

7380-81-6; 15 (Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 61587-08-4; 15 (Ar = *p*-H<sub>3</sub>COC<sub>6</sub>H<sub>4</sub>), 61587-09-5; 15 (Ar = *p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 61587-10-8; 16, 61587-11-9; 17, 61587-13-1; 18, 5633-34-1; 19, 24104-87-8; diethyl disulfide, 110-81-6; 1,2-dithiane, 505-20-4; bis(*p*-methylphenyl) disulfide, 103-19-5; bis(*p*-methoxyphenyl) disulfide, 5335-87-5; bis(*p*-nitrophenyl) disulfide, 100-32-3.

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## Selenium Stabilized Anions. Selenoxide Syn Elimination and Sila-Pummerer Rearrangement of $\alpha$ -Silyl Selenoxides

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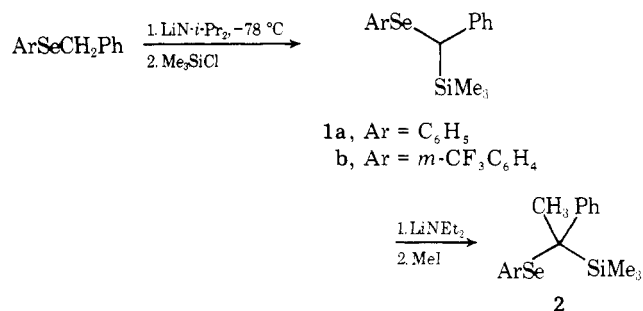
Received August 14, 1975

Several  $\alpha$ -silyl selenides (**2**, **10**) have been prepared by silylation of  $\alpha$ -lithio selenides and alkylation of  $\alpha$ -lithio- $\alpha$ -silyl selenides. Oxidation of these selenides to selenoxides results in competitive selenoxide syn elimination to give vinyl silanes (**4**) and sila-Pummerer rearrangement to give vinyl selenides (**8**) and carbonyl compounds. The ratio can be controlled to some extent by control of reaction conditions, but a more pronounced change (favoring syn elimination) can be achieved by making the arylseleno group more electron withdrawing (*m*-trifluoromethylphenylseleno instead of phenylseleno). These *m*-trifluoromethylphenyl selenides are also deprotonated substantially more rapidly to give  $\alpha$ -lithio selenides than are phenyl selenides. Silaalkene could not be produced by selenoxide syn elimination. The sila-Pummerer rearrangement has been used to prepare  $\alpha$ -silyl ketones.

Functionalized organolithium reagents, in which  $\alpha$ -heteroatom substituents serve both to facilitate preparation of the anion by acidifying  $\alpha$  hydrogens and to mediate subsequent transformations of products derived from the anion, have become important tools for the synthetic organic chemist. As part of our study of selenium stabilized anions,<sup>2</sup> we have developed methods for the generation of several silyl substituted  $\alpha$ -lithio selenides, and explored potentially useful synthetic transformations of products derived from them. Of particular interest is the possibility of forming silaalkenes by selenoxide syn elimination,<sup>3</sup> giving vinyl silanes, and sila-Pummerer rearrangement,<sup>4</sup> giving carbonyl compounds after hydrolysis.

The thermolysis of  $\alpha$ -silyl sulfoxides gives only sila-Pummerer products. It was our feeling that the lower activation energy for selenoxide syn elimination<sup>3a</sup> as compared to sulfide elimination might enable the elimination pathway to compete favorably with the sila-Pummerer reaction in the selenium system.

We chose selenide **2** for our study. Benzyl phenyl selenide<sup>5</sup> was silylated<sup>2a</sup> to give **1a**, which was in turn deprotonated and methylated to give **2a**. Oxidation of **2a** to the selenoxide **3a** was



carried out using *m*-chloroperbenzoic acid. Decomposition of **3a** occurred with a half-life of ca. 30 min at 0 °C (observed by low-temperature NMR), and gave varying mixtures of products resulting from selenoxide syn elimination (path a) and sila-Pummerer rearrangement (path b), presumably via the ylide **5**.

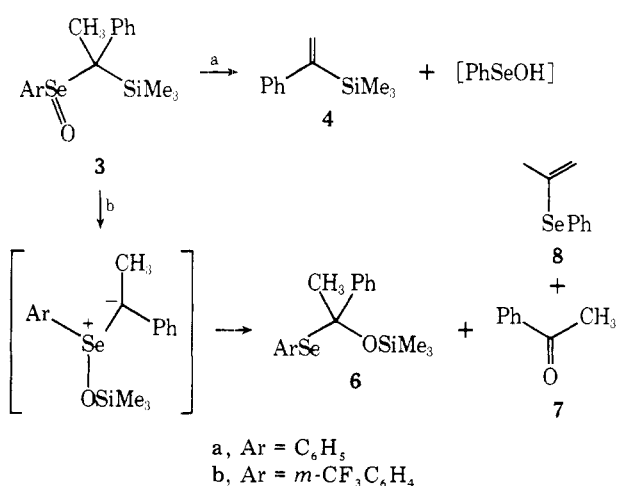
The data in Table I show that significant amounts of both path a and path b occur under all conditions tried. The ratio does not respond in a predictable way to changes in reaction conditions such as solvent polarity, temperature, or pH. The partitioning of intermediate **5** to acetophenone (**6** and **7**) and

Table I. Products from Decomposition of Selenoxide 3

Starting material	Reaction conditions	Products, %			Path a/b
		4	6 + 7	8	
3a	CCl <sub>4</sub> , <sup>a</sup> 80 °C	64	6	6	83/17
3a	CCl <sub>4</sub> , <sup>a,b</sup> 80 °C	55	7	7	80/20
3a	C <sub>2</sub> Cl <sub>4</sub> , <sup>b</sup> 100 °C	55	10	10	63/27
3a	THF, <sup>b</sup> 25 °C	30	22	24	39/61
3a	MeOH, <sup>a,b</sup> 40 °C	51	8	12	72/28
3a	Acetone, <sup>a,b</sup> 56 °C	49	20	17	57/43
3b	CCl <sub>4</sub> , <sup>a</sup> 80 °C	66	<3	<3	>92/8
3b	THF, <sup>b</sup> 25 °C	58	11	<2	>82/18

<sup>a</sup> The cold solution of 3 was added to refluxing solvent. <sup>b</sup> Reaction mixture was buffered (HN-*i*-Pr<sub>2</sub>) during selenoxide decomposition.

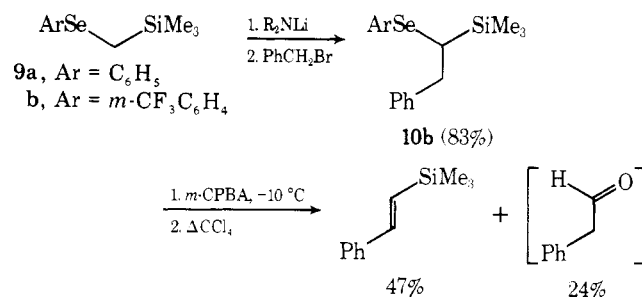
vinyl selenide (8) was also rather insensitive to reaction conditions.



The predominance of path a for selenoxides and path b for sulfoxides can reasonably be ascribed to the fact that the C–Se or C–S bond is breaking during syn elimination, whereas formation of 5 (assuming this to be the rate-determining step) does not involve cleavage of bonds to Se or S. The presence of weaker  $\sigma$  bonds in selenium thus results in greater increase in the rate of path a than path b on going from sulfur to selenium.

It is known that electron-withdrawing substituents accelerate syn elimination of both selenoxides<sup>6</sup> and sulfoxides.<sup>7</sup> One can conclude from the observations of Vedejs and Mullins<sup>4c</sup> that electron withdrawal slows the rate of the sila-Pummerer reaction, since it is faster for alkyl than for aryl sulfoxides. Electron-withdrawing substituents should thus increase the proportion of vinyl silane (path a) in the product. This prediction was tested using the *m*-trifluoromethyl substituted selenide 2b, which was oxidized and pyrolyzed. A substantial decrease in the proportion of sila-Pummerer reaction is observed (last two entries, Table I).

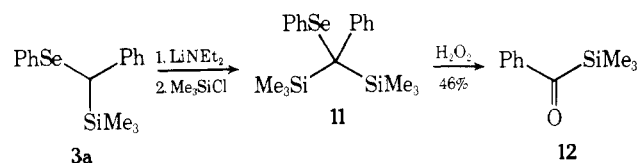
The *m*-CF<sub>3</sub> group also has pronounced effects on the ease of deprotonation of the precursor selenides 1. While 1a is deprotonated slowly by LiNEt<sub>2</sub> in THF at 0 °C, 1b reacts rapidly at –78 °C. Thus a number of phenyl selenides which are not deprotonated readily using amide bases<sup>2a,8</sup> can be deprotonated in the trifluoromethyl series. For example, trimethylsilylphenylselenomethane (9a) is deprotonated in moderate yield by *sec*-BuLi–TMEDA in hexane at 25 °C, but is unaffected by lithium diisopropylamide (LDA). The *m*-CF<sub>3</sub> substituted selenide 9b is deprotonated by LDA even at –78 °C, but more rapidly and cleanly at –40 °C by lithium 2,2,6,6-tetramethylpiperide<sup>9</sup> in THF. Similarly, the *m*-tri-



fluoromethylphenyl methyl, vinyl, and methoxymethyl selenides are deprotonated using amide bases, whereas the unsubstituted phenyl derivatives are not sufficiently acidic for complete deprotonation to occur.<sup>10</sup> Pronounced substituent effects on rates of deprotonation of sulfides have been observed by Shatenshtein (phenyl methyl sulfide undergoes base-catalyzed deuterium exchange 1500 times as fast as cyclohexyl methyl sulfide).<sup>11a</sup> Large differences in equilibrium acidities measured in dimethyl sulfoxide have been observed for PhSO<sub>2</sub>CH<sub>2</sub>X: X = CH<sub>3</sub>S, pK<sub>a</sub> = 23.4; X = PhS, pK<sub>a</sub> = 20.5.<sup>11b</sup>

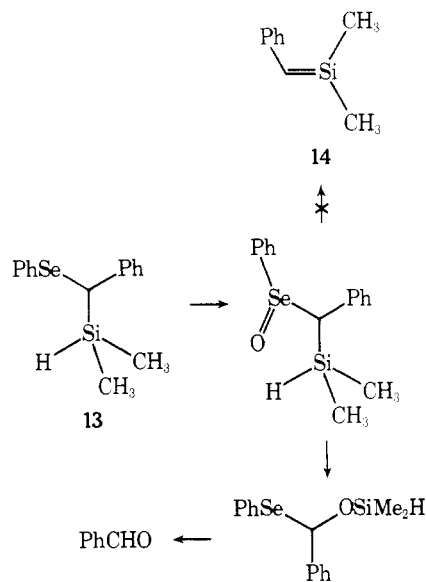
Oxidation of the benzyl alkylation product 10b gives predominantly vinyl silane, but significant quantities of products derived from phenylacetaldehyde are also observed. A more electron-withdrawing aryl substituent might completely suppress attack on silicon.

The sila-Pummerer rearrangement can be used to prepare silyl ketones,<sup>12</sup> as shown by the synthesis of 12. Hydrogen



peroxide oxidation of 11 gives 12 (46%) in addition to a small amount of benzaldehyde (8%).

We have studied the decomposition of the selenoxide obtained by oxidation of 13 to determine if the silaalkene<sup>13</sup> 14



can be produced by selenoxide syn elimination. The only product observed was benzaldehyde (path b). No benzyldimethylsilanol, which would be formed by addition of water to 14, was detected.

### Experimental Section

**General.** Nuclear magnetic resonance spectra were obtained on JEOL MH-100 or FX-60 spectrometers, infrared spectra on a Perkin-Elmer IR-267 spectrophotometer, and mass spectra on an AEI MS-902 spectrometer. NMR spectra were measured in  $\text{CCl}_4$  solution. Unless specified otherwise IR spectra of neat liquid between salt plates were recorded.

Starting materials were commercially available except for diphenyl diselenide and bis(3-trifluoromethyl)phenyl diselenide, which were prepared according to procedures in ref 3b. Butyllithium in hexane was purchased from Foote Mineral Co. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride. Diisopropylamine and diethylamine were distilled from potassium hydroxide and stored over 4A molecular sieves. Solutions of lithium diisopropylamide (LDA), 1 M in THF, were prepared as in ref 3b; THF solutions of lithium diethylamide were prepared as needed. All reactions involving organolithium reagents were run under an atmosphere of dry nitrogen.

Preparative thin layer chromatography (preparative TLC) was carried out using Merck PF-254 silica gel. Elemental analyses were performed by Spang Microanalytical Laboratories.

**Benzyl Phenyl Selenide.** In a 250-mL three-neck flask equipped with a reflux condenser and an addition funnel, diphenyl diselenide (9.30 g, 30 mmol) and 150 mL of absolute ethanol were stirred under  $\text{N}_2$ . Powdered sodium borohydride (2.8 g, 74 mmol) was added in portions. The solution was colorless when all sodium borohydride was added. Benzyl chloride (7.9 g, 62.5 mmol) in 20 mL of absolute ethanol was added over a 10-min period, the resulting solution was stirred for 1 h under  $\text{N}_2$ , 50 mL of 10% HCl was added, and the solution was extracted with  $3 \times 80$  mL of hexane. The combined hexane extracts were washed with 10% HCl, saturated  $\text{NaHCO}_3$ , water, and saturated salt solution and dried ( $\text{Na}_2\text{SO}_4$ ). Benzyl phenyl selenide<sup>5</sup> (13.8 g, 93% yield, mp 31–32 °C) was crystallized from this solution: NMR  $\delta$  4.00 (s, 2 H), 7.1–7.6 (m, 10 H); IR ( $\text{CHCl}_3$ ) 3030, 2995, 1578, 1492, 1475, 1451, 1437, 1178, 1065, 1022  $\text{cm}^{-1}$ .

**$\alpha$ -Trimethylsilylbenzyl Phenyl Selenide (1a).** To a stirred, cooled (dry ice–ethanol) solution of 2.47 g (10 mmol) of benzyl phenyl selenide in 20 mL of THF was added 10.5 mL of 1 M LDA solution under a nitrogen atmosphere. After 5 min, 1.5 mL (11.6 mmol) of trimethylchlorosilane was added, the solution was stirred for an additional 5 min, and the reaction mixture was poured into 10% HCl and extracted with  $3 \times 40$  mL of ether–hexane. The combined organic extracts were washed with water and saturated salt solution and dried, giving 2.66 g (83%) of  $\alpha$ -trimethylsilylbenzyl phenyl selenide (mp 32 °C, crystallized from pentane at 0 °C): NMR  $\delta$  0.36 (s, 9 H), 3.88 (s, 1 H), 7.1–7.6 (m, 10 H); IR ( $\text{CHCl}_3$ ) 2970, 1532, 1459, 1432, 1157, 810, 794  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{16}\text{H}_{20}\text{SeSi}$ , 320.04993) 320.04936.

**1-Phenyl-1-(trimethylsilyl)ethyl Phenyl Selenide (2a).** *n*-Butyllithium (1.55 M, 3.4 mL) was added to a cooled (0 °C) solution of 0.53 mL (5.3 mmol) of diethylamine in 10 mL of THF. After 5 min a THF (5 mL) solution of 1.6 g (5 mmol) of 1a was added. After stirring for 0.5 h, methyl iodide (0.35 mL, 5.5 mmol) was added to this solution, and it was stirred for 10 min, poured into 10% HCl, and worked up as above. A pentane solution of the crude product was cooled to –20 °C overnight to crystallize 1.28 g (77%) of 1-phenyl-1-(trimethylsilyl)ethyl phenyl selenide (2a, mp 40.5 °C): NMR  $\delta$  0.18 (s, 9 H), 1.32 (s, 3 H), 7.1–7.6 (m, 10 H); IR ( $\text{CHCl}_3$ ) 2962, 1480, 1442, 1259, 850  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{17}\text{H}_{22}\text{SeSi}$ , 334.06558) 334.06399.

Anal. Calcd for  $\text{C}_{17}\text{H}_{22}\text{SeSi}$ : C, 61.24; H, 6.65. Found: C, 61.22; H, 6.52.

**Oxidation of 2a.** *m*-Chloroperbenzoic acid (85%, 0.61 g, 3 mmol) in 3 mL of THF was added to a cooled (–78 °C) solution of 1.0 g (3 mmol) of 1-phenyl-1-(trimethylsilyl)ethyl phenyl selenide (2a) in 10 mL of THF. After stirring the reaction mixture at this temperature for 0.5 h, 0.9 mL of diisopropylamine was added and the cold bath was removed. After 1.5 h the reaction mixture was poured into 5%  $\text{Na}_2\text{CO}_3$  solution and extracted with  $2 \times 30$  mL of ether–pentane. The combined organic extracts were washed with 10% HCl and saturated salt solution, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated on a rotary evaporator (bath temperature < 20 °C). The yellow oil thus obtained was dissolved in 10 mL of absolute ethanol in a two-neck flask equipped with a reflux condenser and nitrogen gas inlet. Powdered sodium borohydride was added to this solution in portions until the yellow color had disappeared. To this clear solution was added 0.3 g (3.17 mmol) of chloroacetic acid in 1 mL of ethanol. After stirring the reaction mixture for 20 min it was poured into saturated  $\text{NaHCO}_3$  solution and extracted with  $2 \times 30$  mL of pentane. The combined organic extracts were washed with 10% HCl and saturated salt solution, dried, and concentrated. The crude products was chromatographed on a silica

plate using pentane as solvent to give two bands: band 1 ( $R_f$  0.7), 1-trimethylsilyl-1-phenylethene (4)<sup>12</sup> (0.136 g, 25% yield) [NMR  $\delta$  0.39 (s, 9 H), 5.79 (d,  $J = 3$  Hz, 1 H), 5.98 (d,  $J = 3$  Hz, 1 H), 7.2–7.6 (m, 5 H); IR: 3050, 2965, 1593, 1485, 1403, 1250, 930, 860, 703  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{11}\text{H}_{16}\text{Si}$ , 176.10213) 176.10220]; band 2 ( $R_f$  0.45), 1-phenylseleno-1-phenylethene (8) (0.171 g, 22% yield) [NMR  $\delta$  5.41 (s, 1 H), 5.91 (s, 1 H), 7.2–7.7 (m, 10 H);  $m/e$  (calcd for  $\text{C}_{14}\text{H}_{12}\text{Se}$ , 260.01040) 260.01208].

**Benzyl *m*-Trifluoromethylphenyl Selenide.** In a three-neck round flask equipped with an addition funnel, reflux condenser, and a gas inlet tube 2.24 g (5 mmol) of bis(3-trifluoromethyl)phenyl diselenide and 0.77 g (5 mmol) of sodium formaldehyde sulfoxylate<sup>15</sup> (Rongalite) in 25 mL of ethanol were heated to 50 °C under a nitrogen atmosphere. Alcoholic KOH (3 mL, 5 M) was slowly added to this solution. After 30 min, the solution was decolorized and benzyl chloride (1.2 mL, 10 mmol) was added and stirred for 1 h at 50 °C. The reaction mixture was poured into 10% HCl and extracted with pentane ( $3 \times 40$  mL). The combined organic extracts were washed with water and saturated NaCl solution, dried, and concentrated. The concentrated product on distillation (Kugelrohr, bath 80–85 °C, 0.23 mm) gave 3.052 g (97%) of benzyl *m*-trifluoromethylphenyl selenide: NMR  $\delta$  4.1 (s, 2 H), 7.1–7.9 (m, 9 H); IR 3030, 1494, 1451, 1305, 695  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{14}\text{H}_{11}\text{F}_3\text{Se}$ , 315.99778) 315.99924.

**1-Phenyl-1-(trimethylsilyl)ethyl *m*-Trifluoromethylphenyl Selenide (2b).** Following the procedure given for the preparation of 1a, 1.575 g (5 mmol) of benzyl *m*-trifluoromethylphenyl selenide, 5.5 mL of 1 M LDA, and 0.75 mL (5.75 mmol) of trimethylchlorosilane gave 1.66 g (86% yield) of ( $\alpha$ -trimethylsilyl)benzyl *m*-trifluoromethylphenyl selenide (2b) upon distillation (Kugelrohr, 95–100 °C, 0.2 mm): NMR  $\delta$  0.21 (s, 9 H), 3.8 (s, 1 H), 7.1–7.7 (m, 9 H).

A THF (3 mL) solution of 0.776 g (2 mmol) of 2b was added to a solution of 2.2 mmol of  $\text{LiNEt}_2$  prepared from 0.22 mL of diethylamine and 1.4 mL (1.55 M) of *n*-butyllithium in 2 mL of THF at –78 °C. After stirring the solution for 45 min, 0.2 mL (3.1 mmol) of methyl iodide was added and it was stirred for 10 min. After normal workup, 1-phenyl-1-(trimethylsilyl)ethyl *m*-trifluoromethylphenyl selenide (2b) (0.648 g, 81% yield) was isolated by distillation (Kugelrohr, 105–110 °C, 0.25 mm): NMR  $\delta$  0.39 (s, 9 H), 1.87 (s, 3 H), 7.1–7.7 (m, 9 H); IR 2962, 1420, 1327, 1132, 850, 703  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{18}\text{H}_{21}\text{F}_3\text{SeSi}$ , 402.05295) 402.05246.

Anal. Calcd for  $\text{C}_{18}\text{H}_{21}\text{F}_3\text{SeSi}$ : C, 53.86; H, 5.27. Found: C, 53.82; H, 5.23.

***m*-Trifluoromethylphenyl Trimethylsilylmethyl Selenide (9b).** In a 250-mL three-neck round-bottom flask equipped with a condenser, addition funnel, and a  $\text{N}_2$  gas inlet tube, 4.5 g (10 mmol) of bis(3-trifluoromethyl)phenyl diselenide was dissolved in 60 mL of ethanol. Sodium formaldehyde sulfoxylate (1.54 g, 10 mmol) was added and the reaction mixture was heated to 50 °C. A solution of 1.2 g of NaOH in 10 mL of water was now added and stirred for 0.5 h until the yellow color of the diselenide had disappeared. Chloromethyltrimethylsilane (2.47 g, 20 mmol) was added to the solution. After stirring the reaction mixture for 5 h at 50 °C, it was poured into 75 mL of 10% HCl and extracted with  $4 \times 50$  mL of pentane. The combined extracts were washed with 7%  $\text{NaHCO}_3$  solution and saturated salt solution, dried ( $\text{Na}_2\text{SO}_4$ ), and filtered. The crude product, after removal of solvents, was distilled to give 5.48 g (88%) of *m*-trifluoromethylphenyl trimethylsilylmethyl selenide (9b) (Kugelrohr, 72–74 °C, 0.3 mm): NMR  $\delta$  0.23 (s, 9 H), 2.22 (s, 1 H), 7.2–7.8 (m, 4 H); IR 2962, 1425, 1325, 1130, 845, 697  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{11}\text{H}_{15}\text{F}_3\text{SeSi}$ , 312.00600) 312.00558.

Anal. Calcd for  $\text{C}_{11}\text{H}_{15}\text{F}_3\text{SeSi}$ : C, 42.44; H, 4.86. Found: C, 42.52; H, 4.86.

**$\alpha$ -Dimethylsilylbenzyl Phenyl Selenide (13).** Following the procedure given for preparation of 1a, 0.247 g (1 mmol) of benzyl phenyl selenide and 0.123 g (1 mmol) of chlorodimethylsilane gave 0.276 g (90%) of  $\alpha$ -dimethylsilylbenzyl phenyl selenide (13) after preparative TLC: NMR  $\delta$  0.09 (d,  $J = 3.6$  Hz, 3 H), 0.19 (d,  $J = 3.6$  Hz, 3 H), 3.64 (d,  $J = 3.5$  Hz, 1 H), 4.1 (m, 1 H), 6.9–7.4 (m, 10 H); IR 2965, 2110 (Si–H), 1496, 1481, 1255, 881  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{15}\text{H}_{18}\text{SeSi}$ , 306.03428) 306.03369.

**$\alpha,\alpha$ -Bis(trimethylsilyl)benzyl Phenyl Selenide (11).** *n*-Butyllithium (1.55 M, 2.0 mL) was added to a cooled (0 °C) solution of 0.32 mL (3.2 mmol) of diethylamine in 5 mL of THF. After 5 min a THF (1 mL) solution of crude 1a obtained from 0.741 g (3 mmol) of benzyl phenyl selenide was added to it. After stirring for 0.5 h, 0.4 mL (3.1 mmol) of trimethylchlorosilane was added to the reaction mixture and stirred for 10 min. The solution was poured into 10% HCl and extracted with  $2 \times 30$  mL of pentane. The combined organic extracts were washed with water and saturated NaCl solution and dried. The concentrated pentane solution upon cooling to 0 °C gave 0.60 g (51%)

yield) of  $\alpha,\alpha$ -bis(trimethylsilyl)benzyl phenyl selenide (11, mp 100 °C); NMR  $\delta$  0.16 (s, 18 H), 7.1–7.5 (m, 8 H), 7.8–8.0 (m, 2 H); IR 2965, 1485, 1258, 873, 850  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{19}\text{H}_{28}\text{SeSi}_2$ : C, 58.28; H, 7.21. Found: C, 58.28; H, 7.16.

**Phenyl Trimethylsilyl Ketone (12).** To a stirred solution of 0.391 g (1 mmol) of 11 in 5 mL of dichloromethane was gradually added 2.1 mmol of  $\text{H}_2\text{O}_2$  (0.24 mL of 30%  $\text{H}_2\text{O}_2$  in 0.3 mL of water). The resulting solution was vigorously stirred for 3 h. The reaction mixture was added to 7%  $\text{NaHCO}_3$  solution and extracted with  $3 \times 15$  mL of ether-pentane. The combined extracts were washed with 10% HCl solution and saturated NaCl solution and dried ( $\text{Na}_2\text{SO}_4$ ). After solvent removal preparative TLC gave 0.081 g (46%) of phenyl trimethylsilyl ketone<sup>12</sup> (12) [NMR  $\delta$  0.39 (s, 9 H), 7.3–7.5 (m, 3 H), 7.7–7.9 (m, 2 H); IR 2970, 2900, 1618, 1595, 1580, 1259, 1217, 840, 784, 694  $\text{cm}^{-1}$ ;  $m/e$  (calcd for  $\text{C}_{10}\text{H}_{14}\text{OSi}$ , 178.08139) 178.08138] along with 9 mg (8%) of benzaldehyde.

**Acknowledgment.** We thank the National Science Foundation and the Du Pont Co. for financial support and Mr. David Ting for technical assistance.

**Registry No.**—1a, 56253-59-9; 1b, 61665-38-1; 2a, 61634-66-0; 2b, 61634-67-1; 4, 1923-01-9; 8, 61634-68-2; 9b, 61634-69-3; 11, 61634-70-6; 12, 5908-41-8; 13, 61634-71-7; diphenyl diselenide, 1666-13-3; benzyl chloride, 100-44-7; benzyl phenyl selenide, 18255-05-5;  $\text{Me}_3\text{SiCl}$ , 75-77-4; methyl iodide, 74-88-4; bis(3-trifluoromethyl)phenyl diselenide, 53973-75-4; benzyl *m*-trifluoromethylphenyl selenide, 61634-72-8; chlorodimethylsilane, 1066-35-9.

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## Reaction of $\beta$ -Methylselenium Trichloride with Some Simple Alkenes<sup>1</sup>

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Received October 15, 1976

The addition reaction of  $\beta$ -methylselenium trichloride to (*E*)- and (*Z*)-2-butene, (*E*)- and (*Z*)-1-phenylpropene, propene, methylpropene, 3-methylbutene-1, and 3,3-dimethylbutene-1 gave  $\beta$ -chloroalkyl methyl selenide dichlorides by anti-stereospecific addition. The regiochemistry depends upon the substituents on the double bond: a phenyl substituent gives exclusively the Markownikoff orientation while anti-Markownikoff orientation predominates in the case of alkyl groups.

It is known from previous work that 2,4-dinitrophenyl-selenium trichloride adds to carbon-carbon double bonds in a stereospecific manner.<sup>2</sup> In acetic acid, carbon tetrachloride, chloroform, and methylene chloride, these reactions are suitably interpreted as anti electrophilic additions. Little, however, appears to be known about the addition of the aliphatic analogue to alkenes and alkynes.

Three alkylselenium trichlorides,  $\text{RSeCl}_3$ ,  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and *i*- $\text{C}_3\text{H}_7$ , have been reported.<sup>3</sup> Of these only methylselenium trichloride is reasonably stable. Ethylselenium trichloride may be prepared in situ, but has not been isolated. Isopropylselenium trichloride, although apparently formed in situ, immediately decomposes to isopropyl chloride and selenium tetrachloride.

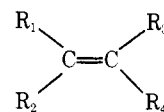
Methylselenium trichloride (MSTC), though first prepared in 1968, has not been the subject of more than very preliminary studies of chemical reactivity.<sup>3</sup> Wynne and George reported<sup>3</sup> the preparation of two distinct forms of MSTC based on their solubility in methylene chloride. The major difference appears to be that the soluble form, hereafter referred to as  $\beta$ -MSTC, is dimeric in solution. The less soluble,  $\alpha$ -MSTC, appears to be monomeric.

As part of our continuing investigations into the mechanism(s) of addition of organic selenium halides to alkenes and

alkynes we have initiated a study of the reactivity of both forms of MSTC. In this paper we wish to report the stereo- and regiochemistry of the products of addition of  $\beta$ -MSTC to a series of simple alkenes.

## Results

As a probe into the stereo- and regiochemistry of this reaction, we have investigated the addition of  $\beta$ -MSTC to two pairs of *E* and *Z* alkenes, the 2-butenes (1 and 2) and the 1-phenylpropenes (3 and 4), and four unsymmetrical terminal



	$\text{R}_1$	$\text{R}_2$	$\text{R}_3$	$\text{R}_4$
1	$\text{CH}_3$	H	H	$\text{CH}_3$
2	$\text{CH}_3$	H	$\text{CH}_3$	H
3	$\text{C}_6\text{H}_5$	H	H	$\text{CH}_3$
4	$\text{C}_6\text{H}_5$	H	$\text{CH}_3$	H
5	$\text{CH}_3$	H	H	H
6	$\text{CH}_3$	$\text{CH}_3$	H	H
7	<i>i</i> - $\text{C}_3\text{H}_7$	H	H	H
8	<i>t</i> - $\text{C}_4\text{H}_9$	H	H	H