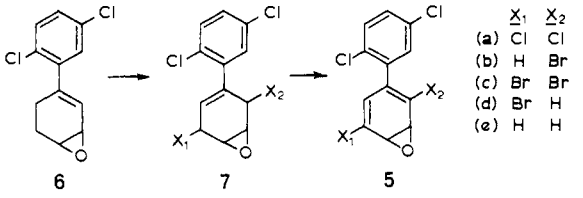
exception is run 7 in Table I, for which the sulfenate-sulfoxide equilibrium may be particularly unfavorable (note, however, that the less hindered alcohol in run 6 works satisfactorily). The sulfenate esters apparently can undergo decomposition reactions if the electrocyclic reactions are too slow.

Runs 3, 4 and 5 demonstrate that all of the isomeric phenylcyclohexadienes can be prepared without loss of regiospecificity. The dienes prepared in runs 8 and 9 were especially susceptible to aromatization and isomerization. Optimum yields were obtained when sulfenate ester formation was performed at −30 °C (3 h), followed by warming to complete the reaction.

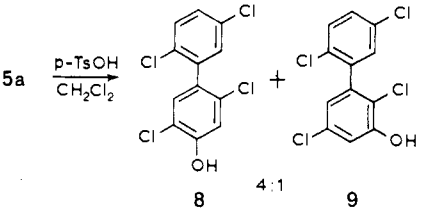
The diene prepared in run 1 is a key intermediate in the synthesis of several arene oxides derived from polychlorinated biphenyls (PCB's). 2,5,2′,5′-Tetrachlorobiphenyl has been extensively studied as a model for the toxic, mutagenic, and carcinogenic effects of PCB mixtures.[10] The arene oxide **5a** has been implicated as an intermediate during the metabolic degradation of this tetrachlorobiphenyl in rhesus monkeys.[10a]

The allyl alcohol **1a** was prepared in 83% yield by addition of unstable 2,5-dichlorophenyllithium[11] to cyclohexenone. Conversion to diene **2a** (Scheme I) and epoxidation gave the



intermediate epoxide **6.** This compound could be monobrominated (22% yield of crystalline **7b,** mp 145–146 °C), dibrominated (50% yield of crystalline **7c,** mp 146–147 °C, based on **2a**), and tribrominated under progressively more vigorous conditions using *N*-bromosuccinimide. The desired tetrachlorobiphenyl oxide **5a**[13] was prepared in highest purity by conversion of **7c** to a mixture of isomeric dichlorides **7a** ($R_4N^+Cl^-$, CH_3CN) followed by chlorination (t-BuOCl, CCl_4, hν) and dehydrochlorination (DBU, CH_2Cl_2, 25°). The compound showed remarkable chemical stability. It could be chromatographed on silica gel with no detectable decomposition and solutions in methanol and dimethyl sulfoxide had half-lives of 20 and 50 days, respectively, at 25 °C.[14]

The structure of **5a** was demonstrated by conversion to the phenols **8** and **9,** whose substitution pattern was unambiguously assigned by analysis of the 270-MHz NMR spectra.[15]



The arene oxides **5c 5d,** and **5e** were similarly prepared by dehydrobromination of the appropriate bromide.

Acknowledgment. We thank the National Institutes of Health (Grant EF00-958 to J. R. Allen, Department of Pathology), the National Science Foundation, and the Wisconsin Alumni Research Foundation for support of this research.

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(6) Election withdrawing[6a–c] and conjugating[6b,d] substituents have been shown to dramatically accelerate sulfoxide and selenoxide syn eliminations, an observation that has important synthetic applications. (a) Emerson, D. W.; Korniski, T. J. *J. Org. Chem.* **1969,** *34,* 4115. (b) Reich, H. J.; Wollowitz, S.; Trend, J. E., Chow, F.; Wendelborn, D. F. *J. Org. Chem.*, **1978,** *43,* 1697. (c) Sharpless, K. B.; Young, M. W. *ibid.*, **1975,** *40,* 947. (d) Trost, B. M.; Bridges, A. J. *ibid.*, **1975,** *40,* 2014. Trost, B. M.; Salzman, T. N.; Hiroi, K. *J. Am. Chem. Soc.*, **1976,** *98,* 4887.
(7) The sulfenic acid generated by syn elimination apparently reacts with 1 equiv of sulfenyl chloride.
(8) The allyl alcohol starting materials were prepared by addition of organometallic reagents to enones (runs 1–3, 8–10), reduction of enones (runs 4, 5), alkylation of the lithium reagent prepared by deprotonation of phenyl prenyl selenide followed by oxidation[2a] (run 11), treatment of aldehyde with α-lithioselenoxide (run 12),[9] or acid-catalyzed rearrangement of allyl alcohols (runs 6, 7).
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(11) Prepared by addition of *n*-BuLi to 2,5-dichloroiodobenzene.[12] Gilman has previously prepared 2-chlorophenyllithium (Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.*, **1956,** *78,* 2217).
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(13) **5a** was purified by TLC on silica gel and crystallization: mp 75–76 °C; 38% yield from **7a;** NMR (δ, $CDCl_3$) 4.23 (dd, J = 3.9, 2.6 Hz, 1 H), 4.31 (d, J = 3.9 Hz, 1 H), 6.34 (d, J = 2.6 Hz, 1 H), 7.21 (dd, J = 2.4, 0.4 Hz, 1 H), 7.29 (dd, J = 8.6, 2.4 Hz, 1 H), 7.37 (dd, J = 8.6, 0.4 Hz, 1 H). Anal. Calcd for $C_{12}H_6Cl_4O$: C, 46.79; H, 1.96. Found: C, 46.73; H, 2.06. If crude dibromide **7a** was used, **5a** could be prepared in 36% yield starting from diene **2b.**
(14) The monochlorobenzene oxides also show increased stability toward aromatization (Selander, H. G.; Jerina, D. M.; Piccolo, D. E.; Berchtold, G. A. *J. Am. Chem. Soc.*, **1975,** *97,* 4428).
(15) Phenol **8** was isolated in pure form: mp 101–102 °C; NMR (δ, acetone-d_6) 3.85 (br s, 1 H), 7.20 (d, J = 0.4 Hz, 1 H), 7.33 (d, J = 0.4 Hz, 1 H), 7.38 (dd, J = 2.6, 0.4 Hz, 1 H), 7.45 (dd, J = 8.5, 2.6 Hz, 1 H), 7.52 (dd, J = 8.5, 0.4 Hz, 1 H). Anal. Calcd. for $C_{12}H_6Cl_4O$: C, 46.79; H, 1.96. Found: C, 46.71; H, 2.09.
(16) A. P. Sloan Fellow, 1975–1979.

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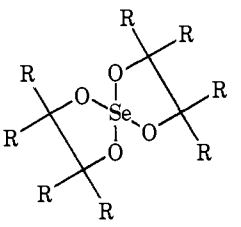
Intramolecular Ligand Reorganization in Five-Membered-Ring Tetraoxyselenuranes

Sir:

The intramolecular ligand reorganization of phosphoranes has received much attention,[1] that of sulfuranes[2] considerably less, and reorganization of selenuranes hardly any at all.[3] Paetzold and Reichenbacher[4] have prepared a number of tetralkoxyselenuranes. In the case of the tetramethoxy compound, the ^1H NMR spectrum indicates that all of the hydrogens of the methoxy groups are equivalent. It was suggested that rapid intramolecular exchange may account for this observation.[5]



1, R = H
2, R = CH_3

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The compounds, **1**[6] and **2**,[7] have now been prepared and their variable-temperature ^1H and ^{13}C spectra have been investigated. The ^1H NMR spectrum, 80 MHz, of **1** in CD_2Cl_2 showed only one resonance at δ 4.05, on cooling to −55 °C a broad two-line pattern was found, and at −85 °C fine structure was observed in the two-line pattern. Addition of *N,N*-diethylaminotrimethylsilane, a known acid and water scavenger, led to an extremely complicated but symmetrical ambient spectrum centered at δ 4.07. It appears that in the untreated sample that ring opening was occurring rapidly on the NMR time scale and this led to the equivalency of the protons. The treated sample shows quite clearly that the pure material has nonequivalent protons and the spectrum is that of an AA'BB' system. The ^{13}C NMR spectrum of either the treated or untreated material had only one resonance at δ +65.65 at ambient temperature and at −75 °C.

The ^1H NMR spectrum of **2** in CH_2Cl_2 at ambient temperature has two resonances at δ 1.20 and 1.25 for hydrogens of nonequivalent pairs of methyl groups. At −110 °C in $CFCl_3$–CD_2Cl_2 a broad absorption was found. The ambient ^{13}C NMR spectrum of **2** in CD_2Cl_2 had absorptions for pairs of nonequivalent methyl group carbons at δ 24.40 and 24.70. A single resonance for quaternary carbons was found at δ 81.40. At −112 °C in $CFCl_3$–CD_2Cl_2 compound **2** exhibited a broad absorption, half-height width of 101 Hz, for methyl group carbons and two absorptions separated by 76 Hz at δ 79.0 and 82.8 for nonequivalent quaternary carbons. The room temperature carbon and ^1H NMR spectra suggest that there is an intramolecular ligand reorganization process between trigonal-bipyramidal (TBP) structures or that **2** is square pyramidal (SP). An ionization process would render the methyl group carbons and hydrogens equivalent. The low-temperature carbon spectrum eliminates an SP structure and strongly supports a TBP or near-TBP structure. The $\Delta G^{\ddagger}$ for the ligand reorganization is 8 kcal/mol[8] with a coalescence temperature of −105 °C.

It is interesting to compare the result of this study with those found for five-membered ring containing oxyphosphoranes and sulfuranes. Many such phosphoranes exist as SP structures in the crystalline state,[9] whereas the sulfuranes favor TBP[10] structures as solids or in solution. The solution structures of the oxyphosphoranes are not known; it is clear though that SP structures have not been eliminated. The structures of **1** and **2** follow the pattern found for the sulfuranes with a very similar activation energy for the ligand reorganization process.[11]

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(6) Compound **1** had the properties reported.[4]
(7) Compound **2** was prepared by allowing selenium tetrachloride, pinacol, and triethylamine to react in THF. The triethylamine hydrochloride was removed by filtration. The THF solution was concentrated and **2** was crystallized at −25 °C. A sublimed sample had mp 89–91 °C. Anal. Calcd for $C_{12}H_{24}O_4Se$; C, 46.30; H, 7.77. Found: C, 46.57; H, 7.73. The ^{77}Se chemical shift of **1** is δ 1261 relative to dimethyl selenide and that of **2** is δ 1203.
(8) The maximum separation may not have been achieved at −112 °C. A further separation of the two resonances would lead to a slightly lower activation energy.
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Book Reviews

Herbicides: Physiology, Biochemistry, Ecology. Second Edition. Volumes I and II. Edited by L. J. AUDUS (Bedford College, London University). Academic Press, New York–London–San Francisco. 1976. Vol I: xii + 608 pp. $48.00. Vol. II: xx + 564 pp. $38.25.

This two-volume set consists of review articles that deal with aspects of herbicides ranging from chemical classification to mechanism of action, from physical behavior to herbicidal selectivity. As such, they will be of greatest interest to researchers specializing in herbicide synthesis, to agricultural chemists, and plant biochemists. Analytical chemists, toxicologists, and ecologists will also discover a wealth of research opportunities in the articles which review the literature of the field to 1974.

Volume **I** is concerned primarily with studies of the mechanism of action of nearly 150 common herbicides. The mechanism studies are discussed in a systematic way, focusing in separate articles on the different sites at which disfunction affects normal growth and development of the plant, i.e., at the level of growth hormone control, cell membrane formation, or by interference with photosynthesis, respiration, metabolism, RNA transcription, or protein synthesis. Encyclopedic reviews of the literature detail the effects of specific herbicides on a wide variety of plant species. A particularly interesting chapter shows the power of electron microscopy in revealing alterations in the fine structure of cellular components induced by chemical treatment. The strategy of using sublethal levels of herbicides to study the mechanisms of control of normal plant development is implicit in the discussion.

The behavior or herbicides in the soil and the fate of the chemicals in the environment are considered in Volume II. Articles describing the known routes of detoxification of herbicides by target plants, biodegradation by other organisms, and nonbiological modes of herbicide decomposition are particularly interesting mechanistically. The point is made that of the 150 chemicals used as herbicides worldwide, few have been completely studied to determine their metabolic and environmental degradation products.

Other articles in Volume II discuss the effects of herbicides on nontarget plants, soil microorganisms, and higher animals. Discussion also focuses on the variables which determine the selectivity and effectiveness of herbicides, with particular emphasis on environmental factors and selectivity resulting from differential absorption or metabolism by various plant species. An extensively referenced article