were established through comparison of VPC retention times and NMR spectral data with those of independently synthesized authentic samples.[9]

2-Hydroxyphenyl Phenyl Selenide and 4-Hydroxyphenyl Phenyl Selenide. A solution of 0.52 g of phenol and 1.40 g of **5** in 12.5 mL of acetonitrile was stirred at 25 °C for 6 days. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel to give 0.24 g (33%) of diphenyl diselenide, 0.08 g (7%) of 2-hydroxyphenyl phenyl selenide and 0.71 g (63%) of 4-hydroxyphenyl phenyl selenide.

The 2-hydroxyphenyl phenyl selenide was further purified by molecular distillation [bath temperature 95 °C (0.7 mm); lit.[9] bp 130–131 °C (0.5 mm)] to give 0.06 g (4%) of product.

The 4-hydroxyphenyl phenyl selenide was recrystallized from hexane to yield 0.53 g (46%) of product, mp 52–53 °C (lit.[9] mp 57 °C).

2-Hydroxy-3-methylphenyl Phenyl Selenide and 4-Hydroxy-3-methylphenyl Phenyl Selenide. A solution of 0.64 g of *o*-cresol and 1.50 g of **5** in 15 mL of acetonitrile was stirred at 25 °C for 9 days. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel with ether–hexane as the eluent to give 0.47 g (61%) of diphenyl diselenide, 0.03 g of crude 2-hydroxy-3-methylphenyl phenyl selenide, and 0.21 g of crude 4-hydroxy-3-methylphenyl phenyl selenide.

Molecular distillation [bath temperature 115 °C (0.8 mm)] of the minor crude product gave 0.02 g (2%) of 2-hydroxy-3-methylphenyl phenyl selenide: ^{1}H NMR ($CDCl_3$) δ 2.28 (3 H, s), 6.50 (1 H, s), 6.78 (1 H, t, J = 7.8 Hz), 7.10–7.65 (2 H, br m), 7.23 (5 H, br s); IR (neat) 3400, 1578, 1478, 1460, 1438, 1422, 1330, 1230, 1160, 1125, 1070, 1018, 841, 760, 725, 680 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}OSe$: C, 59.33; H, 4.60. Found: C, 59.54; H, 5.04.

Molecular distillation [bath temperature 170 °C (1.1 mm)] of the major crude product gave 0.17 g (16%) of 4-hydroxy-3-methylphenyl phenyl selenide: ^{1}H NMR ($CDCl_3$) δ 2.19 (3 H, s), 4.75 (1 H, s), 6.69 (1 H, d, J = 9 Hz), 7.05–7.50 (7 H, m); IR (neat) 3400, 1580, 1485, 1473, 1435, 1395, 1260, 1200, 1168, 1110, 1018, 870, 805, 728, 680 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}OSe$: C, 59.33; H, 4.60. Found: C, 58.86; H, 4.67.

Acknowledgment. We are indebted to the Institute of General Medical Sciences of the National Institutes of Health for Grant GM-22346 which supported this investigation.

Registry No. 4, 34837-55-3; **5**, 80447-92-3; dimethyl sulfide, 75-18-3; aniline, 62-53-3; diphenyl diselenide, 1666-13-3; 4-aminophenyl phenyl selenide, 16089-79-5; *N*-methylaniline, 100-61-8; 4-(methylamino)phenyl phenyl selenide, 80447-93-4; *N,N*-dimethylaniline, 121-69-7; 4-(dimethylamino)phenyl phenyl selenide, 80461-61-6; *N,N*-dimethyl-*o*-toluidine, 609-72-3; 3-methyl-4-(dimethylamino)-phenyl phenyl selenide, 80447-94-5; *N,N*-dimethyl-*o*-anisidine, 700-75-4; 3-methoxy-4-(dimethylamino)phenyl phenyl selenide, 80447-95-6; *N,N*-dimethyl-*m*-toluidine, 121-72-2; 2-methyl-4-(dimethylamino)phenyl phenyl selenide, 80447-96-7; *N,N*-dimethyl-*m*-anisidine, 15799-79-8; 2-methoxy-4-(dimethylamino)phenyl phenyl selenide, 80447-97-8; *N,N*-dimethyl-*p*-toluidine, 99-97-8; 2-(dimethylamino)-5-methylphenyl phenyl selenide, 80447-98-9; *N,N*-dimethyl-*p*-anisidine, 701-56-4; 2-(dimethylamino)-5-methoxyphenyl phenyl selenide, 80447-99-0; anisole, 100-66-3; 2-methoxyphenyl phenyl selenide, 80448-00-6; 4-methoxyphenyl phenyl selenide, 80448-01-7; phenol, 108-95-2; 2-hydroxyphenyl phenyl selenide, 57483-19-9; 4-hydroxyphenyl phenyl selenide, 80448-02-8; *o*-cresol, 95-48-7; 2-hydroxy-3-methylphenyl phenyl selenide, 80448-03-9; 4-hydroxy-3-methylphenyl phenyl selenide, 80448-04-0.

[2,3] Sigmatropic Rearrangement of Ylides Derived from Benzylic Selenonium Salts

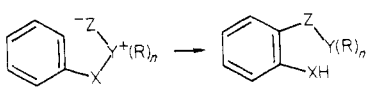
Paul G. Gassman,* Takashi Miura, and Allen Mossman

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received August 24, 1981

The [2,3] sigmatropic rearrangement of a series of ylides derived from benzylic selenonium salts has been observed. These ylides yield alkyl or aryl *o*-methylbenzyl selenides. The competition between nucleophilic displacement and ylide formation in the reaction of base with benzylic selenonium salts has been evaluated.

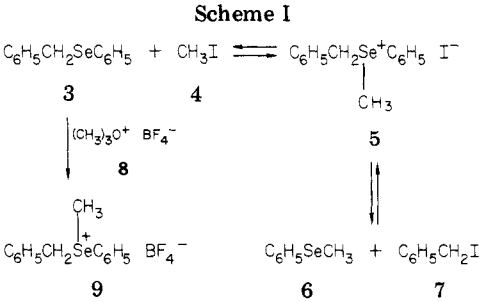
Consideration of the general concept of [2,3] sigmatropic rearrangements for the exclusive ortho substitution of certain aromatic molecules leads one to an analysis of the various possibilities for X, Y, and Z in 1. The first ex-



1 2

ample of the rearrangement of 1 to 2 was reported in 1937 by Sommelet[1] for the case where X = Z = C and Y = N. Extensive investigation of this system by Hauser[2] established this rearrangement of ylides derived from benzylic ammonium salts as the prototype for a potentially large series of different kinds of [2,3] sigmatropic rearrangements. To date, examples have been reported with X, Y, and Z as follows: X = Z = C, Y = N;[1,2] X = Z = C, Y =

Scheme I

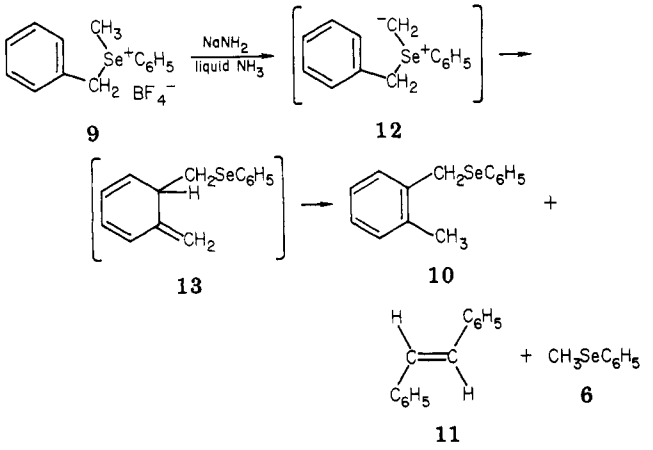


3 4 5 8 9 6 7

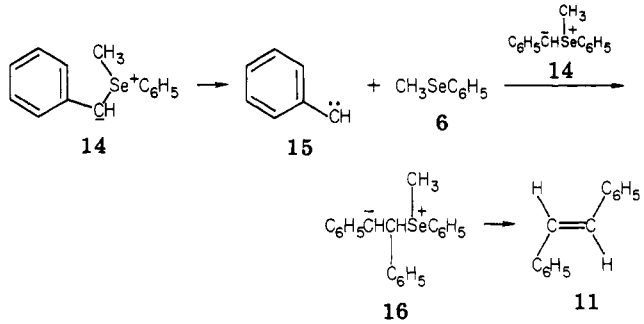
(1) Sommelet, M. *C. R. Hebd. Seances Acad. Sci.* **1937**, *205*, 56.
(2) Kantor, S. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 4122. Jones, G. C.; Hauser, C. R. *J. Org. Chem.* **1962**, *27*, 3572. Jones, G. C.; Beard, W. Q.; Hauser, C. R. *Ibid.* **1963**, *28*, 199. See also: Fery, L. P. A. *Bull. Soc. Chim. Belg.* **1962**, *71*, 376.

0022-3263/82/1947-0954$01.25/0

Scheme II



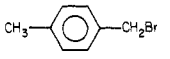
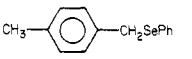
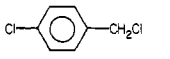
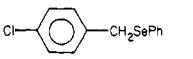
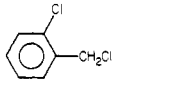
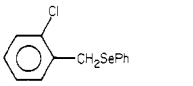
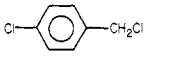
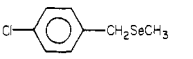
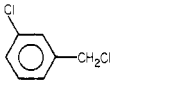
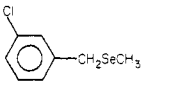
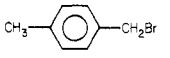
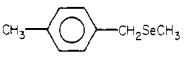
Scheme III



S;[3] X = O, Y = S, Z = C;[4] X = N, Y = S, Z = C;[5] X = Se, Y = S, Z = C;[6] X = Y = S, Z = C.[7] Evaluation of the various possibilities for X, Y, and Z indicates that in excess of 300 variations of this rearrangement might be possible. Of these, only the six listed above and our recently reported[8] example where X = Z = C and Y = Se are known. This paper presents the details of our study of the [2,3] sigmatropic rearrangement of ylides derived from benzylic selenonium salts.[8]

Our initial efforts were devoted to the synthesis of a series of selenonium salts. As part of our preliminary studies, we treated benzyl phenyl selenide (**3**)[9] with methyl iodide. This gave an equilibrium mixture of **3**–**7** (Scheme I), from which **5** could not be readily isolated. On treatment of this mixture with potassium *tert*-butoxide, we found no evidence for the generation of an ylide. Instead, we isolated methyl *tert*-butyl ether, benzyl *tert*-butyl ether, benzyl phenyl selenide (**3**), and methyl phenyl selenide (**6**). Because of the equilibrium between **3**–**7**, it was unclear whether the *tert*-butyl ethers, which were isolated, were derived from nucleophilic attack by *tert*-butoxide anion on **4** and **7** or on **5**. In order to simplify this problem, we treated **3** with Meerwein's reagent, **8**, to produce the salt **9** in 90% yield. Treatment of **9** with potassium *tert*-butoxide gave a 9:1 mixture of **6** and **3** but no product which would have resulted had the appropriate ylide been formed. These experiments demonstrated that salts such as **5** and **9** are extremely susceptible to nucleophilic attack, even by nucleophiles as hindered as *tert*-butoxide anion.

Table I. Products and Yields Obtained in the Preparation of Benzyl Phenyl Selenides and Benzyl Methyl Selenides

starting halide	starting diselenide	product	% yield
$PhCH_2Cl$	PhSeSePh	$PhCH_2SePh$	83
	PhSeSePh		87
	PhSeSePh		86
	PhSeSePh		77
$PhCH_2Cl$	$CH_3SeSeCH_3$	$PhCH_2SeCH_3$	55
	$CH_3SeSeCH_3$		65
	$CH_3SeSeCH_3$		41
	$CH_3SeSeCH_3$		57

As the result of a fairly general survey of the reaction of **9** with bases, we found that the desired ylide formation and subsequent [2,3] sigmatropic rearrangement could be accomplished through the use of sodium amide in liquid ammonia. Addition of **9** to excess sodium amide (Scheme II) gave 17% of the desired rearrangement product, **10**, 22% of *trans*-stilbene (**11**), and 19% of methyl phenyl selenide (**6**). It is presumed that the formation of **10** involves the initial conversion of **9** into the ylide **12** in a standard acid–base reaction. Spontaneous [2,3] sigmatropic rearrangement of **12** would be expected to produce the cyclohexadiene derivative, **13**, which on hydrogen migration and accompanying rearomatization would give **10**. The formation of **6** could be explained in either of two ways. Direct nucleophilic attack of amide anion on the benzylic carbon of **9** would yield **6** directly. An alternate possibility would involve initial removal of the benzylic proton of **9** to yield the ylide **14**. α elimination from **14** would produce **6** and phenyl carbene (**15**)[10] (Scheme III).

(3) Hauser, C. R.; Kantor, S. W.; Brasen, W. R. *J. Am. Chem. Soc.* **1953**, *75*, 2660.
(4) Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1963**, *85*, 3027; **1965**, *87*, 5661, 5670. Burdon, M. G.; Moffatt, J. G. *Ibid.* **1965**, *87*, 4656; **1966**, *88*, 5855; **1967**, *89*, 4725. Pfitzner, K. E.; Marino, J. P.; Olofson, R. A. *Ibid.* **1965**, *87*, 4658. Marino, J. P.; Pfitzner, K. E.; Olofson, R. A. *Tetrahedron* **1971**, *27*, 4181. Olofson, R. A.; Marino, J. P. *Ibid.* **1971**, *27*, 4195. Claus, P. *Monatsh. Chem.* **1971**, *102*, 913. Hayashi, Y.; Oda, R. *J. Org. Chem.* **1967**, *32*, 457. Pettit, G. R.; Brown, T. H. *Can. J. Chem.* **1967**, *45*, 1306. Claus, P. *Monatsh. Chem.* **1968**, *99*, 1034. Claus, P.; Vavra, N.; Schilling, P. *Ibid.* **1971**, *102*, 1072. Doucet, J.; Robert, A. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1971**, *272*, 1562. Claus, P.; Rieder, W. *Tetrahedron Lett.* **1972**, 3879. Gassman, P. G.; Amick, D. R. *Ibid.* **1974**, 3463. Gassman, P. G.; Amick, D. R. *Synth. Commun.* **1975**, *5*, 325. Gassman, P. G.; Amick, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 7611.
(5) Claus, P.; Vycudilik, W. *Monatsh. Chem.* **1970**, *101*, 396. Gassman, P. G.; Huang, C.-T. *J. Chem. Soc., Chem. Commun.* **1974**, 685. Gassman, P. G.; Gruetzmacher, G. D. *J. Am. Chem. Soc.* **1974**, *96*, 5487. Gassman, P. G.; van Bergen, T. J.; Gilbert, D. P.; Cue, B. W., Jr. *Ibid.* **1974**, *96*, 5495. Gassman, P. G.; van Bergen, T. J. *Ibid.* **1974**, *96*, 5508. Gassman, P. G.; Gruetzmacher, G. D., van Bergen, T. J. *Ibid.* **1974**, *96*, 5512. Gassman, P. G.; Gilbert, D. P.; Luh, T.-Y. *J. Org. Chem.* **1977**, *42*, 1340. Gassman, P. G.; Cue, B. W., Jr.; Luh, T.-Y. *Ibid.* **1977**, *42*, 1344. Gassman, P. G.; Parton, R. L. *Tetrahedron Lett.* **1977**, 2055. Gassman, P. G.; Balchunis, R. J. *Ibid.* **1977**, 2235. Gassman, P. G.; Schenk, W. N. *J. Org. Chem.* **1977**, *42*, 3240. Gassman, P. G.; Gilbert, D. P.; Cole, S. M. *Ibid.* **1977**, *42*, 3233. Gassman, P. G.; Parton, R. L. *J. Chem. Soc., Chem. Commun.* **1977**, 694. Gassman, P. G.; Drewes, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 7600.
(6) A 2% conversion for the reaction with X = Se, Y = S, and Z = C has been reported: Detty, M. R. *J. Org. Chem.* **1979**, *44*, 4528.
(7) Gassman, P. G.; Miura, T., submitted for publication.
(8) For a preliminary report of this work see: Gassman, P. G.; Miura, T.; Mossman, A. *J. Chem. Soc., Chem. Commun.* **1980**, 558.
(9) Mayer, R.; Scheithauer, S.; Kunz, D. *Chem. Ber.* **1966**, *99*, 1393. Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204. Entwistle, I. D.; Johnstone, R. A. W.; Varley, J. H. *J. Chem. Soc., Chem. Commun.* **1976**, 61. Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99.

Table II. Products, Yields, and Reaction Conditions for the Preparation of Stable Selenonium Salts

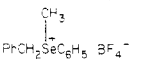
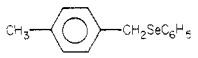
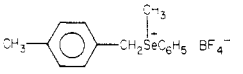
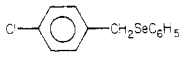
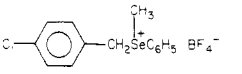
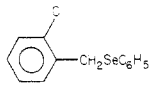
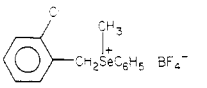
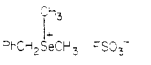
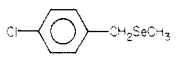
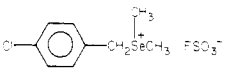
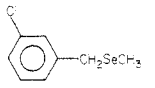
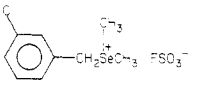
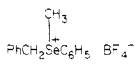
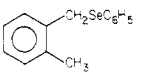
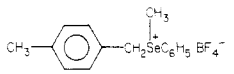
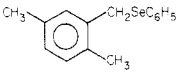
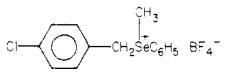
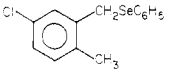
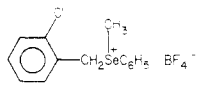
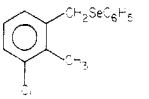
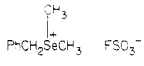
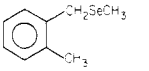
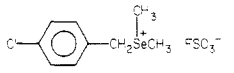
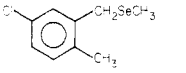
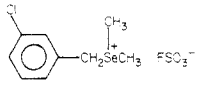
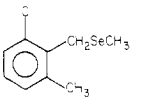
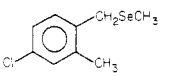
selenide	alkylating agent	reaction temp, °C	product	% yield
$PhCH_2SeC_6H_5$	$(CH_3)_3O^+ BF_4^-$	0		90
	$(CH_3)_3O^+ BF_4^-$	−10		95
	$(CH_3)_3O^+ BF_4^-$	25		92
	$(CH_3)_3O^+ BF_4^-$	0		100
$PhCH_2SeCH_3$	FSO_3CH_3	25		88
	FSO_3CH_3	25		98
	FSO_3CH_3	25		85

Table III. Structures and Yields of [2,3] Sigmatropic Rearrangement Products from the Treatment of Benzylic Selenonium Salts with Sodium Amide in Liquid Ammonia and Byproducts of the Reaction (When Determined)

		% yield		
selenonium salt	rearrangement product	product	6	stilbene[a]
		17	19	22
		38	28	24
		37	16	12
		23	48	28
		43	*b*	*b*
		50	*b*	*b*
		56	*b*	*b*
		14		

[a] The yields of the various *trans*-stilbenes were calculated on the basis of 2 mol of the selenonium salt being required to yield 1 mol of stilbene. [b] Because a different purification procedure was used for these selenides, the yields of dimethyl selenide and the corresponding stilbenes were not determined.

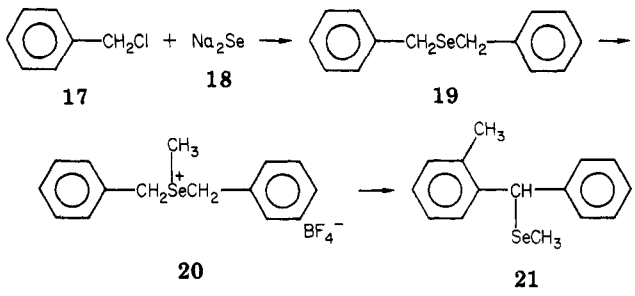
The intermediacy of **15** may be involved in the mechanism of the formation of *trans*-stilbene (**11**). It seems unlikely that **15** would be present in high enough concentration or be long-lived enough under the reaction conditions to form **11** by a simple dimerization process. Instead, we feel it is likely that **15** adds to **14** to form the zwitterion **16**. It would be anticipated that **16** would rapidly lose methyl phenyl selenide to yield **11**. Ample precedent exists for this mechanistic postulate in the work of Swain and Thorton, who demonstrated that benzyldimethylsulfonium salts react with sodium hydroxide to give almost quantitative yields of *trans*-stilbenes.[11] Our mechanism is suggested in analogy to theirs.

Having established the feasibility of the [2,3] sigmatropic rearrangement of ylides derived from benzylic selenonium salts, we investigated the scope of this reaction. In general, the benzylic selenides were prepared by treatment of the

(10) α eliminations to yield carbenoid-type intermediates could also be used to explain the formation of methyl *tert*-butyl ether and benzyl *tert*-butyl ether when potassium *tert*-butoxide was used as a base. We feel this explanation is unlikely because no trace of [2,3] sigmatropic rearrangement product could be found in the reaction of **9** with potassium *tert*-butoxide. In addition, no *trans*-stilbene was observed under these conditions. The significance of this observation is implicit in the mechanism of the formation of the *trans*-stilbene (vide post).

(11) Swain, C. G.; Thorton, E. R. *J. Am. Chem. Soc.* **1961**, *83*, 4033.

Scheme IV



appropriate benzylic chloride with the salt derived from the treatment of a diselenide with sodium borohydride.[9] Table I lists the starting halide, starting diselenide, product, and yields. As can be seen from Table I, the aryl selenoates generally gave better yields than the alkyl selenoates.

With a variety of aryl and alkyl benzyl selenides in hand, two different procedures were used to prepare stable salts. The tetrafluoroborates were prepared by the reaction of the appropriate selenide with trimethyloxonium tetrafluoroborate (Meerwein's reagent) while the fluorosulfonate salts were prepared through the reaction of methyl fluorosulfonate with the the selenides as shown in Table II.

Table III lists the structures and yields of the [2,3] sigmatropic rearrangement products obtained from the treatment of the benzylic selenonium salts with 2 equiv of sodium amide in liquid ammonia. In general, the dimethylselenonium salts gave better yields of [2,3] sigmatropic rearrangement products than did the phenylmethylselenonium salts. It was not apparent whether this difference in yields was due to the greater ease of purification of the products from the dimethylselenonium salts or whether the phenylmethylselenonium salts gave initial ylides which were more prone to follow an α-elimination reaction path.

Of special interest were the results obtained from the (*m*-chlorobenzyl)dimethylselenonium fluorosulfonates. The chlorine appears to direct the attack of the ylide predominantly to the more hindered position ortho to the chlorine. The 4:1 ratio for the ortho to para directing effect clearly indicates the presence of a special directing influence.

The last example studied involved the reaction of benzyl chloride (**17**) with sodium selenide (**18**) to give dibenzyl selenide (**19**) in 60% yield (Scheme IV) according to the literature procedure.[12] Treatment of **19** with trimethyloxonium tetrafluoroborate gave 82% of the selenonium salt **20**. When **20** was allowed to react with 2 equiv of sodium amide in liquid ammonia, we obtained a 68% yield of the diphenylmethane derivative **21**. It seems apparent that the [2,3] sigmatropic rearrangement of benzylic selenonium salts discussed in this paper can be applied to a wide variety of systems.

Experimental Section[13]

Benzyl Phenyl Selenide (3). General Procedure for the Preparation of Benzyl Phenyl Selenides. To a suspension of 9.36 g (30 mmol) of diphenyl diselenide in 75 mL of tetrahydrofuran and 100 mL of water was added slowly 2.70 g of sodium borohydride at 0 °C. To the resulting mixture was added 7.60 g (60 mmol) of benzyl chloride at 25 °C. The reaction mixture was stirred overnight at 25 °C under a nitrogen atmosphere, poured into 50 mL of water, and extracted with three 50-mL portions of ether. The ethereal extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation of the residue gave 12.45 g (83%) of **3**: bp 149–150 °C (2.3 mm) [lit.[9] bp 201 °C (15 mm)]; ^{1}H NMR ($CDCl_3$) δ 4.05 (3 H, s), 7.12–7.55 (10 H, br m).

***p*-Methylbenzyl Phenyl Selenide.** By use of the general procedure outlined above, 11.00 g (60 mmol) of α-bromo-*p*-xylene gave 13.66 g (87%) of the known[9] *p*-methylbenzyl phenyl selenide: bp 149–151 °C (1.4 mm); ^{1}H NMR ($CDCl_3$) δ 2.26 (3 H, s), 4.04 (2 H, s), 7.06 (4 H, br s), 7.10–7.60 (5 H, br m).

***p*-Chlorobenzyl Phenyl Selenide.** By use of the general procedure, 6.44 g (40 mmol) of *p*-chlorobenzyl chloride gave 9.93 g (86%) of the known[9] *p*-chlorobenzyl phenyl selenide: bp 158 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 4.01 (2 H, s), 7.10–7.60 (9 H, br m).

***o*-Chlorobenzyl Phenyl Selenide.** By use fo the general procedure, 9.66 g (60 mmol) of *o*-chlorobenzyl chloride gave 13.27 g (77%) of *o*-chlorobenzyl phenyl selenide: bp 161 °C (1.9 mm); ^{1}H NMR ($CDCl_3$) δ 4.12 (2 H, s), 6.90–7.60 (9 H, br m); exact mass calcd for $C_{13}H_{11}ClSe$ 281.971, found 281.972. This material was further characterized as a stable salt (vide post).

Benzyl Methyl Selenide. General Procedure for the Synthesis of Benzyl Methyl Selenides. Dimethyl diselenide (5.64 g, 30 mmol) was dissolved in a mixture of 30 mL of tetrahydrofuran and 30 mL of water and then 2.66 g (70 mmol) of sodium borohydride was added. The resulting mixture was stirred for 2 h at 25 °C, and 7.60 g (60 mmol) of benzyl chloride was added at 25 °C. The reaction mixture was stirred overnight and then poured into 50 mL of water and extracted with three 25-mL portions of ether. The ethereal extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was fractionally distilled to give 6.27 g (55%) of benzyl methyl selenide:[9] bp 66–68 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.85 (3 H, s), 3.67 (2 H, s), 7.18 (5 H, s).

***p*-Chlorobenzyl Methyl Selenide.** By use of the general procedure 4.54 g (28 mmol) of *p*-chlorobenzyl chloride gave 4.00 g (65%) of *p*-chlorobenzyl methyl selenide: bp 102–103 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 2.20 (3 H, s), 3.94 (2 H, s), 7.33 (4 H, s).

Anal. Calcd for C_8H_9ClSe: C, 43.76; H, 4.13. Found: C, 43.84; H, 4.14.

***m*-Chlorobenzyl Methyl Selenide.** By use of the general procedure, 6.44 g (40 mmol) of *m*-chlorobenzyl chloride gave 3.60 g (41%) of *m*-chlorobenzyl methyl selenide: bp 99 °C (2.3 mm); ^{1}H NMR ($CDCl_3$) δ 1.88 (3 H, s), 3.63 (2 H, s), 7.10–7.30 (4 H, m).

Anal. Calcd for C_8H_9ClSe: C, 43.76; H, 4.13. Found: C, 43.92; H, 4.16.

***p*-Methylbenzyl Methyl Selenide.** By use of the general procedure, 3.70 g (20 mmol) of α-bromo-*p*-xylene gave 2.27 g (57%) of *p*-methylbenzyl methyl selenide:[9] bp 85 °C (1.2 mm); ^{1}H NMR ($CDCl_3$) δ 1.88 (3 H, s), 2.29 (3 H, s), 3.67 (2 H, s), 7.07 (4 H, s).

Benzylmethylphenylselenonium Tetrafluoroborate. To an ice-cooled solution of 4.60 g (31 mmol) of trimethyloxonium tetrafluoroborate[14] in 20 mL of acetonitrile was added dropwise a solution of 7.41 g (30 mmol) of benzyl phenyl selenide in 8 mL of acetonitrile. The resulting mixture was stirred for 1 h, and the solvent was evaporated to give a colorless oil. Addition of ether to the oil followed by cooling in an ice bath gave a white solid which on recrystallization from ethanol yielded 9.46 g (90%) of benzylmethylphenylselenonium tetrafluoroborate: mp 92.5–94.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.02 (3 H, s), 4.88 (2 H, AB q), 7.17 (5 H, br s), 7.51 (5 H, br s).

Anal. Calcd for $C_{14}H_{15}BF_4Se$: C, 48.18; H, 4.33. Found: C, 48.18; H, 4.42.

(*p*-Methylbenzyl)methylphenylselenonium Tetrafluoroborate. To a solution of 3.00 g (21 mmol) of trimethyloxonium tetrafluoroborate[14] in 7 mL of acetonitrile was added slowly a solution of 5.22 g (20 mmol) of *p*-methylbenzyl phenyl selenide in 7 mL of acetonitrile at −10 °C. The reaction mixture was stirred for 0.5 h and the solvent was evaporated to yield a crystalline salt. This solid was recrystallized from acetone–ether to give 6.79 g (95%) of (*p*-methylbenzyl)methylphenylselenonium tetrafluoroborate: mp 101–103 °C; ^{1}H NMR ($CDCl_3$) δ 2.26 (3 H, s), 2.98

(12) Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.
(13) Melting and boiling points are uncorrected. Elemental analyses were obtained from the Scandinavian Microanalytical Laboratories.
(14) Meerwein, H. "Organic Synthesis"; Wiley: New York, 1973; Collect. Vol. V, p 1906.

(3 H, s), 4.86 (2 H, AB q), 6.96 (4 H, s), 7.50 (5 H, br s).

Anal. Calcd for $C_{15}H_{17}BF_4Se$: C, 49.62; H, 4.72. Found: C, 49.59; H, 4.74.

(*p*-Chlorobenzyl)methylphenylselenonium Tetrafluoroborate. To a solution of 3.01 g (21 mmol) of trimethyloxonium tetrafluoroborate[14] in 25 mL of acetonitrile was added dropwise a solution of 5.63 g (20 mmol) of *p*-chlorobenzyl phenyl selenide in 20 mL of acetonitrile at 25 °C. The reaction mixture was stirred for 4 h, and the solvent was evaporated to yield a viscous oil. This oil was dissolved in hot ethanol from which it crystallized to yield 7.13 g (92%) of white, crystalline (*p*-chlorobenzyl)methylphenylselenonium tetrafluoroborate: mp 102.5–104.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.06 (3 H, s), 4.85 (2 H, AB q), 7.06 (4 H, br s), 7.51 (5 H, br s).

Anal. Calcd for $C_{14}H_{14}BClF_4Se$: C, 43.85; H, 3.68. Found: C, 43.63; H, 3.74.

(*o*-Chlorobenzyl)methylphenylselenonium Tetrafluoroborate. To a suspension of 7.40 g (50 mmol) of trimethyloxonium tetrafluoroborate[14] in 25 mL of methylene chloride was added 11.26 g (40 mmol) of *o*-chlorobenzyl phenyl selenide at 0 °C. The reaction mixture was stirred overnight and filtered. Addition of ether to the filtrate gave a white solid, which on recrystallization from ethanol gave 15.23 g (100%) of (*o*-chlorobenzyl)methylphenylselenonium tetrafluoroborate: mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 3.19 (3 H, s), 4.96 (2 H, AB q), 7.18 (4 H, m), 7.48 (5 H, br s).

Anal. Calcd for $C_{14}H_{14}BClF_4Se$: C, 43.85; H, 3.68. Found: C, 43.86; H, 3.67.

Benzyldimethylselenonium Fluorosulfonate. To a solution of 6.27 g (33 mmol) of benzyl methyl selenide in 35 mL of carbon tetrachloride was added dropwise a solution of 4.10 g (36 mmol) of methyl fluorosulfonate in 25 mL of carbon tetrachloride at 25 °C. The reaction mixture was stirred overnight, and the solvent was removed under reduced pressure. The solid residue was recrystallized from methylene chloride–ether to give 8.68 g (88%) of benzyldimethylselenonium fluorosulfonate:[9] mp 90.0–91.5 °C; ^{1}H NMR ($CDCl_3$–CD_3CN) δ 2.58 (6 H, s), 4.59 (2 H, s), 7.40 (5 H, s).

(*p*-Chlorobenzyl)dimethylselenonium Fluorosulfonate. To a solution of 191 mg (0.87 mmol) of *p*-chlorobenzyl methyl selenide in 5 mL of methylene chloride was added slowly 110 mg (0.96 mmol) of methyl fluorosulfonate. The reaction mixture was stirred for 1 h at 25 °C, and the solvent was removed under reduced pressure to give 282 mg (98%) of (*p*-chlorobenzyl)dimethylselenonium fluorosulfonate: mp 121–124 °C. Recrystallization from acetonitrile gave an analytical sample: mp 123.5–125.0 °C; ^{1}H NMR (CF_3CO_2H) δ 2.68 (6 H, s), 4.60 (2 H, s), 7.30 (2 H, d, J = 8.4 Hz), 7.53 (2 H, d, J = 8.4 Hz).

Anal. Calcd for $C_9H_{12}ClFO_3SSe$: C, 32.40; H, 3.62. Found: C, 32.52; H, 3.94.

(*m*-Chlorobenzyl)dimethylselenonium Fluorosulfonate. To a solution of 1.16 g (10.2 mmol) of methyl fluorosulfonate in 10 mL of acetonitrile was added slowly a solution of 2.20 g (10 mmol) of *m*-chlorobenzyl methyl selenide in 10 mL of acetonitrile at 25 °C. The mixture was stirred for 2 h, and the solvent was removed under reduced pressure to give an oil. Treatment of this oil with ethanol–ether resulted in crystallization. Recrystallization from this solvent pair gave 2.85 g (85%) of (*m*-chlorobenzyl)dimethylselenonium fluorosulfonate: mp 130–132 °C; ^{1}H NMR (CF_3CO_2H) δ 2.68 (6 H, s), 4.58 (2 H, s), 7.20–7.60 (4 H, br m).

Anal. Calcd for $C_9H_{12}ClFO_3SSe$: C, 32.40; H, 3.62. Found: C, 32.63; H, 3.94.

Rearrangement of Benzylmethylphenylselenonium Tetrafluoroborate to 2-Methylbenzyl Phenyl Selenide. To a suspension of 297 mg (7.6 mmol) of sodium amide in 20 mL of liquid ammonia at −78 °C was added 1.326 g (3.8 mmol) of benzylmethylphenylselenonium tetrafluoroborate over a 0.5-h period. The resulting mixture was stirred at −78 °C for 1 h, 25 mL of ether was added at −78 °C, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was poured into 25 mL of water and extracted with three 25-mL portions of ether. The ethereal extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give 787 mg of a complex mixture of products which were separated on a 10% SE-30 on 60/80 Chromosorb W column (6 ft) at 185 °C to give 126 mg (19%) of methyl phenyl selenide, 76 mg (22%) of *trans*-stilbene, and 171 mg (17%) of 2-methylbenzyl phenyl selenide:[9] ^{1}H NMR ($CDCl_3$) δ 2.30 (3 H, s), 4.02 (2 H, s), 7.00–7.54 (9 H, br m). The 2-methylbenzyl phenyl selenide was identical in all respects with an authentic sample prepared according to the literature procedure.[9]

Rearrangement of (*p*-Methylbenzyl)methylphenylselenonium Tetrafluoroborate to 2,5-Dimethylbenzyl Phenyl Selenide. To a suspension of 330 mg (8.5 mmol) of sodium amide in 20 mL of liquid ammonia was added 1.430 (4.0 mmol) of (*p*-methylbenzyl)methylphenylselenonium tetrafluoroborate at −78 °C over 0.5 h. The reaction mixture was stirred at −78 °C for 1 h, 25 mL of ether was added, and the mixture was stirred at room temperature until the ammonia had evaporated. The reaction mixture was then poured into water and extracted with two 25-mL portions of ether. The ethereal extracts were dried over anhydrous magnesium sulfate and filtered, and the filtrate was fractionally distilled to give 0.19 g (28%) of methyl phenyl selenide, bp 55 °C (1.2 mm). The pot residue was recrystallized from 60–70 °C petroleum ether to yield 0.10 g (24%) of *trans*-4,4′-dimethylstilbene.[15]

The solvent was removed under reduced pressure from the filtrate of the above-described recrystallization, and the residue was distilled to give 0.40 g (38%) of 2,5-dimethylbenzyl phenyl selenide: bp 158–160 °C (1.5 mm) ^{1}H NMR ($CDCl_3$) δ 2.19 (3 H, s), 2.27 (3 H, s), 4.03 (2 H, s), 6.77–7.60 (8 H, br m).

Anal. Calcd for $C_{15}H_{16}Se$: C, 65.45; H, 5.86. Found: C, 65.88; H, 5.86.

Rearrangement of (*p*-Chlorobenzyl)methylphenylselenonium Tetrafluoroborate to 2-Methyl-5-chlorobenzyl Phenyl Selenide. To a suspension of 0.39 g (10 mmol) of sodium amide in 25 mL of liquid ammonia was added over a 0.5-h period 1.92 g (5 mmol) of (*p*-chlorobenzyl)methylphenylselenonium tetrafluoroborate at −78 °C. The reaction mixture was stirred for 1.5 h at −78 °C, 25 mL of ether was added, and the solution was then stirred at room temperature until the ammonia evaporated. The reaction mixture was poured into 30 mL of water and extracted with three 25-mL portions of ether. The ethereal extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The residue was distilled to give 0.28 g (16%) of methyl phenyl selenide: bp 64–65 °C (2.5 mm). Addition of 5 mL of petroleum ether (bp 60–70 °C) to the pot residue precipitated 0.08 g (12%) of *trans*-4,4′-dichlorostilbene: mp 175–176 °C (lit.[15] mp 176.0–176.5 °C).

The solvent was removed under reduced pressure from the filtrate, and the residue was distilled to give 0.54 g (37%) of 2-methyl-5-chlorobenzyl phenyl selenide: bp 173–175 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 2.23 (3 H, s), 3.93 (2 H, s), 6.80–7.50 (8 H, br m).

Anal. Calcd for $C_{14}H_{13}ClSe$: C, 56.87; H, 4.43. Found: C, 57.03; H, 4.45.

Rearrangement of (*o*-Chlorobenzyl)methylphenylselenonium Tetrafluoroborate to 2-Methyl-3-chlorobenzyl Phenyl Selenide. By use of the general procedure outlined for the *p*-chloro isomer, 1.54 g (4.0 mmol) of (*o*-chlorobenzyl)-methylphenylselenonium tetrafluoroborate was allowed to react with 0.32 g (8.2 mmol) of sodium amide. After the workup, the reaction mixture was distilled to give 0.32 g (48%) of methyl phenyl selenide: bp 53–54 °C (0.6 mm). The pot residue was recrystallized from petroleum ether (bp 60–70 °C) to give 0.14 g (28%) of 2,2′-dichlorostilbene, mp 96–97 °C (lit.[15] mp 98.5–99.0 °C).

Concentration of the filtrate and molecular distillation of the residue gave 0.26 g (23%) of 2-methyl-3-chlorobenzyl phenyl selenide: ^{1}H NMR ($CDCl_3$) δ 2.36 (3 H, s), 4.09 (2 H, s), 6.80–7.60 (8 H, br m).

Anal. Calcd for $C_{14}H_{13}ClSe$: C, 56.87; H, 4.43. Found: C, 57.59; H, 4.41.

Rearrangement of Benzyldimethylselenonium Fluorosulfonate to 2-Methylbenzyl Methyl Selenide. To a stirred suspension of 314 mg (8.0 mmol) of sodium amide in 30 mL of liquid ammonia was added slowly 1.992 g (6.7 mmol) of ben-

(15) Hoeg, D. F.; Lusk, D. I. *J. Organomet. Chem.* **1966**, *5*, 1.

zyldimethylselenonium fluorosulfonate at −78 °C over a 30-min period. The reaction mixture was stirred for 1 h at −78 °C, 20 mL of ether was added, and the mixture was allowed to warm to room temperature. When the ammonia had evaporated, 30 mL of water was added, the organic layer was separated, and the aqueous phase was extracted with two 20-mL portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give 894 mg of crude product. Distillation of the material yielded 558 mg (43%) of pure 2-methylbenzyl methyl selenide: bp 82–83 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.90 (3 H, s), 2.33 (3 H, s), 3.71 (2 H, s), 7.09 (4 H, br s).

Anal. Calcd for $C_9H_{12}Se$: C, 54.28; H, 6.07. Found: C, 54.33; H, 6.04.

Rearrangement of (*p*-Chlorobenzyl)dimethylselenonium Fluorosulfonate to 2-Methyl-5-chlorobenzyl Methyl Selenide. By use of the procedure described above, 0.30 g (8 mmol) of sodium amide was allowed to react with 1.34 g (4 mmol) of (*p*-chlorobenzyl)dimethylselenonium fluorosulfonate. Distillation of the product gave 0.47 g (50%) of 2-methyl-5-chlorobenzyl methyl selenide: bp 111–114 °C (13 mm): ^{1}H NMR ($CDCl_3$) δ 1.94 (3 H, s), 2.32 (3 H, s), 3.67 (2 H, s), 7.10 (3 H, br s).

Anal. Calcd for $C_9H_{11}ClSe$: C, 46.28; H, 4.75. Found: C, 46.34; H, 4.72.

Rearrangement of (*m*-Chlorobenzyl)dimethylselenonium Fluorosulfonate to 2-Methyl-6-chlorobenzyl Methyl Selenide and 2-Methyl-4-chlorobenzyl Methyl Selenide. By use of the procedure outlined above, 0.30 g (8 mmol) of sodium amide was allowed to react with 1.32 g (4 mmol) of (*m*-chlorobenzyl)dimethylselenonium fluorosulfonate. Distillation of the crude product gave 0.66 g (70%) of a 4:1 mixture of 2-methyl-6-chlorobenzyl methyl selenide and 2-methyl-4-chlorobenzyl methyl selenide, respectively; bp 107–115 °C (0.8 mm). The ratio of the major to minor products was determined by both NMR and GC analysis. The two products were separated by preparative GC on a 10% SE-30 on Chromosorb W column.

The major product was 2-methyl-6-chlorobenzyl methyl selenide (56%). Its IR spectrum showed the typical pattern for a 1,2,3-trisubstituted benzene in the 1660–2000-cm^{-1} region: ^{1}H NMR ($CDCl_3$) δ 2.03 (3 H, s), 2.41 (3 H, s), 3.97 (2 H, s), 6.95–7.30 (3 H, br m).

Anal. Calcd for $C_9H_{11}ClSe$: C, 46.28; H, 4.75. Found: C, 46.30; H, 4.81.

The minor product was 2-methyl-4-chlorobenzyl methyl selenide (14%). Its IR spectrum showed the typical pattern for a 1,2,4-trisubstituted benzene in the 1660–2000-cm^{-1} region: ^{1}H NMR ($CDCl_3$) δ 1.90 (3 H, s), 2.32 (3 H, s), 3.67 (2 H, s), 7.05–7.30 (3 H, br m).

Anal. Calcd for $C_9H_{11}ClSe$: C, 46.28; H, 4.75. Found: C, 46.17; H, 4.76.

Dibenzyl Selenide (19). Dibenzyl selenide was prepared from benzyl chloride and sodium selenide according to the literature procedure:[12] 60% yield; mp 42–44 °C (lit.[12] mp 44–45 °C).

Dibenzylmethylselenonium Tetrafluoroborate (20). To a suspension of 7.40 g (50 mmol) of trimethyloxonium tetrafluoroborate in 50 mL of methylene chloride was added dropwise a solution of 11.79 g (45 mmol) of **19** in 25 mL of methylene chloride at 0 °C. The mixture was stirred at 25 °C overnight. The solvent was removed under vacuum, and 50 mL of ether was added. This resulted in the formation of a white precipitate which was collected by filtration and recrystallized to give 13.38 g (82%) of **20**: mp 113.5–115.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.43 (3 H, s), 4.65 (4 H, AB q), 7.39 (10 H, s).

Anal. Calcd for $C_{15}H_{17}BF_4Se$: C, 49.62; H, 4.72. Found: C, 49.51; H, 4.68.

Rearrangement of 20 to 2-Methylbenzhydryl Methyl Selenide (21). To a suspension of 0.31 g (8 mmol) of sodium amide in 20 mL of liquid ammonia was added 1.45 g (4 mmol) of **20** over a 30-min period at −78 °C. The resulting mixture was stirred for 2 h at −78 °C, 25 mL of ether was added, and the mixture was allowed to warm to 25 °C. After the ammonia had evaporated, the reaction mixture was poured into 25 mL of water and extracted with two 25-mL portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure to give 1.10 g of crude product. Distillation gave 0.73 g (68%) of 2-methylbenzhydryl methyl selenide (**21**): bp 158–159 °C (1.0 mm); ^{1}H NMR ($CDCl_3$) δ 1.84 (3 H, s), 2.31 (3 H, s), 5.49 (1 H, s), 7.00–7.70 (9 H, br m).

Anal. Calcd for $C_{15}H_{16}Se$: C, 65.45; H, 5.86. Found: C, 65.36; H, 5.85.

Acknowledgment. We are indebted to the Institute of General Medical Sciences of the National Institutes of Health for Grant GM-22346, which supported this investigation, and to Mr. T. Guggenheim for aid in the preparation of *p*-chlorobenzyl methyl selenide.

Registry No. **3**, 18255-05-5; **6**, 4346-64-9; **9**, 75772-14-4; **10**, 18255-12-4; **11**, 103-30-0; **17**, 100-44-7; **19**, 1842-38-2; **20**, 80447-77-4; **21**, 80447-78-5; diphenyl diselenide, 1666-13-3; α-bromo-*p*-xylene, 104-81-4; *p*-methylbenzyl phenyl selenide, 18255-06-6; *p*-chlorobenzyl chloride, 104-83-6; *p*-chlorobenzyl phenyl selenide, 59305-51-0; *o*-chlorobenzyl chloride, 611-19-8; *o*-chlorobenzyl phenyl selenide, 78808-27-2; dimethyl diselenide, 7101-31-7; benzyl methyl selenide, 5925-78-0; *p*-chlorobenzyl methyl selenide, 75772-21-3; *m*-chlorobenzyl chloride, 620-20-2; *m*-chlorobenzyl methyl selenide, 80447-79-6; *p*-methylbenzyl methyl selenide, 80447-80-9; (*p*-methylbenzyl)methylphenylselenonium BF_4^-, 80447-82-1; (*p*-chlorobenzyl)methylphenylselenonium BF_4^-, 75772-16-6; (*o*-chlorobenzyl)methylphenylselenonium BF_4^-, 80447-84-3; benzyldimethylselenonium FSO_3^-, 75772-19-9; (*p*-chlorobenzyl)dimethylselenonium FSO_3^-, 75772-23-5; (*m*-chlorobenzyl)dimethylselenonium FSO_3^-, 80447-86-5; *trans*-4,4′-dimethylstilbene, 18869-29-9; 2,5-dimethylbenzyl phenyl selenide, 80447-87-6; *trans*-4,4′-dichlorostilbene, 1657-56-3; 2-methyl-5-chlorobenzyl phenyl selenide, 75772-17-7; *trans*,2,2′-dichlorostilbene, 25144-38-1; 2-methyl-3-chlorobenzyl phenyl selenide, 80447-88-7; 2-methylbenzyl methyl selenide, 75772-20-2; 2-methyl-5-chlorobenzyl methyl selenide, 75772-18-8; 2-methyl-6-chlorobenzyl methyl selenide, 80447-89-8; 2-methyl-4-chlorobenzyl methyl selenide, 80447-90-1.