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PHENYLSELENOTRIMETHYLSILANE. A NOVEL SOURCE OF PHENYLSELENIDE ANION

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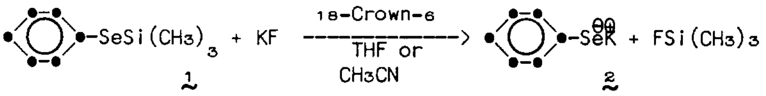
Although the utility of aryl selenides for effecting a wide variety of synthetic transformations is well established, use of such reagents has been limited to the addition of the substrate to a preformed equivalent of the aryl selenide.[1] We report here the utility of phenylselenotrimethylsilane (**1**) as a potassium phenylselenide source in which the anion is slowly generated in the presence of the substrate. Such a method should permit selective anionic attack in substrates where two or more sites can react.

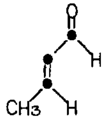
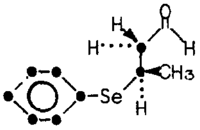
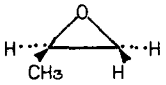
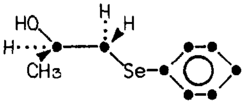
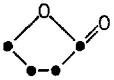
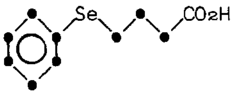
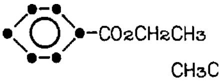
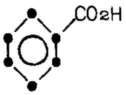
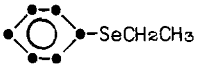
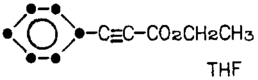
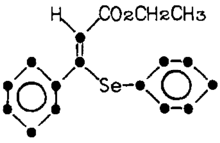
When a solution of phenylselenotrimethylsilane (**1**) in degassed tetrahydrofuran (THF) or acetonitrile was treated at reflux with 1.1 eq of potassium fluoride in the presence of 0.05 eq of 18-crown-6, quantitative conversion to potassium phenylselenide (**2**) and fluorotrimethylsilane was realized. The consumption of **1** was complete after ~**2** hr (TLC analysis). Bubbling a slow stream of air through the reaction mixture gave a 100% yield of diphenyl diselenide.



The reagent **1** has been prepared by treating phenylselenol and chlorotrimethylsilane with triethylamine in benzene.[2] Although this method gives **1** in moderate yield, it suffers frequently from incomplete reaction. In addition to being the source of an extremely unpleasant stench, the unreacted phenylselenol is difficult to separate from starting material. We avoid the use of phenylselenol by treating diphenyl diselenide with sodium metal in tetrahydrofuran according to the procedure of Liotta[1a] and quenching the resulting sodium phenylselenide <u>in situ</u> with chlorotrimethylsilane. This procedure gave **1** in 60-70% yield as an air-sensitive, foul-smelling, colorless oil, bp 110-115° at 18 torr.

A less satisfactory method of preparing **1** consisted of treating phenylselenol and a threefold excess of trimethylsilane in degassed benzene with chlorotris(triphenylphosphino)rhodium(I) at 0°.[3] After evolution of hydrogen was complete, the catalyst was removed by filtration. Distillation of the filtrate gave **1** in 43-55% yield; the remainder of the reaction mixture was diphenyl diselenide.

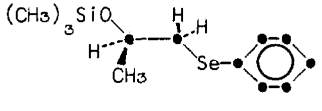
Table I. Reactions of Phenselenotrimethylsilane with Organic Substrates.

Substrate	Solvent	Reflux Time (hr)	Product	Isolated Yield (%)
	CH3CN THF	4 4	 3	62 73
	THF	4	 4	60
	THF	4	 5	81
	CH3CN THF	4 2	 6	92 95
CH3CH2Br	THF	2	 7	88
	THF	2	 8	42

The reagent is stored in a septum equipped vial under argon at 0°. Alternatively, stock solutions in tetrahydrofuran may be prepared by dilution, which are stable for several weeks at 0° under argon. The reagent should be transferred in dry syringes.

The potassium phenylselenide (2) generated from 1 was a potent nucleophile with various organic substrates. Table I lists representative reactions of 2 with α,β-unsaturated carbonyls, epoxides, lactones, esters, and alkyl halides. In a typical procedure, the organic substrate (2 mmole) and 1 (2 mmole) were dissolved in 5 ml of degassed THF or acetonitrile in an argon atmosphere.[4] The potassium fluoride (2.2 mmole) and 18-crown-6 (0.1 mmole) were added in one portion. The resulting mixture was then warmed to reflux. Appropriate workup (aqueous dilution, acidification, methylene chloride extraction) gave the products listed in the table.[5] In general, reaction times were much shorter than those reported for other methods.[1]

Attempts to use a catalytic amount of potassium fluoride or potassium cyanide with 1 as described for phenylthiotrimethylsilane[6] gave variable yields and product mixtures. Such reactions were difficult to drive to completion, and oxygen functionalities were not completely silylated. When propylene oxide was treated with 1.1 eq of 1, 0.05 eq of 18-crown-6 and 0.05 eq of potassium fluoride in THF as described, two products were obtained in a ratio of 85:15. The minor component was identified as 4 while the major component was identified as the trimethylsilyloxy compound 9. Crotonaldehyde reacted sluggishly under similar conditions (~50% reaction after 18 hr) to give a 1:1 mixture of 3 and 10 as products.



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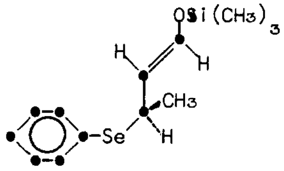

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References and Notes

1. (a) D. Liotta, W. Markiewicz, and H. Santiesteban, Tetrahedron Lett., 4365 (1977); (b) D. Liotta and H. Santiesteban, ibid., 4369 (1977); (c) R. M. Searborough, Jr. and Amos B. Smith, III, ibid., 4361 (1977); (d) K. B. Sharpless and R. F. Lauer, J. Amer. Chem. Soc., 95, 2697 (1973); (e) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, ibid., 95, 6137 (1973); (f) P. A. Grieco, S. Gilman, and N. Nishizawa, J. Org. Chem., 41, 1485 (1976); (g) R. Ahmad, J. Saa, and M. P. Cava, ibid., 42, 1228 (1977).

2. N. Y. Derkach, N. A. Pasmurtseva, and E. S. Levchenko, Zh. Org. Khim., 7, 1543 (1971).

3. E. W. Abel, D. A. Armitage, and D. B. Brady, J. Organomet. Chem., 5, 130 (1966).
4. Degassing the solvent with argon minimizes the formation of diphenyl diselenide due to dissolved oxygen.
5. All compounds gave satisfactory IR, NMR, and mass spectral data. All new compounds gave satisfactory elemental analyses.
6. D. A. Evans, K. G. Grimm, and L. K. Truesdale, J. Amer. Chem. Soc., 97, 3229 (1975).

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