Further Studies of Selenosulfonation. Photoaddition of Bis(*p*-tolylsulfonyl) Selenide and Alkaneselenosulfonates to Alkenes and the Selenosulfonation of β-Pinene and 1,6-Heptadiene

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Some extensions of the selenosulfonation of olefins of possible synthetic utility have been investigated: (a) Photoaddition of bis(*p*-tolylsulfonyl)selenide (**7**), $ArSO_2SeSO_2Ar$ (Ar = *p*-$CH_3C_6H_4$), to alkenes leads to *Se*-β-(*p*-tolylsulfonyl)alkyl *p*-tolueneselenosulfonates, $ArSO_2C(<)–C(<)SeSO_2Ar$, and bis(β-*p*-tolylsulfonylalkyl) diselenides, $(ArSO_2C(<)–C(<)Se–)_2$, the latter probably resulting from photodecomposition of the former. Both compounds can be easily converted to the corresponding β-(*p*-tolylsulfonyl)alkyl selenocyanate, $ArSO_2C(<)–C(<)SeCN$. (b) *Se*-Phenyl alkaneselenosulfonates (**6**), $PhSeSO_2R$, can be synthesized by the reaction of benzeneseleninic acid with the appropriate alkanesulfinic acid, RSO_2H. When R is an *n*-alkyl group photoaddition of **6** to alkenes yields the β-phenylseleno sulfone resulting from 1,2-addition. When R = $PhCH_2$, however, desulfonylation of the RSO_2· radical is faster than its addition to the alkene, and benzyl phenyl selenide is formed. (c) Free radical addition of **1** (Ar = *p*-$CH_3C_6H_4$) to β-pinene occurs with opening of the four-membered ring and gives **14** in 91% yield. Oxidative elimination of the PhSe group in **14** affords 7-(*p*-tolylsulfonyl)-1,8(9)-*p*-menthadiene (**15**) in 94% yield. Photoaddition of **1** to 1,6-heptadiene gives a mixture of the 1,2-addition product (**18**) and the disubstituted cyclopentane derivative (**19**).

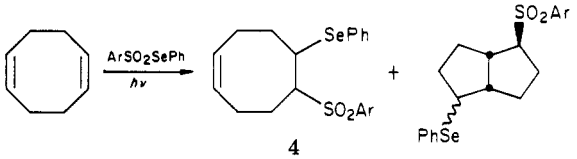
Arenesulfinic acids react readily with benzeneseleninic acid in ethanol at 0 °C to give *Se*-phenyl areneselenosulfonates (**1**), eq 1. Such selenosulfonates undergo facile

$$PhSeO_2H + 2\ ArSO_2H \xrightarrow[EtOH]{0\ °C} \underset{\mathbf{1}}{PhSeSO_2Ar} + ArSO_3H + H_2O \quad (1)$$

free-radical addition to alkenes to give β-phenylseleno sulfones (**2**), which can then be converted in excellent yield by oxidative elimination of the phenylseleno group to synthetically valuable α,β-unsaturated sulfones (**3**), eq 2.[1,2]

$$\underset{\mathbf{1}}{ArSO_2SePh} + RCH{=}CH_2 \xrightarrow[\text{or } \Delta]{h\nu} \underset{\mathbf{2}}{ArSO_2CH_2CH(SePh)R} \xrightarrow{[O]} \xrightarrow{-PhSeOH} \underset{\mathbf{3}}{ArSO_2CH{=}CHR} \quad (2)$$

It has also been shown that free-radical addition of **1** to 1,5-cyclooctadiene (eq 3) gives a mixture of approximately



(3)

4 **5**

equal amounts of **4** (the 1,2-adduct) and **5** (the product from transannular addition of the initial adduct radical prior to reaction with **1**), thereby demonstrating that with appropriate substrates selenosulfonation can result in structurally more varied products than the simple 1,2-adducts (**2**) of eq 2.

The objective of the present work is to ascertain the viability of certain extensions of eq 1–3 of possible synthetic utility. The following points are addressed: (1) preparation of alkaneselenosulfonates, RSO_2SePh (**6**), and bis(arylsulfonyl) selenides, $ArSO_2SeSO_2Ar$ (**7**), by reactions analogous to eq 1; (2) free-radical addition of **6** and **7** to simple alkenes; (3) selenosulfonation (using **1**) of other substrates (β-pinene, 1,6-heptadiene) that, like 1,5-cyclooctadiene, are known[3,4] to undergo intramolecular processes during the course of certain radical additions.

Results and Discussion

Formation of Alkaneselenosulfonates. Both 1-dodecanesulfinic acid[5] (an alkanesulfinic acid) and phenylmethanesulfinic acid[6] (an aralkanesulfinic acid) react readily with benzeneseleninic acid in ethanol at 0 °C to give the corresponding alkaneselenosulfonate (**6**) in reasonable yield (eq 4). Reaction of sulfinic acids with

$$PhSeO_2H + 2\ RSO_2H \rightarrow \underset{\substack{\mathbf{6a},\ R = n\text{-}C_{12}H_{25}\ (80\%)\\ \mathbf{6b},\ R = PhCH_2\ (54\%)}}{PhSeSO_2R} + RSO_3H + H_2O \quad (4)$$

$PhSeO_2H$ to afford selenosulfonates is therefore not restricted to arenesulfinic acids only.

Reaction of *p*-Toluenesulfinic Acid with Selenium Dioxide. Formation of Bis(*p*-tolylsulfonyl) Selenide. Thirty years ago Foss[7] showed that $Se(O)Cl_2$ reacts with $ArSO_2Na$ as outlined in eq 5a and obtained **7** (Ar = *p*-

$$Se(O)Cl_2 + 3\ ArSO_2Na \rightarrow \underset{\mathbf{7}}{ArSO_2SeSO_2Ar} + ArSO_3Na + 2\ NaCl \quad (5a)$$

$CH_3C_6H_4$) in approximately 50% yield. This and the nature of reaction 1 suggested that **7** might also be formed by reacting the sulfinic acid with selenium dioxide. This is indeed the case (eq 5b). The reaction is considerably

$$3\ ArSO_2H + SeO_2 \rightarrow ArSO_2SeSO_2Ar + ArSO_3H + H_2O \quad (5b)$$

slower and the yields of **7** are lower than those of **1** from eq 1. The best yield of **7** (60%) was obtained by allowing *p*-toluenesulfinic acid (3 mol) and selenium dioxide (1 mol) to react in tetrahydrofuran for 24 h at room temperature.

(1) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899.
(2) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249.
(3) (a) Bordwell, F. G.; Hewett, W. A. *J. Am. Chem. Soc.* **1957**, *79*, 3493. (b) Oldroyd, D. M.; Fisher, G. S.; Goldblatt, L. A. *Ibid.* **1950**, *72*, 2407.
(4) (a) Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.* **1966**, 434. (b) Huyser, E. S. "Free Radical Chain Reactions"; Wiley-Interscience: New York, 1970; p 182. (c) Brace, N. O. *J. Am. Chem. Soc.* **1964**, *86*, 523; *J. Org. Chem.* **1966**, *31*, 2897.
(5) Marvel, C. S.; Johnson, R. S. *J. Org. Chem.* **1948**, *13*, 822.
(6) Kice, J. L.; Engebrecht, R. H. *J. Org. Chem.* **1962**, *27*, 4654.
(7) Foss, O. *Acta Chem. Scand.* **1952**, *6*, 508.

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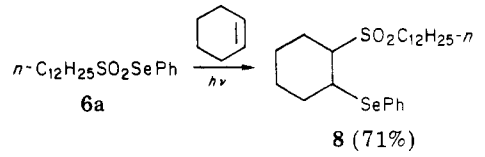
Photoaddition of Alkaneselenosulfonates to Alkenes. Photoaddition of *Se*-phenyl 1-dodecaneselenosulfonate (**6a**) to cyclohexene under the same conditions used[1] for the photoaddition of 1 to alkenes gives 1-phenylseleno-2-(*n*-dodecylsulfonyl)cyclohexane (**8**) in 71% yield (eq 6).[8] On the other hand, attempted photoaddition



6a 8 (71%) (6)

of **6b** to the same alkene gives no olefin–**6b** adduct. Instead benzyl phenyl selenide is isolated in greater than 90% yield.

The difference in behavior of **6a** and **6b** is easily explained. Alkylsulfonyl radicals can undergo desulfonylation (eq 7); the more stable the radical R′·, the more easily

$$R'SO_2\cdot \rightarrow R'\cdot + SO_2 \quad (7)$$

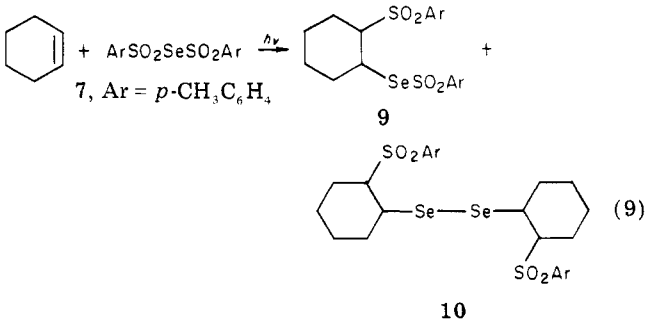
this process will occur.[9] Once formed, the R′· radical undergoes a transfer reaction with a molecule of selenosulfonate (eq 8) in preference to addition to a molecule of

$$R'\cdot + PhSeSO_2R' \rightarrow R'SePh + R'SO_2\cdot \quad (8)$$

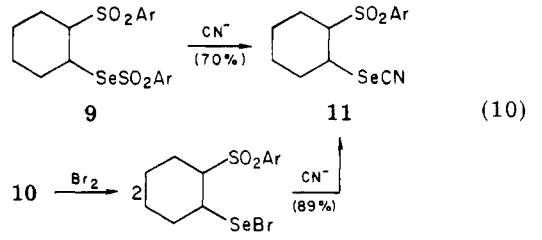
alkene ($R'\cdot + CH_2{=}CHR \rightarrow R'CH_2\dot{C}HR$). With **6a**, where R′ = n-$C_{12}H_{25}$, desulfonylation of $R'SO_2\cdot$ is slow compared to its rate of addition to cyclohexene, and **8** is formed in good yield. With **6b**, where R′· is a resonance-stabilized benzyl radical, desulfonylation is rapid and an almost quantiative yield of $PhCH_2SePh$ is obtained.

Kobayashi and co-workers[10] have examined the thermal decomposition of several other alkaneselenosulfonates in the presence of alkenes and have obtained results that are in accord with those for **6a** and **6b** and the interpretation presented above. Free-radical selenosulfonation of alkenes by alkaneselenosulfonates ($PhSeSO_2R'$) is therefore feasible only in those cases (such as R′ = Me, Et, or n-C_nH_{2n+1}) where the lack of stabilization for R′· causes eq 7 to be slow compared to the rate of addition of $R'SO_2\cdot$ to the alkene.

Photoaddition of Bis(*p*-tolylsulfonyl) Selenide to Alkenes. In carbon tetrachloride photoaddition of **7** (Ar = *p*-$CH_3C_6H_4$) to cyclohexene occurs readily. During the reaction some elemental selenium precipitates from the solution. The other identifiable products, separated by preparative thin-layer chromatography, are **9**, the product of 1,2-addition of **7** to the alkene, 0.45 mol/mol of **7**, and bis2-(*p*-tolylsulfonyl)cyclohexyl diselenide (**10**), 0.19 mol/mol of **7** (eq 9). The identity of **9** and **10** was established from their spectral data and by the conversion of each in high yield, via the reaction sequences shown in eq 10, to the same compound, *trans*-2-(*p*-tolylsulfonyl)-



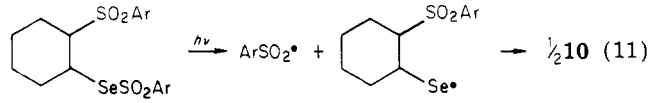
(9)



(10)

cyclohexyl selenocyanate (**11**) (J_{ab} = 10 Hz for $CH_a(SeCN)CH_b(SO_2Ar)$). The $ArSO_2$ and Se groups in **9** and **10** are therefore trans.

We believe that diselenide **10** is not a primary product of the reaction of **7** with cyclohexene but is rather formed from **9** in a subsequent reaction.[11] One route by which it might be formed is shown in eq 11. Compound **9**, being



→ ½**10** (11)

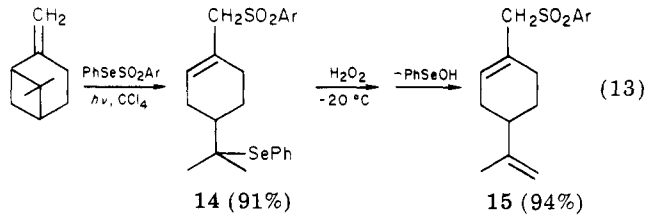
itself a selenosulfonate, can undergo photodissociation. Recombination of selenenyl radicals (**12**) from this photodissociation would afford **10**.

Photoaddition of **7** to styrene under the same conditions as for its reaction with cyclohexene gives a high yield (0.5 mol/mol of **7**) of diselenide **13** and no significant amount

$$PhCH{=}CH_2 \xrightarrow[h\nu]{ArSO_2SeSO_2Ar} \underset{13}{(ArSO_2CH_2CH(Ph)\text{-}Se\text{-})_2} \quad (12)$$

of the 1,2-addition product of **7** to $PhCH{=}CH_2$. Apparently the process that transforms the 1,2-addition product to the diselenide occurs more readily than with **9**.

Photoaddition of 1 to β-Pinene and 1,6-Heptadiene. Photoaddition of *Se*-phenyl *p*-tolueneselenosulfonate (**1a**, Ar = *p*-$CH_3C_6H_4$), 1.0 M, to β-pinene (1.5 M) in carbon tetrachloride solution affords a 91% yield of a 1:1 adduct of **1a** and β-pinene whose NMR spectrum (olefinic proton resonance at δ 5.4, 1 H) shows the compound to be 8-(phenylseleno)-7-(*p*-tolylsulfonyl)-Δ^1-*p*-menthene (**14**). Oxidative elimination of the PhSe group from **14** gives 7-(*p*-tolylsulfonyl)-1,8(9)-*p*-menthadiene (**15**) in 94% yield (eq 13).



(13)

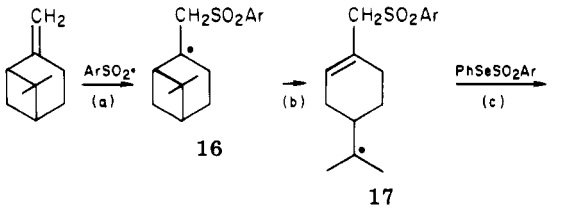
Addition of an $ArSO_2\cdot$ radical to β-pinene (eq 14, step a) will give radical **16**. The formation of **14** in >90% yield demonstrates that the transfer reaction of this radical with **1** (which would yield the simple 1,2-adduct) is much slower than opening of the strained, four-membered ring in **16** to give **17**. Except for cases where the addend is an extremely reactive chain transfer agent (such as $CH_3C(O)SH$),[3a] this is what has also been observed in other radical additions[3b] to β-pinene.

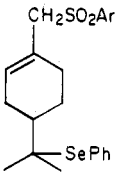
(8) The photoaddition of **1** to cyclohexene is highly stereoselective and gives the trans adduct.[1] By analogy, the **8** formed in eq 6 should be almost entirely the trans isomer.

(9) Kice, J. L. "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 2, pp 731–737 and references cited therein.

(10) Kobayashi, M., Tokyo Metropolitan University, private communication.

(11) This is based on the observation (from TLC of the reaction mixture at various times during the reaction) that the ratio **10**:**9** increases as the photoaddition proceeds.

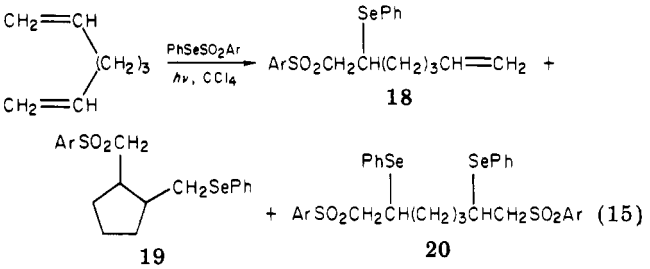




(14)

Free-radical additions to 1,6-heptadiene are known[4] to afford disubstituted cyclopentane derivatives in competition with simple 1,2-addition. If in the selenosulfonation of 1,6-heptadiene cyclization can compete effectively with transfer, **19** should be formed, and this, after oxidative elimination of the PhSe group, should yield 1-methylene-2((*p*-tolylsulfonyl)methyl)cyclopentane (**23**), a compound of possible interest as a synthetic intermediate.

Investigation of the photoaddition of **1a** (1.0 M) to 1,6-heptadiene (1.5 M) in carbon tetrachloride reveals that three products (separable by chromatography) are formed. Their structures, deduced from appropriate spectral data are **18** (70% of the adduct mixture), **19** (19%), and **20** (11%) (eq 15). Compound **20** results from addition of **1a** to **18**.



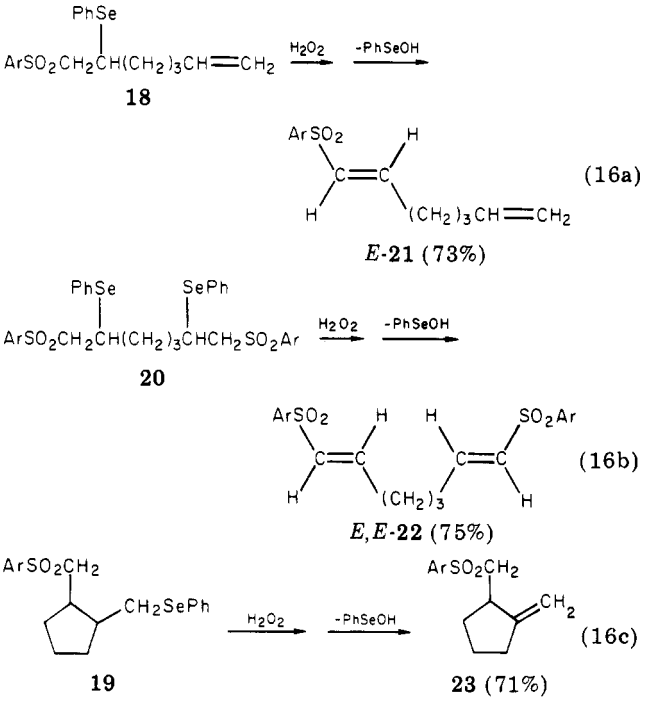
(15)

Use of more dilute solutions of **1a** and 1,6-heptadiene leads to an increase in the percentage of **19** in the total adduct mixture. When the addition was carried out using a solution initially 0.1 M in **1a** (and 0.15 M in diene) the proportions of the three products in the mixture were **18**, 51%, **19**, 44%, **20**, 5%.

These results unfortunately indicate that **1a** is too reactive as a chain-transfer agent for formation of **19** to predominate over formation of **18** at initial concentrations of **1a** and diene in the convenient range for synthetic work. For this reason, even though oxidative elimination of the PhSe group from **19** does lead to **23** (vide infra), selenosulfonation of 1,6-heptadiene by **1a** does not provide a useful practical route to **23**.

Oxidative elimination of **18** (eq 16a) gives a 73% yield of a compound whose ^{1}H NMR and IR spectra are consistent with those expected for the *E* isomer of **21** (J_{ab} = 15 Hz for $ArSO_2CH_a{=}CH_bCH_2{-}$). Formation of the *E* isomer, and of the α,β-unsaturated sulfone without any significant amount of the isomeric β,γ-unsaturated sulfone, is in accord with previous experience[1,2] with the oxidative elimination of β-phenylseleno sulfones. Similarly, **20** undergoes oxidative elimination of both PhSe groups to give *E,E*-**22** in 75% yield (eq 16b).

Oxidative elimination of the PhSe group in **19** affords a single alkene in 71% yield. The ^{1}H NMR spectrum clearly shows a $CH_2{=}C <$ group [δ 4.98 (d, J = 2 Hz, 1 H), 4.79 (d, J = 2 Hz, 1 H)]; its structure is therefore **23**. The

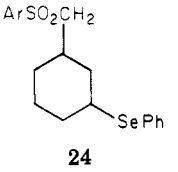


(16a)

(16b)

(16c)

formation of **23** provides proof that the cyclization leads to **19** and not to the isomeric cyclohexane derivative **24**



that would result from addition of the carbon free radical to the other carbon of the carbon–carbon double bond.

Experimental Section

Preparation and Purification of Materials. Phenylmethanesulfinic acid, mp 66–70 °C (lit.[6] 64–69 °C), was prepared from phenylmethanesulfonyl chloride[12] by the procedure of Kice and Engebrecht.[6] 1-Dodecanesulfinic acid, mp 36.5–37.5 °C (lit.[5] 29–30 °C), was prepared as described by Marvel and Johnson.[5] *Se*-Phenyl *p*-tolueneselenosulfonate (**1a**), mp 76–78 °C, was synthesized by the method of Gancarz and Kice.[1] Benzeneseleninic acid (Aldrich Chemical), *p*-toluenesulfinic acid (Aldrich), β-pinene (Aldrich), selenium dioxide (Alfa Chemical), and 1,6-heptadiene (Pfaltz and Bauer) were obtained from commercial sources. Cyclohexene, styrene, and 1,6-heptadiene were redistilled before use.

Reaction of Benzeneseleninic Acid with Alkanesulfinic Acids. Benzeneseleninic acid (0.94 g, 5.0 mmol) was dissolved in 20 mL of ethanol and the solution was cooled to 0 °C. To this was then added 10.0 mmol of the alkanesulfinic acid, and the reaction mixture was stirred vigorously for 3 h at 0 °C in the dark. The reaction mixture was cooled to −20 °C and the precipitate of the selenosulfonate was filtered off. The product from the reaction involving 1-dodecanesulfinic acid was recrystallized twice from ethanol giving 1.56 g (80%) of *Se*-phenyl 1-dodecaneselenosulfonate (**6a**): mp 32–33 °C; IR (KBr) 2957, 2922, 2850, 1469, 1300 (s, SO_2), 1118, 1111 (s, SO_2), 742, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.9–7.0 (m, 5 H), 3.25 (t, J = 7.5 Hz, 2 H, CH_2SO_2), 2.5–1.15 (series of m, 23 H). Anal. Calcd for $C_{18}H_{30}O_2SSe$: C, 55.51; H, 7.76. Found: C, 55.71; H, 7.78.

Se-Phenyl phenylmethaneselenosulfonate (**6b**), 0.84 g (54%), mp 79–79.5 °C, was isolated from the reaction involving phenylmethanesulfinic acid: IR (KBr) 3063, 3032, 3014, 2962, 2908, 1583, 1572, 1491, 1475, 1454, 1440, 1406, 1321, 1238, 1195, 1138, 1114, 1072, 873, 775, 744, 700, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz)

(12) Sprague, J. M.; Johnson, T. B. *J. Am. Chem. Soc.* **1937**, *59*, 1837.

δ 7.75–7.10 (m, 10 H), 4.48 (s, 2 H).

Reaction of *p*-Toluenesulfinic Acid with Selenium Dioxide. *p*-Toluenesulfinic acid (0.47 g, 3 mmol) and selenium dioxide (0.11 g, 1 mmol) were stirred vigorously in 25 mL of tetrahydrofuran at room temperature for 24 h in the dark. Ether (25 mL) and water (50 mL) were then added. The organic layer was washed five times with 25 mL of water and dried ($MgSO_4$), and the solvent was removed under reduced pressure at room temperature. The residue was recrystallized from ethanol giving 0.217 g (57%) of bis(*p*-tolylsulfonyl)selenide (**7**): mp 110 °C dec (lit.[7] 121 °C in a *preheated* bath); IR (KBr) 3047, 2970, 2918, 2868, 1591, 1489, 1454, 1446, 1399, 1340, 1315, 1303, 1296 (s, SO_2), 1182, 1126 (s, SO_2), 1072, 1014, 815, 700, 646 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_4S_2Se$: C, 43.19; H, 3.60. Found: C, 43.32; H, 3.67.

Photoaddition of 6a to Cyclohexene. Cyclohexene (0.123 g, 1.5 mmol) and **6a** (0.390 g, 1.0 mmol) were dissolved in 1 mL of degassed carbon tetrachloride and the solution was irradiated under nitrogen in a closed pyrex vessel in a Rayonet reactor (RPR-2537 lamp). After 1.5 h TLC indicated no **6a** remained. Removal of the solvent and excess cyclohexene and recrystallization of the residue twice from hexane gave 0.335 g (71%) of 1-(phenylseleno)-2-(*n*-dodecylsulfonyl)cyclohexane (**8**): mp 45.5–46 °C; IR (KBr) 3070, 3057, 2922, 2850, 1475, 1467, 1437, 1286, 1276 (s, SO_2), 1186, 1118 (s, SO_2), 740, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–7.15 (m, 5 H), 4.0 (m, 1 H), 3.3–2.7 (m, 3 H), 2.5–1.1 (series of m, 28 H), 0.95 (t, J = 5 Hz, 3 H). Anal. Calcd for $C_{24}H_{40}O_2SSe$: C, 61.12; H, 8.55. Found: C, 61.29; H, 8.32.

Photodecomposition of 6b in the Presence of Alkenes. The alkene (1.5 mmol) and **6b** (0.312 g, 1.0 mmol) were dissolved in 1 mL of degassed carbon tetrachloride and the solution was irradiated in the same manner as described above until TLC showed no **6b** remained (1.5 h). The solvent and excess alkene were then removed under reduced pressure.

In the case of cyclohexene the residue (0.236 g) consisted entirely of phenyl benzyl selenide: mp 32.5–33.5 °C (lit.[13] 34–35 °C); ^1H NMR ($CDCl_3$) δ 7.55–6.90 (m, 10 H), 4.0 (s, 2 H). In the case of styrene preparative TLC (SiO_2, CH_2Cl_2–benzene, 1:1) separated the residue into phenyl benzyl selenide 0.195 g (79%), mp 31–32 °C, and a small amount (0.03 g) of a product obtained as a white solid after trituration with hexane. The IR (strong absorptions at 1307 and 1122 cm^{-1} due to a sulfonyl group) and the ^1H NMR of this material were consistent with those expected for the 1,2-addition product of **6b** to styrene.

Photoaddition of Bis(*p*-tolylsulfonyl) Selenide (7) to Cyclohexene. A solution of cyclohexene (0.124 g, 1.5 mmol) and **7** (0.390 g, 1.0 mmol) in 2 mL of carbon tetrachloride was irradiated in the manner previously described for **6a**. During the irradiation a small amount of red-purple solid separated from the solution.

The solvent and excess alkene were removed under reduced pressure and a small amount of chloroform was added. The chloroform solution was filtered to remove the red-purple solid (0.02 g), which was identified as elemental selenium. The chloroform-soluble material was separated by preparative TLC (SiO_2, ethyl acetate) into two fractions. Each fraction was dissolved in the minimum amount of chloroform, hexane was added, and the solutions were cooled to −20 °C. From the solution containing the fraction of lower R_f value there was obtained 0.120 g (0.19 mmol) of bis(2-(*p*-tolylsulfonyl)cyclohexyl) diselenide (**10**) as a faintly yellow solid: mp 66–70 °C; IR (KBr) 3063, 3049, 3030, 2937, 2856, 1595, 1494, 1446, 1402, 1311, 1302, 1288 (s, SO_2), 1147 (s, SO_2), 1086, 868, 814, 717, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.2 (m, 8 H), 3.6–3.1 (m, 4 H, 2 $CHSO_2Ar$ and 2 CHSe), 2.45 (s, 6 H, 2 $CH_3C_6H_4$), 2.2–1.3 (series of m, 16 H); mass spectrum, m/e 634 (M^+, ^{80}Se, ^{80}Se), 632 (M^+, ^{80}Se, ^{78}Se), 630 (M^+, ^{78}Se, ^{78}Se).

On cooling the chloroform–hexane solution of the higher R_f value fraction an oil separated. The solvent was removed by decantation, and the last traces of solvent were removed from this oil by subjecting the material to an oil-pump vacuum. This left 0.213 g (0.45 mmol) of *Se*-2-(*p*-tolylsulfonyl)cyclohexyl *p*-tolueneselenosulfonate (**9**) as a yellow semisolid: IR (neat) 3063, 3048, 3030, 2935, 2856, 1595, 1491, 1448, 1402, 1315, 1302, 1290 (s, SO_2), 1147, 1134 (s, SO_2), 1086, 1074, 814, 717, 702, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.2 (m, 8 H), 4.32 (m, 1 H), 3.75 (m, 1 H), 2.47 (s, 6 H, 2 $CH_3C_6H_4$), 2.2–1.4 (m, 8 H).

Conversion of 9 to 2-(*p*-Tolylsulfonyl)cyclohexyl Selenocyanate (11). Selenosulfonate **9** (0.236 g, 0.5 mmol) was dissolved in 2.5 mL of ethanol–ethyl acetate (5:1) and a solution of 0.033 g (0.5 mmol) of potassium cyanide in the minimum amount of water was added slowly with stirring at room temperature. The reaction was complete when the addition was finished. The reaction mixture was then allowed to stand in the freezer, and the solid that had precipitated was filtered off, washed with a little hot water, and recrystallized from ethanol, giving 0.120 g (70%) of *trans*-2-(*p*-tolylsulfonyl)cyclohexyl selenocyanate (**11**) as a colorless solid: mp 140–142 °C; IR (KBr) 2943, 2920, 2864, 2143 (CN), 1595, 1448, 1300–1278 (s, SO_2), 1172, 1141 (s, SO_2), 1082, 812, 758, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95–7.25 (AA'BB' pattern, 4 H), 3.9–3.0 (two m, 2 H, $CHSO_2Ar$ and CHSeCN, J_{ab} = 10 Hz), 2.48 (s, 3 H, $CH_3C_6H_4$), 2.3–1.0 (m, 8 H). Anal. Calcd for $C_{14}H_{17}NO_2SSe$: C, 49.12; H, 5.01. Found: C, 48.95; H, 5.04.

Conversion of 10 to 11. Diselenide **10** (0.063 g, 0.1 mmol) was dissolved in 1 mL of dry chloroform and 0.016 g (0.1 mmol) of bromine was added with stirring. Reaction was rapid. Removal of the chloroform left a shiny, reddish-brown solid. This solid was treated with a solution of 0.3 mmol of potassium cyanide dissolved in 6.5 mL of 90% ethanol, and the reaction mixture was warmed briefly on a steam bath. The solvent was removed under reduced pressure at room temperature. The residue was then washed several times with hot water and finally recrystallized from ethanol, giving 0.061 g (89%) of **11**, mp 140–142 °C, identical in all respects with the material obtained from the reaction of **9** with cyanide ion.

Photoaddition of 7 to Styrene. Styrene (0.078 g, 0.75 mmol) and **7** (0.195 g, 0.5 mmol) in 2 mL of carbon tetrachloride was irradiated in the same manner as for the reaction of **7** with cyclohexene. After removal of the solvent and excess olefin the residue was treated with a small amount of hot chloroform and filtered to remove a small amount of elemental selenium. Ethanol was added to the chloroform filtrate, and the solution was cooled to −20 °C. The precipitate that separated was filtered off and recrystallized from chloroform, giving 0.17 g (0.25 mmol) of bis(2-(*p*-tolylsulfonyl)-1-phenylethyl) diselenide (**13**): mp 184–185 °C; IR (KBr) 3061, 3028 2978, 2918, 1597, 1493, 1460, 1411, 1311, 1302 (s, SO_2), 1253, 1163, 1134 (s, SO_2), 1082, 912, 814, 752, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60–6.85 (m, 18 H), 4.37 (t, J= 7 Hz, 2 H, 2 CHPh), 3.75 (d, J = 7 Hz, 4 H, 2 CH_2SO_2Ar), 2.38 (s, 6 H, 2 $CH_3C_6H_4$). Anal. Calcd for $C_{30}H_{30}O_4S_2Se_2$: C, 53.25; H, 4.47. Found: C, 52.90; H, 4.51.

Photoaddition of 1a to β-Pinene. β-Pinene (0.204 g, 1.5 mmol) and **1a** (0.312 g, 1.0 mmol) were dissolved in carbon tetrachloride (1 mL) and the solution was irradiated and worked up in the usual manner. Recrystallization of the residue twice from hexane gave 0.408 g (91%) of 8-(phenylseleno)-7-(*p*-tolylsulfonyl)-Δ^1-*p*-menthene (**14**) as a white solid: mp 64–64.5 °C; IR (KBr) 3068, 3057, 2960, 2920, 2837, 1664, 1597, 1473, 1452, 1437, 1404, 1367, 1313, 1303, 1285 (s, SO_2), 1140 (s, SO_2), 1114, 1086, 1020, 815, 748, 742, 727, 694, 648 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.1 (m, 9 H), 5.4 (m as a br s, 1 H, CH=C), 3.67 (s, 2 H, CH_2SO_2Ar), 2.43 (s, 3 H, $CH_3C_6H_4$), 2.30–1.73 (m, 7 H), 1.35 (s, 3 H, CH_3C), 1.28 (s, 3 H, CH_3C). Anal. Calcd for $C_{23}H_{28}O_2SSe$: C, 61.76; H, 6.31. Found: C, 61.87; H, 6.47.

Conversion of 14 to 15. A sample of **14** (0.447 g, 1.0 mmol) was dissolved in 4 mL of tetrahydrofuran, the solution was cooled to −20 °C, and 1.5 mL of cold 30% hydrogen peroxide was added. After 2 h 0.5 mL of triethylamine was added and the solution was allowed to warm to room temperature and stand overnight. Carbon tetrachloride (~15 mL) was added, the organic layer was washed several times with water and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The solid residue was recrystallized from hexane, giving 0.272 g (94%) of 7-(*p*-tolylsulfonyl)-1,8(9)-*p*-menthadiene (**15**) as long needles: mp 86–87 °C; IR (KBr) 3060, 2960, 2910, 2845, 1640, 1590, 1490, 1445, 1430, 1405, 1370, 1300, 1285 (s, SO_2), 1245, 1180, 1145 (s, SO_2), 1120, 1085, 885, 815, 732, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.1 (AA'BB' pattern, 4 H), 5.45 (m as a br s, 1 H, CH=C), 4.67 (s, 2 H, CH_2=C), 3.67 (s, 2 H, CH_2SO_2Ar), 2.43 (4 H, $CH_3C_6H_4$ and (CH)C=CH_2), 2.35–1.85 (4 H, —CH_2CH=C(CH_2SO_2Ar)CH_2—), 1.72 (br s, 5 H, $(CH_3)C$= and (CH_2CH)C=CH_2). Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64. Found: C, 69.89; H, 7.63.

(13) Lapkin, I. I.; Bogoslovskii, N. V.; Zenkova, N. I. *Zh. Obsch. Khim.* **1971**, *41*, 2452.

Photoaddition of 1a to 1,6-Heptadiene. Irradiation (1.5 h) of a solution of 1,6-heptadiene (0.144 g, 1.5 mmol) and **1a** (0.312 g, 1.0 mmol) in 1 mL of carbon tetrachloride gave, upon workup, an oily residue (0.423 g) that could be separated into three fractions by chromatography on silica gel using benzene, methylene chloride, and chloroform successively as eluants. The compounds eluted were as follows: (a) An oil (0.136 g), assigned the structure 6-(phenylseleno)-7-(*p*-tolylsulfonyl)-1-heptene (**18**): IR (neat) 3060, 2920, 2855, 1633, 1590, 1572, 1473, 1437, 1398, 1311, 1298 (s, SO_2), 1140 (s, SO_2), 1081, 1018, 996, 910, 813, 738, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75–7.10 (m, 9 H), 6.1–5.4 (br m, 1 H, C*H*=CH_2), 5.2–4.7 (m appearing as a d, 2 H, CH_2=CH), 3.42 (m, 3 H, CHSePh and CH_2SO_2Ar), 2.43 (s, 3 H, C$H_3C_6H_4$), 2.20–1.65 (m, 6 H, —$(CH_2)_3$—). (b) An oil (0.036 g), which is 1-((phenylseleno)methyl)-2-((*p*-tolylsulfonyl)methyl)cyclopentane 1-((phenylseleno)methyl)-2-((*p*-tolylsulfonyl)methyl]cyclopentane (**19**): IR (neat) 3057, 3026, 2955, 2874, 1597, 1577, 1477, 1452, 1437, 1404, 1313, 1302, 1288 (s, SO_2), 1147 (s, SO_2), 1087, 1022, 817, 758, 738, 692, 689, 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95–7.10 (m, 9 H), 3.55–2.65 (two m, 4 H, CH_2SePh and CH_2SO_2Ar), 2.43 (s, 3 H, C$H_3C_6H_4$), 2.40 (m, 2 H, C*H*CH_2SO_2Ar and C*H*CH_2SePh), 2.00–1.35 (m, 6 H). Anal. Calcd for $C_{20}H_{24}O_2SSe$: C, 58.96% H, 5.93. Found: C, 58.74; H, 6.16. (c) An oil (0.038 g), assigned the structure 2,6-bis(phenylseleno)-1,7-bis(*p*-tolylsulfonyl)heptane (**20**): IR (neat) 3050, 2915, 2850, 1590, 1575, 1473, 1435, 1398, 1312, 1298 (s, SO_2), 1140 (s, SO_2), 1081, 1018, 813, 739, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (m, 18 H), 3.42 (m, 6 H, 2 CHSePh and 2 CH_2SO_2Ar), 2.43 (s, 6 H, 2 C$H_3C_6H_4$), 2.25–1.50 (m, 6 H, —$(CH_2)_3$—).

To study the effect of a change in the initial concentration of **1a** on the product distribution more dilute solutions of **1a** and 1,6-heptadiene were irradiated. A solution of 1.0 mmol of **1a** and 1.5 mmol of 1,6-heptadiene in 5 mL of carbon tetrachloride gave 0.146 g of **18**, 0.071 g of **19**, and 0.042 g of **20**, while a solution of 5.0 mmol of **1a** and 7.5 mmol of 1,6-heptadiene in 50 mL of carbon tetrachloride gave 0.329 g of **18**, 0.283 g of **19**, and 0.051 g of **20**.

Oxidative Elimination of the Phenylseleno Groups in 18, 19, and 20. Each of the 1,6-heptadiene–**1a** adducts (**18**, **19**, **20**) was subjected to the same oxidative procedure described for the conversion of **14** to **15**.

Formation of 21. Upon workup of the reaction mixture from the oxidation of 0.407 g (1.0 mmol) of **18** there was obtained, after chromatography on silica gel using ethanol as eluant, 0.181 g (73%) of (*E*)-1-(*p*-tolylsulfonyl)-1,6-heptadiene (*E*-**21**) as an oil: IR (neat) 3060, 3043, 2925, 2860, 1635, 1595, 1490, 1450, 1433, 1311, 1300, 1280 (s, SO_2), 1143 (s, SO_2), 1085, 1014, 995, 967, 915, 814, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (AA′BB′ pattern, 4 H), 6.93 (dt, J_1 = 15 Hz, J_2 = 6 Hz, 1 H, C*H*=CHSO_2Ar), 6.28 (dt, J_1 = 15 Hz, J_2 = 1.5 Hz, 1 H, CH=C*H*SO_2Ar), 6.1–5.4 (br m, 1 H, C*H*=CH_2), 5.2–4.7 (2 H, CH_2=CH), 2.43 (s, 3 H, C$H_3C_6H_4$), 2.33–1.33 (m, 6 H, —$(CH_2)_3$—). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25. Found: C, 66.97; H, 7.18.

Formation of 22. Workup of the reaction mixture from the oxidation of 0.180 g (0.25 mmol) of **20** gave 0.064 g (75%) of a gummy solid whose structure was assigned to be (*E*,*E*)-1,7-di-(*p*-tolylsulfonyl)-1,6-heptadiene on the basis of its IR and ^1H NMR spectra: IR (neat) 3061, 3043, 2928, 2860, 1928, 1815, 1718, 1635, 1595, 1494, 1450, 1433, 1311, 1300, 1280 (s, SO_2), 1143 (s, SO_2), 1086, 1014, 981 (s, *trans* C=C), 868, 814, 738, 659 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (AA′BB′ pattern, 8 H) 6.89 (dt, J_1 = 15 Hz, J_2 = 6 H, 2 H, 2 C*H*=CHSO_2Ar), 6.25 (dt, J_1 = 15 Hz, J_2 = 1.5 Hz, 2 H, 2 CH=C*H*SO_2Ar), 2.43 (s, 6 H, 2 C$H_3C_6H_4$), 2.35–1.30 (m, 6 H, —$(CH_2)_3$—).

Formation of 23. Oxidation of **19** (0.306 g, 0.75 mmol) gave upon workup a yellow oil that could be separated into two fractions by TLC (SiO_2, CH_2Cl_2–benzene, 1:1, with two drops of EtOH per 5 mL of solvent). The higher R_f value was diphenyl diselenide (0.01 g), and the lower R_f value fraction was an oil (0.175 g) that consisted primarily of 1-methylene-2-(*p*-tolylsulfonylmethyl)-cyclopentane (**23**), but with the latter still contaminated with a small amount of **19**. Since a variety of attempts to separate **23** from **19** by preparative TLC were unsuccessful, an analytically pure sample of **23** could not be obtained. The structure for **23** was assigned on the basis of the following spectral data: IR (neat) 3068, 2957, 2872, 1653, 1597, 1315, 1302, 1288 (s, SO_2), 1145 (s, SO_2) 1087, 885, 817, 761, 659 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07–7.15 (AA′BB′ pattern, 4 H), 4.98 (d, J = 2 Hz, 1 H), 4.79 (d, J = 2 Hz, 1 H), 3.5–1.35 (series of m, 12 H). The yield of **23** (71%) was determined from the total weight of the second fraction and the integrated intensity of the signals for the CH_2=C group in **23** in the ^1H NMR spectrum of the fraction.

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Registry No. **1a**, 68819-94-3; **6a**, 89165-51-5; **6b**, 89165-52-6; **7**, 60513-62-4; **8**, 89165-53-7; **9**, 89165-55-9; **10**, 89165-54-8; **11**, 89165-56-0; **13**, 89165-57-1; **14**, 89165-58-2; **15**, 89165-59-3; **18**, 89165-60-6; **19**, 89165-61-7; **20**, 89165-62-8; (*E*)-**21**, 89165-63-9; (*E*,*E*)-**22**, 89165-64-0; **23**, 89165-65-1; benzeneseleninic acid, 6996-92-5; 1-dodecanesulfinic acid, 26535-63-7; phenylmethanesulfinic acid, 4403-73-0; *p*-toluenesulfinic acid, 536-57-2; selenium dioxide, 7446-08-4; cyclohexene, 110-83-8; styrene, 100-42-5; phenyl benzyl selenide, 18255-05-5; β-pinene, 127-91-3; 1,6-heptadiene, 3070-53-9.

Optical Rotatory Dispersion Studies. 137.[1] Synthesis and Chiroptical Properties of α- and β-Deuterium Substituted Aliphatic Aldehydes and Ketones

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The synthesis and chiroptical properties of (2*R*)-2-deuterio-3-hexanone (**8a**), (2*R*)-2-deuterio-4-methylpentanone (**8b**), (2*R*)-2-deuteriopentanal (**9a**), (2*R*)-2-deuterio-3-methylbutanal (**9b**), and (3*R*)-3-deuteriohexanal (**13**) are described. All exhibit Cotton effects consistent with the preferred eclipsed conformation of the carbonyl/α-alkyl moiety. The β-deuterio aldehyde **13** shows a sign change in accordance with the "proximity rule" previously observed in CD studies.

Introduction

In spite of the large amount of work published on the chiroptical properties of cyclic carbonyl compounds, relatively little has been done in acyclic systems. Because of their conformational mobility, the latter are expected to give rotations substantially lower than those of their cyclic counterparts, as was borne out by Djerassi and Geller in their early (1959) study of a series of optically active methyl-substituted aldehydes and ketones.[2] The rotations

(1) For the preceding paper, see Lu, Y.; Barth, G.; Kieslich, K.; Strong, P. S.; Duax, W. L.; Djerassi, C. *J. Org. Chem.* **1983**, *48*, 4549.

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