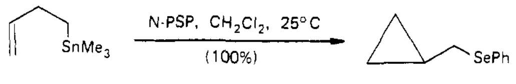
Scheme II. Cyclopropane Synthesis



23 24

of these new organoselenium compounds (N-PSP and N-PSS) in the construction of carbon–carbon bonds was demonstrated by the efficient formation of *cyclopropanes* (Scheme II). For example, the unsaturated organotin derivative **23** on treatment with N-PSP (1.1 equiv) in methylene chloride at 25 °C under acid catalysis (vide supra) is quantitatively converted to the phenylselenocyclopropane **24**.

The ready access, relative stability of the described selenium reagents (N-PSP and N-PSS), and the demonstration of their versatile nature as carriers of the PhSe group should make them useful and selective reagents for a number of selenium-based synthetic operations. The design, synthesis, and chemistry of novel organoselenium reagents and their application to the synthesis of natural and "unnatural" products is continuing in these laboratories.[18]

References and Notes

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(5) For a Pd(0)-initiated macrolide synthesis by C–C bond formation, see ref 13a.

(6) After our initial reports[12c,d] of the phenylselenocycloetherification reaction, a macrolide synthesis based on this cyclization principle appeared: Petrzilka, M. *Helv. Chim. Acta* **1978,** *61*, 3075.

(7) *N*-Phenylselenophthalimide was prepared as follows. A 250-mL round-bottom three-necked flask fitted with an Ar inlet was charged with potassium phthalimide (3.00 g, 16.2 mmol) and phenylselenenyl chloride (2.87 g, 15 mmol). After several evacuations and purges with Ar, dry and degassed hexane (15 mL, distilled from CaH_2 under Ar) was added and the mixture was vigorously stirred for 2 h at 25 °C (all PhSeCl dissolves). Dry methylene chloride (100 mL, distilled from CaH_2 under Ar) was added and the solution was filtered to remove solid materials. The solution was concentrated on the rotary evaporator to ~20 mL and dry hexane (80 mL) was added. The crystalline solid was collected by filtration and washed thoroughly with dry hexane: yield, 3.92 g (88%); colorless crystals; mp 171–175 °C dec. This product is sufficiently pure for use. An analytical sample was obtained by recrystallization from methylene chloride–ether (or hexane) as colorless crystals: mp 171–175 °C dec; IR (KBr) ν_{max} 1720 (vs) cm^{-1}; NMR (60 MHz, $CDCl_3$) τ 2.0–2.8 (m); exact mass calcd for $C_{14}H_9O_2NSe$ *m/e* 302.9798, found 302.9798; Anal. ($C_{14}H_9O_2NSe$) C, H, N, Se.

(8) *N*-Phenylselenosuccinimide, the first member of this general class of reagents, was first mentioned by Sharpless and Frejd (Frejd, T.; Sharpless, K. B. *Tetrahedron Lett.* **1978,** 2239. We thank Professor K. B. Sharpless and Dr. T. Hori for the experimental procedure for the preparation of this compound. For details of the synthesis and some other aspects of the chemistry of this reagent, see Sharpless, K. B.; Hori, T. *J. Org. Chem.*, in press.

(9) All new compounds showed satisfactory spectral and analytical data.

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(11) For the use of "PhSeOH" [10] in cyclization of dienes, see Scarborough, S., Smith, A. B., III; Barnette, W. E.; Nicolaou, K. C. *J. Org. Chem.*, in press.

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(13) For some recent macrolide forming methodology based on C–C bond formation, see the following. (a) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1977,** *99*, 3867. (b) Takahashi, T.; Hashiguchi, S.; Kasuga, K.; Tsuji, J. *ibid.* **1978,** *100*, 7424. (c) Burri, K. F.; Cardone, R. A.; Chen, W. Y.; Rosen, P. *ibid.* **1978,** *100*, 7069.

(14) Although a high dilution (syringe drive) experiment produced the monomeric lactones in somewhat higher yields (~5–8%), the inconvenience of the procedure does not seem to be worth the gain.

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Additions and Corrections

Steric and Electronic Effects on ^{15}N Chemical Shifts of Saturated Aliphatic Amines and Their Hydrochlorides [*J. Am. Chem. Soc.*, **100,** 3889 (1978)]. By Rudolph O. Duthaler and John D. Roberts,* Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125.

Page 3892, column 2; second sentence in the third paragraph (line 26) should read: "Thus, the shifts of the tertiary amine hydrochlorides of **29–41,** like those of the secondary amine hydrochlorides, **21, 23,** and **24,** are downfield of those predicted."

Structures and Energetics of Planar and Tetrahedral Dilithiomethane. A Near Degeneracy of Singlet and Triplet Electronic States [*J. Am. Chem. Soc.*, **100,** 5972 (1978)]. By William D. Laidig and Henry F. Schaefer,* Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

Several corrections must be made in Table II. The table in corrected form follows:

Table II. Relative Energy Predictions for Dilithiomethane. The Absolute Energies for the Tetrahedral Singlet are −53.8362 hartrees (SCF) and −54.0277 hartrees (CI)

	E (SCF), kcal	μ (SCF), D	*E* (CI), kcal	*E* (CI),[a] kcal
planar singlet	3.2	4.85	4.0	4.2
planar triplet	−15.8	−1.22	2.4	5.9
tetrahedral singlet	0.0	5.42	0.0	0.0
tetrahedral triplet	−16.6	−0.76	1.3	4.7

[a] Corrected for unlinked clusters.

Reactivity in Methyl Transfer Reactions. 3. Equilibria and Rates in Transfers between Substituted Thiophenoxides [*J. Am. Chem. Soc.*, **101,** 417 (1979)]. By Edward S. Lewis* and Semyon Kukes, Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77001.