatography indicated that the residue (0.6 g, 81%) was quite pure *endo*-tosylate: IR (KBr) 2960, 2880, 1600, 1455, 1360 (s, SO_2), 1180 (s, SO_2), 1100, 985, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (AA′BB′ pattern, 4 H), 5.0–4.53 (m, 1 H, CHOTs), 2.43 (s, 3 H), 2.73–1.00 (complex, 12 H).

The *endo*-tosylate (0.30 g, 1.1 mmol) was dissolved in 3 mL of dimethylformamide, 4 mL of a 1 M solution of the sodium salt of *p*-thiocresol in 90% dimethylformamide was added, and the solution was allowed to stand under nitrogen at room temperature until TLC showed that no tosylate remained (~28 h). At that point 20 mL of ether was added, and the organic layer was washed successively with water, 10% sodium carbonate, and again with water. It was then dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel (carbon tetrachloride), giving 0.176 g (69%) of *exo*-2-(*p*-tolylthio)-*cis*-bicyclo[3.3.0]octane: ^1H NMR ($CDCl_3$) δ 7.60–7.10 (m, 4 H), 3.15–3.05 (m, 1 H, CHS), 2.42 (s, 3 H), 2.80–1.20 (complex, 12 H). This sulfide was dissolved in 5 mL of glacial acetic acid, 0.5 mL of 30% hydrogen peroxide was added, and the solution was heated to 85 °C for 3 h. The solution was then cooled to room temperature, poured into water, and extracted with ether. The ether extracts were washed successively with water, 10% sodium bicarbonate, and water and then dried ($MgSO_4$). Removal of the ether gave a residue which was purified by preparative TLC on silica gel (toluene–ether, 5:1), giving 0.121 g (60%) of *exo*-2-(*p*-toluenesulfonyl)-*cis*-bicyclo[3.3.0]octane (**21**) as an oil: IR (KBr) 2950, 2870, 1600, 1455, 1300 (s, SO_2), 1150 (s, SO_2), 1100, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (AA′BB′ pattern, 4 H), 3.05–2.50 (complex, 3 H), 2.40 (s, 3 H), 2.10–1.70 (complex, 4 H), 1.70–1.00 (complex, 4 H); mass spectrum, *m/e* 264 (M^+). Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.18; H, 7.63. Found: C, 68.40; H, 7.45.

Formation of α,β-Unsaturated Sulfones from Selenosulfonate–Olefin Adducts. 1-(*p*-Toluenesulfonyl)-1-cyclohexene. A solution of *trans*-**7c** (0.393 g, 1 mmol) in 4 mL of tetrahydrofuran was cooled to −20 °C, 1.5 mL of cold 30% hydrogen peroxide was added, and the solution was kept at −20 °C for 2 h, at which time TLC showed that no starting material remained. Then 0.5 mL of triethylamine was added, and the solution was allowed to warm to room temperature and stand for 12 h. Carbon tetrachloride (~15 mL) was added, the organic layer was washed several times with water and dried ($MgSO_4$) and the solvent was evaporated. The crystalline residue was recrystallized from ethanol–water, giving 0.196 g (83%) of 1-(*p*-toluenesulfonyl)-1-cyclohexene (**10c**): mp 82–85 °C (lit.[31] mp 82–83 °C); ^1H NMR ($CDCl_3$) δ 7.8–7.2 (AA′BB′ pattern, 4 H), 6.96 (t, 1 H, J = 4 Hz), 2.37 (s, 3 H), 2.37–2.00 (m, 4 H), 1.70–1.30 (m, 4 H).

(*E*)-1-Phenyl-2-(*p*-toluenesulfonyl)ethene. Reaction of **7b** (0.230 g, 0.55 mmol) with hydrogen peroxide in the same manner as described for *trans*-**7c** gave upon workup 0.110 g (77%) of (*E*)-1-phenyl-2-(*p*-toluenesulfonyl)ethene ((*E*)-**10b**): mp 121–122 °C (lit.[11] mp 122–123 °C); ^1H NMR ($CDCl_3$) δ 7.87 (d, 2 H), 7.69 (d, 1 H, J = 15 Hz), 7.60–7.30 (complex, 7 H), 6.88 (d, 1 H, J = 15 Hz), 2.46 (s, 3 H); mass spectrum, *m/e* 258 (M^+).

(*E*)-1-(*p*-Toluenesulfonyl)-1-hexene was obtained from **7a** by the same procedure. Instead of crystallization the crude product was purified by preparative TLC (SiO_2/CCl_4), yielding 0.148 g (62%) of (*E*)-1-(*p*-toluenesulfonyl)-1-hexene ((*E*)-**10a**) as an oil: ^1H NMR ($CDCl_3$) δ 7.8–7.2 (AA′BB′ pattern, 4 H), 6.94 (dt, J_1 = 15 Hz, J_2 = 7 Hz, 1 H), 6.28 (d, J = 15 Hz, 1H), 2.42 (s, 3 H), 2.20 (q, $J_1 = J_2$ = 7 Hz, 2 H), 1.70–1.10 (m, 4 H), 0.86 (t, 3 H); mass spectrum, *m/e* 238 (M^+). Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.52; H, 7.61. Found: C, 65.80; H, 7.67.

Kinetics of Reaction of Cyanide with Selenosulfonates and Thiosulfonates in Tris Buffers. A solution of cyanide ion [(1.0–2.0) × 10^{-3} M] in a 1:1 tris/tris-H^+ buffer (0.01 M in each component) in 80% acetonitrile–20% water was placed in one of the reservoir syringes of a Durrum Model D-110 stopped-flow spectrophotometer. A solution of the appropriate areneselenosulfonate (4 × 10^{-5} M) in anhydrous acetonitrile was placed in the other reservoir syringe. The two solutions were then mixed, and the decrease in absorbance with time at 245 nm was monitored on the storage oscilloscope.

The runs with the thiosulfonate were so much slower that they were followed by conventional spectrophotometry. A solution of cyanide ion [(1.0–2.0) × 10^{-3} M] in a 1:1 tris/tris-H^+ buffer (0.01 M in each component) was made up in 90% acetonitrile–10% water, and 3.5 mL of the solution was placed in a thermostated cell in a spectrophotometer. For initiation of the reaction, 35 μL of a 2 × 10^{-2} M solution of the thiosulfonate in acetonitrile was added, and the decrease in absorbance with time at 275 nm was followed.

Registry No. 1a, 76200-60-7; **2a**, 68819-94-3; **2b**, 60805-71-2; **2c**, 76200-59-4; **7a**, 77332-91-3; **7b**, 76649-85-9; **7c**, 76649-90-6; **8**, 70312-74-2; (*E*)-**10a**, 71964-05-1; (*E*)-**10b**, 16212-08-1; **10c**, 67963-03-5; **13c**, 77332-93-5; **14c**, 77332-92-4; **14d**, 79272-74-5; **15c**, 77398-77-7; **15d**, 79355-43-4; **19**, 79272-75-6; *exo*-**20**, 79272-76-7; *endo*-**20**, 79355-44-5; **21**, 79272-77-8; **22a**, 79272-78-9; **22b**, 79272-79-0; **23**, 24454-38-4; **24**, 79272-80-3; benzeneseleninic acid, 6996-92-5; *p*-toluenesulfinic acid, 536-57-2; benzenesulfinic acid, 618-41-7; *p*-chlorobenzenesulfinic acid, 100-03-8; cyclohexene, 110-83-8; 1-hexene, 592-41-6; styrene, 100-42-5; 1,1-diphenylethylene, 530-48-3; 2,5-norbornadiene, 121-46-0; 1,5-cyclooctadiene, 111-78-4; diphenyl diselenide, 1666-13-3; *endo*-2-tosyloxy-*cis*-bicyclo[3.3.0]octane, 14352-97-7; *exo*-2-(*p*-tolylthio)-*cis*-bicyclo[3.3.0]octane, 79299-86-8.

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(31) Bordwell, F. G.; Kern, R. J. *J. Am. Chem. Soc.* **1955**, *77*, 1141.