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SYNTHESIS OF β-SILOXYALKYL PHENYL SELENIDES BY THE REACTION OF PHENYL TRIMETHYLSILYL SELENIDE WITH EPOXIDES

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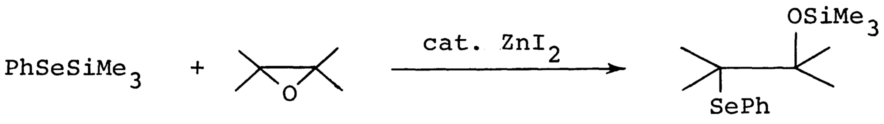
The reaction of phenyl trimethylsilyl selenide with epoxides using zinc iodide or n-butyllithium as a catalyst gave β-siloxyalkyl phenyl selenides in good yield.

In the preceding paper,$^{1)}$ we have reported the reaction of phenyl trimethylsilyl selenide(1)$^{2)}$ with alkyl acetates and lactones. This paper describes the reaction of phenyl trimethylsilyl selenide(1) with various epoxides in the presence of a Lewis acid (ZnI_2) or a base (n-BuLi) as a catalyst. Recently Detty has briefly reported the reaction of 1,2-epoxypropane with potassium phenyl selenolate.$^{2b)}$ Others have also reported the reaction of epoxides with sodium phenyl selenolate, which is generated from diphenyl diselenide and sodium borohydride.$^{3)}$



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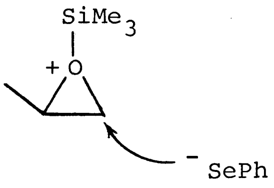
In a typical procedure, the epoxide(2)(5 mmol) and phenyl trimethylsilyl selenide(1)(6 mmol) were dissolved in the solvent(5 ml) under nitrogen atmosphere. A catalytic amount of zinc iodide(16 mg; 0.05 mmol) was added at the reaction temperature(cited in Table I) with stirring.$^{4)}$ The reaction mixture was quenched by adding a small amount of pyridine. After filtration of precipitates of pyridine-zinc iodide complex, the solvent was removed *in vacuo* and then the yellow residual oil was distilled to give the product (3). The results of the reaction of silyl selenide(1) with various epoxides are shown in Table I.

Reaction of cyclohexene oxide(2a) with the silyl selenide (1) in tetrachloromethane or dichloromethane gave stereospecifically trans-2-trimethylsilylcyclohexyl phenyl selenide(3a) in 87 % yield. No cis isomer was detected. 1,2-Epoxypropane(2d), 1,2-epoxybutane(2e) and epichlorohydrin(2g) underwent ring opening exclusively at the terminal carbon atom to give primary selenide. 2-Methyl-2,3-epoxybutane(2i) underwent fairly selective ring opening at low temperature with predominant formation of tertiary selenide.
No selectivity, however, was observed in the case of 2-methyl-1,2-epoxypropane (2h) under weakly acidic conditions(ZnI_2).

The results obtained from the present work indicate that the facility of carbon-oxygen bond scission in epoxides decreases in the following order when zinc iodide is used as a catalyst; tertiary > primary > secondary.
It is interesting to note that this order is in agreement with that previously observed in the cases of ZnI_2 catalyzed reaction of esters and lactones with 1.1) Thus, the ring opening is likely to involve S_N2-like cleavage of a silyl oxonium ion (4), which may be sensitive to steric factor, or partially stabilized carbonium ion (5), which may be sensitive to the nature and numbers of the substituents, as the two extreme cases when zinc iodide has been used as the catalyst. The low partial rate factor at the secondary center in these two mechanisms may account for the selectivity observed.



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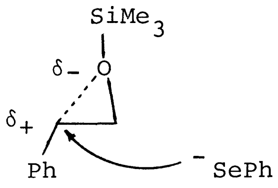

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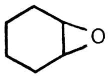
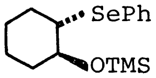
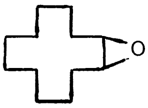
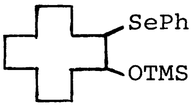
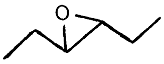
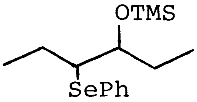
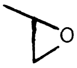
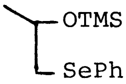
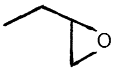
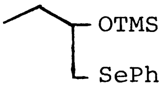
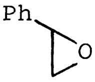
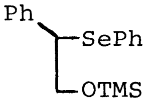
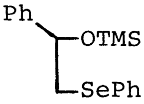
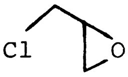
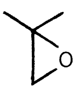
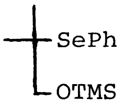
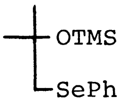
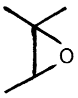
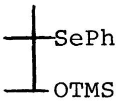
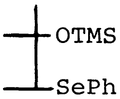
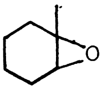
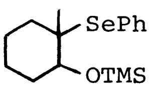
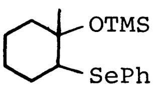
Furthermore, when a base such as n-BuLi was used as the catalyst, the selectivity of the ring opening has been changed almost completely. The actual catalyst species may be lithium phenyl selenolate(PhSeLi) and the steric factor would be important in these base catalyzed ring opening.

Further studies on the utilization of silyl selenide(1) for synthetic transformation are currently under investigation.

Table I Reaction of Epoxides with Phenyl Trimethylsilyl Selenide[a]

Epoxide(2)		Solvent(cat.)	Temp(°C)	Time(h)	Products(3)	(ratio)		Yield(%)[b]
2a		$CCl_4(ZnI_2)$	15	24	3a 			87
		$CCl_4(ZnI_2)$	50	2				84
		$CH_2Cl_2(ZnI_2)$	0	8				87
2b		$CH_2Cl_2(ZnI_2)$	0	1	3b 			74
2c		$CH_2Cl_2(ZnI_2)$	0	1	3c 			75
2d		$CH_2Cl_2(ZnI_2)$	0	0.5	3d 			84
2e		$CH_2Cl_2(ZnI_2)$	0	2	3e 			78
2f		$CCl_4(ZnI_2)$	50	5	 3f	(90 : 10)	 3g	70
		$CH_2Cl_2(ZnI_2)$	0	2		(100 : 0)		69
		$CH_2Cl_2(ZnI_2)$	-20	20		(100 : 0)		83
		THF(n-BuLi)	15	2		(12 : 88)		91[c]
2g		$CH_2Cl_2(ZnI_2)$	25	72	3h 			76
2h		$CH_2Cl_2(ZnI_2)$	0	6	 3i	(66 : 34)	 3j	58
		THF(n-BuLi)	15	2		(3 : 97)		78[c]
2i		$CH_2Cl_2(ZnI_2)$	0	2	 3k	(90 : 10)	 3l	30
		$CH_2Cl_2(ZnI_2)$	-20	6		(91 : 9)		60
		$CH_2Cl_2(ZnI_2)$	-20	10		(92 : 8)		67
		$CH_2Cl_2(ZnI_2)$	-70	6		(91 : 9)		57
2j		$CH_2Cl_2(ZnI_2)$	-20	6	 3m	(59 : 41)	 3n	79
		THF(n-BuLi)	15	3		(3 : 97)		88[c]

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a) Epoxide(5 mmol), $PhSeSiMe_3$(6 mmol), ZnI_2(0.05 mmol).

b) Isolated yield based on epoxide used.

c) Epoxide(5 mmol) was added after treatment of 1(6 mmol) with n-BuLi(0.5 mmol) in THF(5 ml) at -78°, the mixture was stirred for 2 or 3 h at 15°.

References and Notes

1) N. Miyoshi, H. Ishii, S. Murai, and N. Sonoda, Chem. Lett., 1979, 873.

2) (a) N. Y. Derkach, N. A. Pasmurtseva and E. S. Levchenko, Zh. Org. Khim., 7 1543(1971); (b) M. R. Detty, Tetrahedron Lett., 1978, 5087; (c) D. Liotta, P. B. Paty, J. Johnston and G. Zima, ibid., 1978, 5091; (d) N. Miyoshi, H. Ishii, K. Kondo, S. Murai and N. Sonoda, Synthesis, 1979, 300.

3) (a) K. B. Sharpless and R. F. Lauer, J. Am. Chem. Soc., 95, 2697(1973); (b) G. H. Posner and D. Z. Rogers, ibid., 99, 8208(1977).

4) All of these reactions were monitored by NMR measurements. The products were adequately characterized by elemental analysis and spectroscopies. B. P. and NMR data of the products (3a-n) are give below. (3a); NMR(CCl_4) δ0.07 (s, 9H, OTMS), 1.01-2.13(m, 8H, ring methylene), 2.97-3.25(td, J= 4,8Hz, 1H, $C\underline{H}SePh$), 3.45-3.75(td, J= 4,8Hz, 1H, $C\underline{H}OTMS$), 7.06-7.25(m, 3H), 7.41-7.65(m, 2H); b.p. 123-125°(3 mm). (3b); 0.09(s, 9H, OTMS), 1.06-1.86(m, 20H, ring methylene), 3.10-3.30(m, 1H, $C\underline{H}SePh$), 3.76-4.02(m, 1H, $C\underline{H}OTMS$), 7.06-7.20(m, 3H), 7.32-7.46(m, 2H); b.p. 176-179°(1 mm). (3c) 0.06(s, 9H, OTMS), 0.83(t, J= 7Hz, 3H, $CH(SePh)CH_2C\underline{H}_3$), 1.04(t, J= 7Hz, 3H, $CH(OTMS)CH_2C\underline{H}_3$), 1.43-1.85(c, 4H, methylene), 1.86(dt, J= 5, 8Hz, 1H, $C\underline{H}SePh$), 3.75(dt, J= 5, 8Hz, 1H, $C\underline{H}OTMS$), 7.05-7.23(m, 3H), 7.35-7.55(m, 2H); b.p. 96-97°(1 mm). (3d); 0.06 (s, 9H, OTMS), 1.24(d, J= 6Hz, 3H, $CH(OTMS)C\underline{H}_3$), 2.78(dd, J= 12.5, 6Hz, 1H, $C\underline{H}_2SePh$), 2.98(dd, J= 12.5, 6Hz, 1H, CH_2SePh), 3.92(dq, J= 6, 6.5Hz, 1H, $C\underline{H}OTMS$), 7.04-7.24(m, 3H), 7.28-7.60(m, 2H); b.p. 87-88°(2 mm). (3e); 0.06(s, 9H, OTMS), 0.90(t, J= 8Hz, 3H, $CH_2C\underline{H}_3$), 1.38-1.74(m, 2H, $C\underline{H}_2CH_3$), 2.90(d, J= 6Hz, 2H, $C\underline{H}_2SePh$), 3.58-3.90(m, 1H, $C\underline{H}OTMS$), 7.10-7.26(m, 3H), 7.34-7.56(m, 2H); b.p. 103-104(2 mm). (3f); -0.06(s, 9H, OTMS), 3.76-4.06(c, 2H, $C\underline{H}_2OTMS$), 4.14-4.36 (c, 1H, $C\underline{H}SePh$), 6.96-7.62(m, 10H); b.p. 147-148°(0.5 mm). (3g); 0.06(s, 9H, OTMS), 3.02(dd, J= 12, 6Hz, 1H, $C\underline{H}_2SePh$), 3.22(dd, J= 8, 12Hz, 1H, $C\underline{H}_2SePh$), 4.83 (dd, J= 8, 6Hz, 1H, $C\underline{H}OTMS$), 7.08-7.38(m, 8H), 7.38-7.64(m, 2H); b.p. 147.5-150° (4 mm). (3h); 0.08(s, 9H, OTMS), 2.92(dd, J= 12.5, 5.5Hz, 1H, $C\underline{H}_2SePh$), 3.10(dd, J= 12.5, 5.5Hz, 1H, $C\underline{H}_2SePh$), 3.47(dd, J= 10.5, 5.5Hz, 1H, $C\underline{H}_2Cl$), 3.49(dd, J= 5.5, 10.5Hz, 1H, $C\underline{H}_2Cl$), 3.93(quintet, J= 5.5Hz, 1H, $C\underline{H}OTMS$), 7.09-7.25(m, 3H), 7.33-7.53(m, 2H); b.p. 107-108°(2 mm). (3i); 0.08(s, 9H, OTMS), 1.26(s, 6H, $CH(C\underline{H}_3)_2$), 3.48(s, 2H, $C\underline{H}_2OTMS$)), 7.05-7.29(m, 3H), 7.31-7.65(m, 2H); b.p. 106-122°(10 mm). (3j); 0.10(s, 9H, OTMS), 1.34(s, 6H, $C(C\underline{H}_3)_2$, 3.00(s, 2H, $C\underline{H}_2SePh$), 7.04-7.20(m, 3H), 7.32-7.54(m, 2H); b.p. 87-88°(2 mm). (3k); 0.07(s, 9H, OTMS), 1.25(s, 6H, $CH(C\underline{H}_3)_2$), 1.26(d, J= 6Hz, 3H, $CH(OTMS)C\underline{H}_3$), 3.73(q, J= 6Hz, 1H, $C\underline{H}SePh$), 7.09-7.29(m, 3H), 7.45-7.65(m, 2H); b.p. 95-96° (2 mm). (3m); 0.10(s, 9H, OTMS), 1.27(s, 3H, $C\underline{H}_3$), 3.76(dd, J= 4, 8Hz, 1H, $C\underline{H}OTMS$), 7.08-7.28(m, 3H), 7.42-7.62(m, 2H); b.p. 112.5-117°(2 mm). (3n); 0.10(s, 9H, OTMS), 1.36(s, 3H, $C\underline{H}_3$), 3.24(dd, J= 4, 8Hz, 1H, $C\underline{H}SePh$), 7.08-7.28(m, 3H), 7.42-7.62(m, 2H); b.p. 132-133°(3 mm).

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