Direct Selenation of Electron-Rich Aromatic Compounds with (Phenylseleno)dimethylsulfonium Tetrafluoroborate

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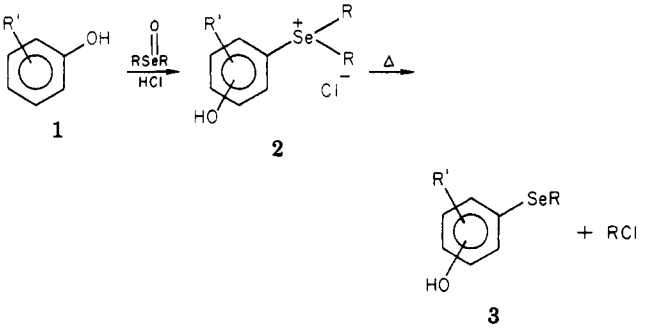
(Phenylseleno)dimethylsulfonium tetrafluoroborate was found to be a highly reactive selenating agent for electron-rich aromatic compounds such as aromatic amines, phenols, and aromatic ethers. Reaction took place readily at 0–25 °C to give ca. 50% yields of substitution para to the activating substituent. In general, anilines gave better yields than anisoles or phenols.

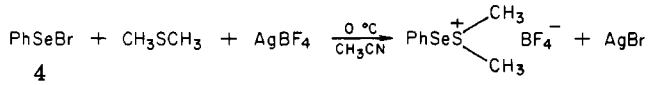
As part of our general studies of [2,3] sigmatropic rearrangements in the selective ortho substitution of aromatic systems,[1-3] we became interested in the properties of (arylseleno)dimethylsulfonium salts. In particular, we were concerned with the possibility of generating an ylide, which would then undergo a [2,3] sigmatropic rearrangement to yield an ortho-disubstituted aromatic.[4] In the course of this investigation, we found that (arylseleno)-dimethylsulfonium tetrafluoroborates were powerful electrophiles, which reacted with certain electron-rich aromatic compounds at 0 °C. This paper describes our findings on the arylselenation of aromatic amines, phenols, and ethers.

Of the many methods available for the selenation of an aromatic ring, most involve either the reaction of an organometallic reagent with an appropriate selenium derivative[5,6] or nucleophilic aromatic substitution.[7-12] In terms of electrophilic aromatic substitution, arylselenenyl halides have been used for the substitution of both anilines[15] and phenols,[16] as have been arylselenenyl thiocyanates.[16] Among the more general methods for selenation of phenols was that of Sonoda and co-workers, who developed a two-step process involving conversion of **1** into **2** followed by thermal decomposition of **2** to **3**.[17]



1 **2** **3**

We have found (phenylseleno)dimethylsulfonium tetrafluoroborate (**5**) to be an extremely reactive reagent for



4 **5**

selenation of electron-rich aromatic compounds. This reagent was prepared in 92% yield by the reaction of phenylselenenyl bromide (**4**)[18] with dimethyl sulfide in the presence of silver tetrafluoroborate. The ^1H NMR spectrum of **5** showed a six-proton singlet at δ 2.92 and a five-proton multiplet at δ 7.5–8.0. This salt stored well at 0 °C, but above room temperature it slowly decomposed.

In general, slightly different procedures were used for the anilines and anisoles (or phenols); the aromatic amines were run at 0 °C for 1 h while the anisoles and phenols were run at 25 °C for periods of 6–9 days. Table I lists the starting materials, reaction conditions, products, and yields for a series of compounds. A major byproduct of each of these reactions was diphenyl diselenide. As shown in Table I, unsubstituted, ortho-substituted, and meta-substituted anilines reacted very similarly and gave exclusive substitution para to the activating amino function. In contrast, para-substituted anilines gave only trace amounts of arylselenation product, and in these cases, the selenation occurred ortho to the amino group. With the anisidines, the amino moiety was the controlling function.

The phenols and anisole required more vigorous conditions than the anilines, and in general the yields were lower. In addition, while the oxygen-containing group was activating, it was less directing than the amino function. As shown in Table I, both phenols and anisole underwent

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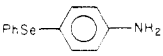
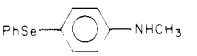
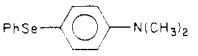
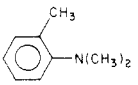
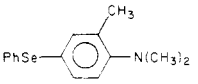
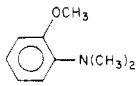
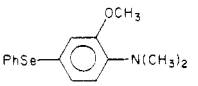
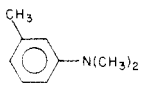
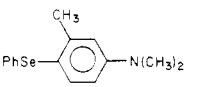
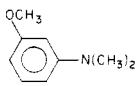
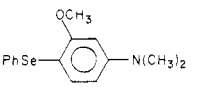
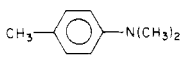
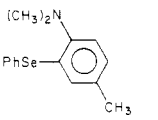
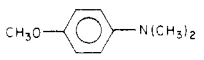
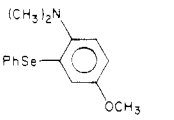
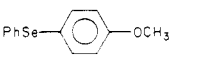
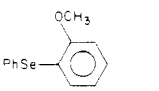
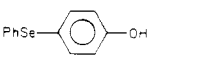
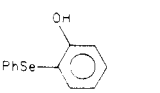
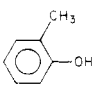
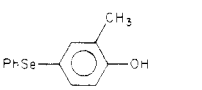
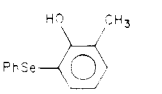
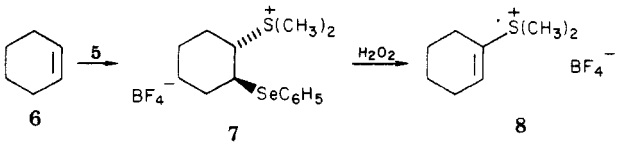
Table I. Products from the Reaction of (Phenylseleno)dimethylsulfonium Tetrafluoroborates with Electron-Rich Aromatic Compounds in Acetonitrile

starting material	reaction temp, time	product	% yield: product	% yield: diphenyl diselenide
$PhNH_2$	0 °C, 1 h		33	25
$PhNHCH_3$	0 °C, 1 h		58	11
$PhN(CH_3)_2$	25 °C, 1 h		54	*a*
	0 °C, 1 h		49	21
	0 °C, 1 h		48	18
	0 °C, 1 h		56	19
	0 °C, 1 h		49	23
	0 °C, 1 h		2	85
	0 °C, 1 h		6	83
$PhOCH_3$	25 °C, 7 days		34	54
			5	
PhOH	25 °C, 6 days		46	33
			4	
	25 °C, 9 days		16	61
			2	

[a] The yield of diselenide was not determined in this reaction.

both ortho and para phenylselenation.

In summary, we have shown that **5** is an efficient reagent for the selenation of electron-rich aromatic rings.[18] As might be expected from the observed electrophilicity of **5**, the presence of any electron-rich aliphatic unsaturation is incompatible with the selenation. For example, **5** readily adds to cyclohexene (**6**) to give **7** in high yield.[19] Treatment of **7** with hydrogen peroxide then produced **8**.[19]



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(19) Gassman, P. G.; Miura, T.; unpublished results.

Experimental Section[20]

(Phenylseleno)dimethylsulfonium Tetrafluoroborate (5). To an ice-cooled solution of 0.70 g (11.3 mmol) of dimethyl sulfide and 1.95 g (10.0 mmol) of silver tetrafluoroborate in 30 mL of acetonitrile was added a solution of phenylselenenyl bromide which had been prepared in situ from 1.56 g (5.0 mmol) of diphenyl diselenide and 0.80 g (5.0 mmol) of bromine in 20 mL of methylene chloride. The resulting mixture was stirred for 15 min at 0 °C. The reaction mixture was filtered, the filtrate was concentrated under reduced pressure, and the residue was washed twice with 60-mL portions of dry ether to yield a pale yellow oil. Upon being dried in vacuo, the oil crystallized to give 2.81 g (9.2 mmol, 92%) of **5**: mp 81–83 °C; ^1H NMR (CD_3CN) δ 2.92 (6 H, s), 7.5–8.0 (5

(20) Melting points and boiling points are uncorrected. Microanalyses were performed by the Scandinavian Microanalytical Laboratory.

H, m); IR (KBr) 3040, 2995, 2980, 1570, 1470, 1435, 1420, 1315, 1300, 1120–1020, 970, 735, 680 cm^{-1}.

N,N-Dimethylaniline Derivatives. *N,N*-Dimethylaniline and *N,N*-dimethyl-*p*-toluidine were obtained commercially. All of the other *N,N*-dimethylaniline derivatives studied were prepared by methylation of the appropriate aniline with trimethyl phosphate according to the literature procedure.[21]

General Procedure for the Selenation of Aniline Derivatives with (Phenylseleno)dimethylsulfonium Tetrafluoroborate. To an ice-cooled solution of 6.0 mmol of an aniline derivative in 10 mL of acetonitrile was added a solution of 5.0 mmol of **5** in 6 mL of acetonitrile. The mixture was stirred at 0 °C for 1 h and then poured into 30 mL of saturated sodium bicarbonate solution. The solution was extracted with two 30-mL portions of ether, and the combined extracts were washed with two 30-mL portions of water and dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated to give a residue which was distilled and/or chromatographed on 25–30 g of silica gel with ether–hexane as the eluent.

4-Aminophenyl Phenyl Selenide. By use of the general procedure described above, 1.40 g of aniline was allowed to react with 1.83 g of **5**. After the workup, the residue was partially distilled to give 0.71 g of aniline, bp 51 °C (2.1 mm). The distillation residue was poured into 150 mL of 2 N hydrochloric acid and extracted with two 30-mL portions of ether. This organic phase was dried and concentrated, and the residue was chromatographed to give 0.24 g (25%) of diphenyl diselenide, mp 62 °C.

The aqueous phase was neutralized with sodium carbonate and extracted with two 50-mL portions of ether. The extract was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated to give a dark brown solid. The solid was purified by chromatography to afford 0.50 g (33%) of 4-aminophenyl phenyl selenide, mp 92–93 °C (lit.[22] mp 93–94 °C).

4-(Methylamino)phenyl Phenyl Selenide. By use of the general procedure, 0.46 g of *N*-methylaniline and 1.11 g of **5** were allowed to react. After the workup, the residue was chromatographed to give 0.06 g (11%) of diphenyl diselenide (mp 61 °C), and 0.75 g (81%) of 4-(methylamino)phenyl phenyl selenide. Molecular distillation [bath temperature 120 °C (1.0 mm)] gave 0.55 g (58%) of 4-(methylamino)phenyl phenyl selenide which crystallized on cooling: mp 41.0–41.5 °C; ^1H NMR ($CDCl_3$) δ 2.80 (3 H, s), 3.80 (1 h, br s), 6.68 (2 H, d, J = 9 Hz)8 7.35 (5 H, m), 7.57 (2 H, d, J = 9 Hz); IR (KBr) 3410, 1593, 1573, 1500, 1470, 1317, 1290, 1263, 1180, 1016, 810, 732, 682 cm^{-1}; exact mass calcd for $C_{13}H_{13}NSe$ 263.020, found 263.020.

Anal. Calcd for $C_{13}H_{13}NSe$: C, 59.55; H, 5.00. Found: C, 59.35; H, 4.68.

4-(Dimethylamino)phenyl Phenyl Selenide. By use of the general procedure, 1.17 g of *N,N*-dimethylaniline was allowed to react with 2.96 g of **5**. After a chromatographic workup, the reaction gave 1.45 g (54%) of the known[16] 4-(dimethylamino)-phenyl phenyl selenide: mp 67–68 °C (lit.[16] mp 67–68 °C); ^1H NMR ($CDCl_3$) δ 2.29 (6 H, s), 6.67 (2 H, d, J = 8.4 Hz), 7.22 (5 H, m), 7.50 (2 H, d, J = 8.4 Hz).

3-Methyl-4-(dimethylamino)phenyl Phenyl Selenide. By use of the general procedure, 0.60 g of *N,N*-dimethyl-*o*-toluidine was allowed to react with 1.12 g of **5**. After the workup, chromatography gave 0.12 g (21%) of diphenyl diselenide and a mixture of *N,N*-dimethyl-*o*-toluidine and the selenation product. Vacuum distillation gave 0.07 g of *N,N*-dimethyl-*o*-toluidine. The residue was molecularly distilled [bath temperature 135 °C (20 mm)] to give 0.53 g (49%) of 3-methyl-4-(dimethylamino)phenyl phenyl selenide: ^1H NMR ($CDCl_3$) δ 2.24 (3 H, s), 2.63 (6 H, s), 6.88 (1 H, d, J = 9 Hz), 7.05–7.50 (7 H, complex m); IR (neat) 3050, 2930, 2820, 2770, 1577, 1473, 1435, 1310, 1150, 1110, 938, 810, 724, 680 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NSe$: C, 62.07; H, 5.90. Found: C, 62.09; H, 5.93.

3-Methoxy-4-(dimethylamino)phenyl Phenyl Selenide. By use of the general procedure, 0.83 g of *N,N*-dimethyl-*o*-anisidine was allowed to react with 1.40 g of **5**. After the workup, chromatography gave 0.13 g (18%) of diphenyl diselenide and a mixture of *N,N*-dimethyl-*o*-anisidine and the desired product. The *N,N*-dimethyl-*o*-anisidine (0.22 g) was removed by fractional distillation, and the residue was molecularly distilled [bath temperature 140 °C (1.9 mm)] to yield 0.68 g (48%) of 3-methoxy-4-(dimethylamino)phenyl phenyl selenide: ^1H NMR ($CDCl_3$) δ 2.76 (6 H, s), 3.79 (3 H, s), 6.72 (1 H, d, J = 8.4 Hz), 6.90–7.40 (7 H, complex m); IR (neat) 3042, 2930, 2820, 2770, 1575, 1490, 1430, 1385, 1320, 1225, 1115, 1015, 935, 840, 800, 725, 680 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NOSe$: C, 58.83; H, 5.59. Found: C, 58.82; H, 5.60.

2-Methyl-4-(dimethylamino)phenyl Phenyl Selenide. According to the general procedure, 0.83 g of *N,N*-dimethyl-*m*-toluidine was allowed to react with 1.56 g of **5**. The workup, as described for the ortho isomer, gave 0.15 g (19%) of diphenyl diselenide, 0.11 g of *N,N*-dimethyl-*m*-toluidine, and, after molecular distillation [bath temperature 135 °C (0.1 mm)], 0.83 g (56%) of 2-methyl-4-(dimethylamino)phenyl phenyl selenide: mp 36–38 °C; ^1H NMR ($CDCl_3$) δ 2.37 (3 H, s), 2.94 (6 H, s), 6.50 (1 H, dd, J = 3.0, 8.4 Hz), 6.64 (1 H, d, J = 3 Hz), 7.13 (5 H, br s), 7.49 (1 H, d, J = 8.4 Hz); IR (KBr) 1590, 1490, 1470, 1353, 1270, 1227, 1202, 1155, 1060, 1016, 830, 790, 727, 680 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NSe$: C, 62.07; H, 5.90. Found: C, 62.11; H, 5.98.

2-Methoxy-4-(dimethylamino)phenyl Phenyl Selenide. By use of the general procedure, 0.92 g of *N,N*-dimethyl-*m*-anisidine was allowed to react with 1.56 g of **5**. After the workup, chromatography gave 0.18 g (23%) of diphenyl diselenide, 0.33 g of *N,N*-dimethyl-*m*-anisidine, and 0.86 g (55%) of 2-methoxy-4-(dimethylamino)phenyl phenyl selenide, mp 75–77 °C. Recrystallization of this sample from ether–hexane gave product: 0.75 g (49%); mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 2.91 (6 H, s), 3.76 (3 H, s), 6.26 (2 H, m), 7.18 (6 H, m); IR (KBr) 1590, 1548, 1502, 1470, 1435, 1360, 1267, 1240, 1163, 1060, 1045, 1010, 970, 803, 768, 732, 682 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NOSe$: C, 58.83; H, 5.59. Found: C, 58.85; H, 5.58.

2-(Dimethylamino)-5-methylphenyl Phenyl Selenide. By use of the general procedure, 0.77 g of *N,N*-dimethyl-*p*-toluidine was allowed to react with 1.47 g of **5**. After the workup, chromatography gave 0.64 g (85%) of diphenyl diselenide and a mixture of *N,N*-dimethyl-*p*-toluidine and the desired selenation product. Fractional distillation gave 0.30 g of the starting amine. The residue was purified by thick-layer chromatography to give 0.04 g (2%) of 2-(dimethylamino)-5-methylphenyl phenyl selenide: ^1H NMR ($CDCl_3$) δ 2.11 (3 H, s), 2.71 (6 H, s), 6.6–7.8 (8 H, complex m); IR (neat) 3050, 2970, 2930, 2850, 2820, 2775, 1480, 1445, 1432, 1300, 1155, 1040, 1015, 935, 865, 845, 810, 730, 680 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NSe$: C, 62.07; H, 5.90. Found: C, 61.83; H, 5,83.

2-(Dimethylamino)-5-methoxyphenyl Phenyl Selenide. By use of the general procedure, 0.86 g of *N,N*-dimethyl-*p*-anisidine was allowed to react with 1.45 g of **5**. After the workup, chromatography gave 0.62 g (83%) of diphenyl diselenide, 0.47 g of starting amine, and 0.13 g (8%) of the selenation product. Molecular distillation of the desired product [bath temperature 110 °C (1.9 mm)] gave 0.10 g (6%) of pure 2-(dimethylamino)-5-methoxyphenyl phenyl selenide: ^1H NMR ($CDCl_3$) δ 2.68 (6 H, s), 3.51 (3 H, s), 6.26 (1 H, d, J = 2.4 Hz), 6.58 (1 H, dd, J = 2.4, 8.4 Hz), 7.01 (1 H, d, J = 8.4 Hz), 7.10–7.80 (5 H, complex m); IR (neat) 3040, 2925, 2815, 2765, 1585, 1470, 1275, 1218, 1173, 1150, 1030, 930, 840, 795, 730, 680 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NOSe$: C, 58.83; H, 5.59. Found: C, 58.97; H, 5.61.

2-Methoxyphenyl Phenyl Selenide and 4-Methoxyphenyl Phenyl Selenide. A solution of 2.70 g of anisole and 2.75 g of **5** in 15 mL of acetonitrile was stirred at 25 °C for 7 days. The solvent was removed under reduced pressure, and the residue was chromatographed on 50 g of silica gel to give 0.76 g (54%) of diphenyl diselenide and 0.92 g of a 1:7 mixture of 2-methoxyphenyl phenyl selenide (5% yield) and 4-methoxyyphenyl phenyl selenide (34% yield). Yields were obtained by VPC, and the structures

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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.

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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

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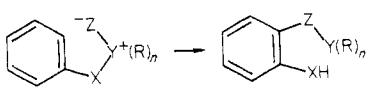
The [2,3] sigmatropic rearrangement of a series of ylides derived from benzylic selenonium salts has been observed. These ylides yield alkyl or aryl *o*-methylbenzyl selenides. The competition between nucleophilic displacement and ylide formation in the reaction of base with benzylic selenonium salts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

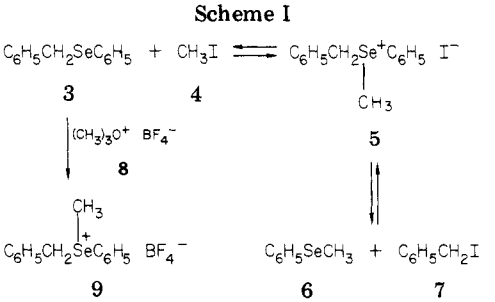
Consideration of the general concept of [2,3] sigmatropic rearrangements for the exclusive ortho substitution of certain aromatic molecules leads one to an analysis of the various possibilities for X, Y, and Z in 1. The first ex-



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

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