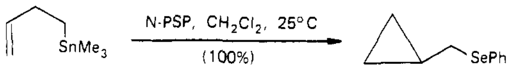
Scheme II. Cyclopropane Synthesis



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

(1) Sharpless, K. B.; Gordon, K. M., Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975,** *8A,* 9.

(2) (a) Reich, H. J. In "Oxidation in Organic Chemistry, Part C", Trahanovsky, W., Ed.; Academic Press: New York, 1978; p 1. (b) Reich, H. J. *Acc. Chem. Res.* **1979,** *12*, 22.

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(4) (a) Nicolaou, K. C. *Tetrahedron* **1977,** *33*, 683 and references cited therein. (b) Masamune, S., Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977,** *16*, 585 and references cited therein. (c) Back, T. G. *Tetrahedron* **1977,** *33*, 3041 and references cited therein.

(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.

(10) (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973,** *95*, 2697. (b) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978,** *43*, 1689. (c) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *ibid.* **1978,** *43*, 1697. (d) Labar, D.; Krief, A.; Hevesi, L. *Tetrahedron Lett.* **1978,** 3967.

(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.

(15) Nicolaou, K. C.; Barnette, W. E.; Claremon, D. A., unpublished results.

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(17) Moore, B. P.; Brown, W. V. *Aust. J. Chem.* **1976,** *29*, 1365.

(18) We gratefully acknowledge partial financial support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Merck Sharp and Dohme, U.S.A. We thank The Middle Atlantic Regional NMR Facility (NIH No. RR542) at The University of Pennsylvania directed by Dr. G. McDonald for the 360-MHz ^1H NMR spectra. We also thank Professor K. B. Sharpless for helpful discussions.

(19) Fellow of the Alfred P. Sloan Foundation.

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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.

Page 417: For eq 2 substitute the following.

$$\frac{K^{1/2}}{2A_0}\ln\left|\frac{CK^{-1/2}-C+A_0}{CK^{-1/2}+C-A_0}\right| = k_+t \qquad (2)$$

The calculations using eq 2 do not require correction.

Structures and Mass Spectral Behavior of the Inositol Cyclic Boronic Esters [*J. Am. Chem. Soc.*, **101,** 979 (1979)]. By JACEK WIECKO and WILLIAM R. SHERMAN,* Departments of Psychiatry and Biological Chemistry, Washington University School of Medicine, St. Louis, Missouri 63110.

On p 982, column 2, paragraph 2, line 7, the text should read: "In the spectra of these inositol butaneboronates the ratio of abundances of *m/e* 126 to *m/e* 139 is about 3:1, whereas in the spectra of the other inositol butaneboronates the ratio is 1:3 or greater."

Nonchair Conformations in Phosphorus-Containing Cyclohexanes. Crystal and Molecular Structures of *cis*- and *trans*-2-Phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes and *cis*-2-Phenyl-5-*tert*-butyl-1,3,2-dithiaphosphorinane [*J. Am. Chem. Soc.*, **101,** 1600 (1979)]. By ROBERT O. HUTCHINS,* BRUCE E. MARYANOFF,* MARIO J. CASTILLO, KARL D. HARGRAVE, and ANDREW T. MCPHAIL,* Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104; Chemical Research Department, McNeil Laboratories, Fort Washington, Pennsylvania 19034; and Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706.

Structure **5** should read R_1 = Se, R_2 = NH-*t*-C_4H_9, R_3 = CH_3 (R_3 was inadvertently omitted).

A Pair-Specific Osmium Reagent for Polynucleotides [*J. Am. Chem. Soc.*, **101,** 2251 (1979)]. By H. FORD, C.-H. CHANG, and E. J. BEHRMAN,* Department of Biochemistry, The Ohio State University, Columbus, Ohio 43210.

Line 14: VIII, not VII.
Line 21: ($k_0 + k$[L]), not ($k_0 + k$)[L].
Acknowledgments: Insert, "We are very grateful to John W. Fowble for the NMR spectra."

Book Reviews

Atmospheric Chemistry. By JULIAN HEICKLEN. Academic Press, New York. 1976. xiii + 406 pp. $38.00.

The author has presented a systematic organization of the vast amount of new information provided during the recent surge of interest in atmospheric processes. The monograph provides a synthesis of these results, mainly those of the Climatic Impact Assessment Program, through 1974. The emphasis is on experimental results. The book discussues both the lower and upper atmosphere neutral and ion chemistry.

The first chapter is a presentation of the physical and chemical structure of the atmosphere. A review of the spectroscopy of the main atmospheric constituents is included. Chapter Two presents an analysis of the neutral chemistry of the atmosphere, beginning with the photochemistry of neutral oxygen and successively introducing more species as the chemical structure is developed in detail. The analysis is closely related to in situ observations and explained using simple steady-state arguments. A brief summary of the stratospheric effects of NO_x and the chlorofluorocarbons concludes this chapter. Chapter Three briefly presents the chemistry of the ionosphere. Chapter Four considers the major atmospheric pollutants: CO, CO_2, NO_x, hydrocarbons, oxidants, halogenated compounds, sulfur compounds, and particulate matter. The concern of this chapter is not the chemistry of these species but rather to catalog their known sources and environmental insult. The detailed chemistry of hydrocarbon combustion, photochemical smog, ozone and singlet oxygen, SO_2, and aerosols is presented in succeeding chapters. The final chapter presents an interesting analysis of attempts at controlling atmospheric pollutants, including a controversial suggestion for chemical control of photochemical smog through large-scale dispersion of a radical scavenger.

This book must be compared with "Chemistry of the Atmosphere", by McEwan and Phillips, published two years earlier, which covers much the same material, although the present book is slightly more current. However, the style is quite different. The present author, in attempting to present a vast amount of precise experimental detail, has had to sacrifice, to an extent, readability. The earlier book, although not as rich in detail, is easier to absorb.

Thomas J. O'Brien, *Texas Tech University*

Polyvinylidene Chloride. By RITCHIE A. WESSLING (Dow Chemical Co.). Gordon and Breach Science Publishers, New York. 1977. xii + 199 pp. $25.00.

This well-organized book fills a real need for a review of significant aspects of vinylidene chloride copolymers, best known in formulations of the Dow Chemical Company as Saran packaging films and coatings of low moisture permeability. Wessling not only has reviewed the extensive literature critically but has included historical, polymerization, properties, and applications data contributed by his named colleagues of Dow. The commercialization of Saran is credited to Ralph M. Wiley and coworkers at Midland in 1933 to 1940.

Wessling uses "polyvinylidene chloride", abbreviated PVDC, to include the VDC copolymers. In fact, there are relatively few data available on the unmodified homopolymers. The book includes excellent chapters on the monomer, copolymerization (including heterogeneous, graft and ionic), copolymer structure, transitions, and degradation, as well as a short chapter on application technology. The latter contains some disclosures about Saran copolymer compositions. For example, packaging films are lower in vinyl chloride units than commercial shrink films, and acrylonitrile is a comonomer along with alkyl acrylate or methacrylate for copolymers used as coatings of low moisture permeability.

Among the features of the book are photomicrographs of a wide variety of VDC copolymer morphologies obtained from different copolymerization systems and from different solvents. Areas needing further research are pointed out, for example, branching, morphology, and the conformations of the crystalline polymers.

Perhaps Wessling might have given more attention to problems of toxicity. The commercial VDC monomer may contain some vinyl chloride. VDC in air forms peroxides which decompose to phosgene and formaldehyde. Pyrolysis of Saran gives HCl gas as well as carbons having interesting electrical properties. The book gives many patent and other references as well as both subject and author indexes.

C. E. Schildknecht, *Gettysburg College*

Organometallic Polymers. Edited by CHARLES E. CARRAHER, JR. (Wright State University), JOHN E. SHEATS (Rider College), and CHARLES U. PITTMAN, JR. (University of Alabama). Academic Press, New York. 1978. v-xii + 353 pp. $18.50.

Polymeric materials combining the thermal and oxidative stability of organic polymers and the interesting optical and electrochemical properties of metal complexes have much obvious potential: thus, the study of organometallic polymers is becoming an important area of research and development activity. This book consists of a series of papers (33) presented as part of a three-day Symposium on Organometallic Polymers held at the ACS National Meeting in New Orleans, March 1977. The book is divided into seven major sections dealing