3

$a_\alpha^H = 7.33$ (2 H), 1.40 (2 H) G

$a_\beta^H = 0.48$ (2 H) G

$g = 2.00494$
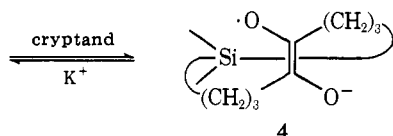
4

$a_\alpha^H = 3.6$ (2 H), 2.3 (2 H) G

$g = 2.00507$

silacyclononane-1,2-semidiones as the ion-paired (**3**) and free ion (**4**), respectively.

References and Notes

(1) Aliphatic Semidiones. 37.
(2) G. A. Russell, G. Wallraff, and J. L. Gerlock, *J. Phys. Chem.*, **82**, 1161 (1978).
(3) With Li⁺ only the cis ion pair can be detected, whereas with Cs⁺ only the trans semidione is observed: G. A. Russell, D. F. Lawson, H. L. Malkus, R. D. Stephens, G. R. Underwood, T. Takano, and V. Malatesta, *J. Am. Chem. Soc.*, **96**, 5830 (1974).
(4) H. C. Heller, *J. Am. Chem. Soc.*, **86**, 5346 (1964); C. Corvaja, P. L. Nordio, and G. Giacommeti, *ibid.*, **89**, 1751 (1967).
(5) Prepared by the disproportionation of α-hydroxycyclopentanone in Me₂SO in the presence of K⁺CH₃SOCH₂⁻. To obtain the spectra in the presence of Li⁺, Na⁺, or (C₂H₅)₄N⁺ the K⁺ salt of the semidione was treated with a slight excess of [2.2.2] cryptand to give the free semidione ion to which the new counterion was added as the iodide or perchlorate salt.
(6) Experiment performed by Mr. B. Graether.
(7) a^K is not observed for 1,2-semidiones even in the presence of crown ethers (which for Na⁺ greatly reduces the rate of the exchange; semidione⁻·, Na⁺ + *Na⁺ ⇌ semidione⁻·, *Na⁺ + Na⁺).² a^K can be observed in Me₂SO for semidione radical dianions (unpublished work with Mr. T. Takano), such as that shown.
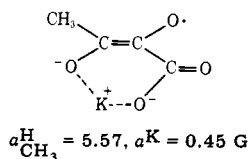
$a_{CH_3}^H = 5.57, a^K = 0.45$ G

(8) a_{CO}^C in cis-dimethylsemidione increases from 1.1 (K⁺, Me₂SO) to 1.4 (Na⁺, Me₂SO), 1.8 (Li⁺, Me₂SO), 1.9 (K⁺, *tert*-butyl alcohol). In Me₂SO a^H increases from 7.0 (K⁺) to 7.1 (Na⁺) to 7.4 (Li⁺).³
(9) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).
(10) National Science Foundation Fellow, 1975–1978.

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Conversion of Allyl Alcohols to Dienes by Sulfoxide and Selenoxide Syn Elimination. Synthesis of PCB Arene Oxides

Sir:

Of the many procedures and reagents available for the dehydration of alcohols, few work well for the conversion of allyl alcohols to dienes, and even fewer provide for regiospecific dehydration. We report here a new procedure (Scheme I, Y = S, Se) for the 1,4 dehydration of allyl alcohols, and application of this method as a key step in the synthesis of chlorinated and brominated biphenyl oxides.

Treatment of alcohol **1a** with 2-nitro-4-methylbenzeneselenenyl chloride in refluxing dichloromethane leads to diene

Table I. 1,4-Dehydration of Allyl Alcohols Using 2,4-Dinitrobenzenesulfenyl Chloride–Triethylamine

run	allyl alcohol	diene		yields, %^{a}
1	**1a**	**2a**		83^b
2	**1b**	**2b**		66^b
3	**1c**	**2c**		79^b
4	(structure)	(structure)		68^c
5	(structure)	(structure)		77^c
6	(structure)	(structure)	C_6H_5	71^c
7			$2,5$-Cl_2-C_6H_3	<10^c
8	(structure)	(structure)	C_6H_5	75^b
9			$2,5$-Cl_2-C_6H_3	58^b
10	(structure)	(structure)		74^b
11	(structure)	(structure)		73^b
12	(structure)	(structure)		54^{c,d}

^{a} Reactions were carried out on 1–10 mmol of allyl alcohol; products were purified chromatographically or by distillation. ^{b} Reaction in CH_2Cl_2 at 25–40 °C. ^{c} Reaction in $ClCH_2CH_2Cl$ at 80 °C. ^{d} The diene was a 60:40 mixture of *E,E* and *E,Z* isomers.

Scheme I

(a) $2,5$-Cl_2-C_6H_3-
(b) 4-Cl-C_6H_4-
(c) C_6H_5-
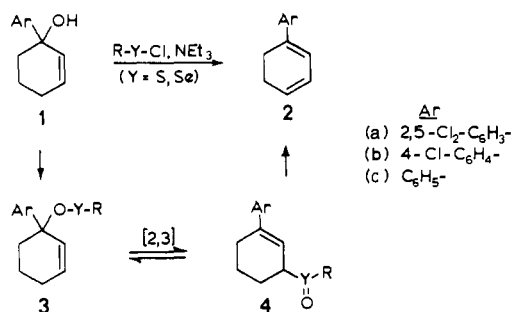
2a (65% yield). The reaction must proceed by [2,3]-sigmatropic rearrangement of selenenate ester **3** to the allyl selenoxide **4**, which fragments to diene.¹ There are several reported examples of allyl selenoxide to selenenate rearrangements,²,⁵ but this is the first demonstration of the allyl selenenate to selenoxide conversion.

In the course of attempting to generalize the process described above a number of readily available selenenyl (PhSeCl, 2,4-(NO₂)₂C₆H₃SeBr) and sulfenyl (CCl₃SCl, 2-NO₂C₆H₄SCl, 2,4-(NO₂)₂C₆H₃SCl) halides were examined. It was hoped that the powerful electron-attacting substituents in the sulfenyl halides, together with the acceleration provided by the allylic nature of the sulfoxide intermediate, would lead to sufficiently fast sulfoxide syn elimination⁶ to accommodate the mild reaction conditions desirable for the synthesis of reactive dienes. 2,4-Dinitrobenzenesulfenyl chloride is the reagent currently showing the most promise. Of a variety of reaction conditions tried, treatment with 2.4 equiv⁷ of the sulfenyl chloride and 3 equiv of triethylamine in dichloromethane (−30 to 40 °C) or 1,2-dichloroethane (20 to 80 °C) gave the highest yields. Table I presents several examples using these conditions.⁸ At its current stage of development, the reaction proceeds in acceptable yield for a variety of allyl alcohols. One

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

	X_1	X_2
(a)	Cl	Cl
(b)	H	Br
(c)	Br	Br
(d)	Br	H
(e)	H	H
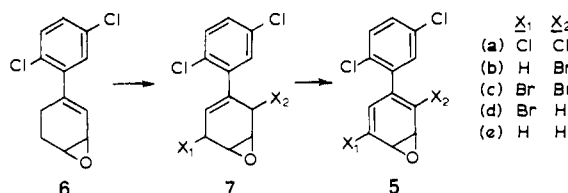
intermediate epoxide **6**. This compound could be monobrominated (22% yield of crystalline **7b**, mp 145–146 °C), dibrominated (50% yield of crystalline **7c**, mp 146–147 °C, based on **2a**), and tribrominated under progressively more vigorous conditions using *N*-bromosuccinimide. The desired tetrachlorobiphenyl 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 phenols **8** and **9**, whose substitution pattern was unambiguously assigned by analysis of the 270-MHz NMR spectra.[15]
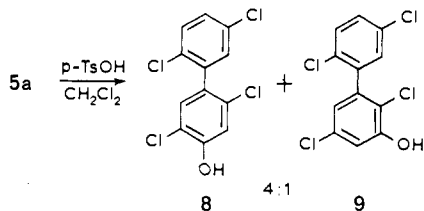
The arene oxides **5c 5d**, and **5e** were similarly prepared by dehydrobromination of the appropriate bromide.

References and Notes

(1) A related procedure for diene preparation involving thermolysis of allylic sulfinamides has been reported recently: Hori, T.; Singer, S. P.; Sharpless, K. B. *J. Org. Chem.*, **1978**, *43*, 1456.
(2) There are two reported examples of competing syn elimination and [2,3]-sigmatropic rearrangement of allyl selenoxides[3a] and one involving a propargyl selenoxide.[3b] Pyrolysis of allyl sulfoxides leads to [1,3]-sigmatropic rearrangement in the absence of a sulfenate trap.[4]
(3) (a) Reich, H. J. *J. Org. Chem.*, **1975**, *40*, 2570. Salmond, W. G.; Barta, M. A.; Cain, A. M.; Sobala, M. C. *Tetrahedron Lett.*, **1977**, 1683. (b) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.*, **1977**, *99*, 263.
(4) Evans, D. A.; Andres, G. C., *Acc. Chem. Res.*, **1974**, *7*, 147. Kwart, H.; George, T. J. *J. Am. Chem. Soc.*, **1977**, *99*, 5214.
(5) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.*, **1972**, *94*, 7154.
(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).
(9) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.*, **1975**, *97*, 3250.
(10) (a) Hsu, I. C.; Van Miller, J. P.; Allen, J. R. *Bull. Environ. Contam. Toxicol.*, **1975**, *14*, 233. (b) Hsu, I. C.; Van Miller, J. P., Seymour, J. L.; Allen, J. R. *Proc. Soc. Exp. Biol. Med.*, **1975**, *150*, 185. Gardner, A. M.; Chen, J. T.; Roach, J. A. G.; Ragelis, E. P. *Biochem. Biophys. Res. Commun.*, **1973**, *55*, 1377.
(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).
(12) De Crauw, Th. *Recl. Trav. Chim. Pays-Bas*, **1931**, *50*, 753.
(13) **5a** was purified by TLC on silica gel and crystallization: mp 75–76 °C; 38% yield from **7a**; NMR (δ, CDCl₃) 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 C₁₂H₆Cl₄O: 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-d₆) 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 C₁₂H₆Cl₄O: 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 = CH₃