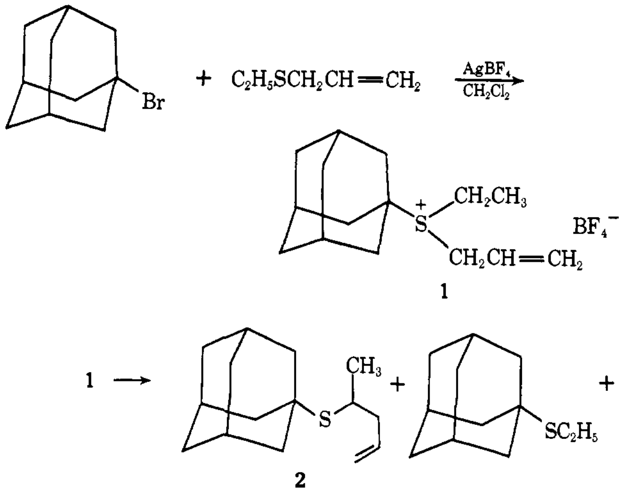
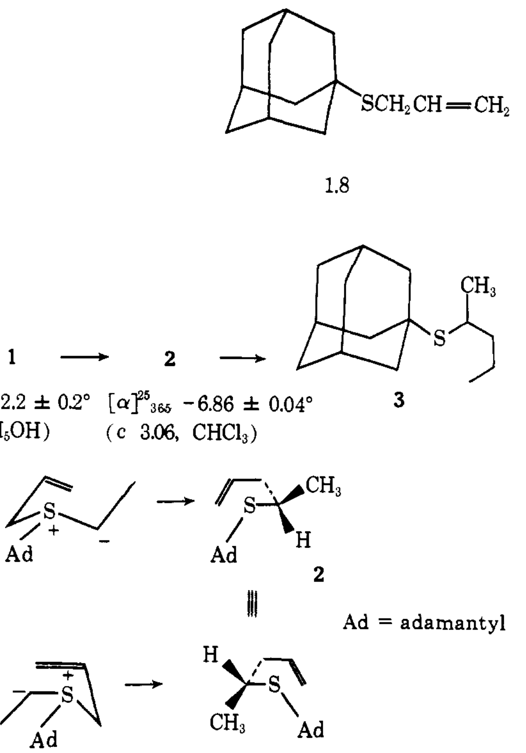
Scheme II. Preparation and [2,3] Sigmatropic Rearrangement of Optically Active Ylide



	2	
$KOC(CH_3)_3$-$(CH_3)_3COH$	30.8%	13.3%
$KOC(CH_3)_3$-$(CH_3)_3COH$-PhH-crown ether[a]	74.4	17.4
$KOC(CH_3)_3$-$(CH_3)_3COH$-$PhCH_3$	62.3	10.4



[a] Crown ether employed was dicyclohexyl-18-crown-6 ether.

A brief discussion of the mechanism of the [2,3] sigmatropic rearrangement is in order.[12–14] Obviously, the faithful translation of optical activity from sulfur to carbon supports the concerted nature of the rearrangement. Assuming the folded envelope conformation, obtention of the *R* enantiomer of sulfide requires the conformations depicted in Scheme II for the *R* and *S* configurations of π sulfurane. Of the possible reactive conformations of the *S* enantiomer, the one depicted minimizes nonbonded interactions, whereas the one depicted for the *R* enantiomer maximizes the nonbonded interactions. On this basis the *S* configuration may be assigned to the starting salt. The observation of such high optical induction for the [2,3] sigmatropic rearrangement has important implications in relation to the formation of presqualene and its monoterpene analog chrysanthemol.[15,16]

Acknowledgment. We wish to thank the National Institutes of Health and the National Science Foundation for their generous support of our program.

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(12) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, (1969); R. W. C. Cose, A. M. Davies, W. D. Ollis, C. S. Smith, and I. O. Sutherland, *Chem. Commun.*, 293 (1969).

(13) For an oxygen analog see J. E. Baldwin and J. E. Patrick, *J. Amer. Chem. Soc.*, **93**, 3556 (1971); V. Rautenstrauch, *Chem. Commun.*, 4 (1970). For transfer of chirality from nitrogen to carbon in a Stevens rearrangement, see R. K. Hill and T. H. Chan, *J. Amer. Chem. Soc.*, **88**, 866 (1966).

(14) For a nitrogen analog see R. W. Jemison and W. D. Ollis, *Chem. Commun.*, 294 (1969); S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *ibid.*, 1494 (1971).

(15) B. M. Trost, P. Conway, and J. Stanton, *ibid.*, 1639 (1971).

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(17) Recipient of Camille and Henry Dreyfus Teacher-Scholar Award.

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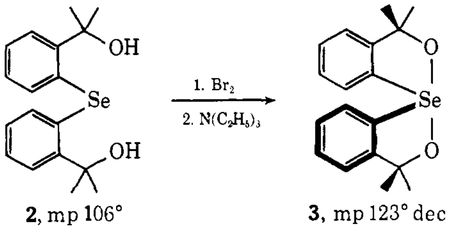
Organoselenium Stereochemistry. Configurational Stability of Dialkoxydiarylselenium Compounds

Sir:

We wish to report the synthesis and characterization of several new cyclic chiral dialkoxydiarylselenuranes,[1,2] and some results of a study of their configurational stability, including the first example of the separation of diastereomers differing in configuration at tetracoordinate selenium.

The reaction of dimethyl 2,2′-selenodibenzoate[4c] (1) with methyllithium gave the tertiary glycol 2[7a] which could be cyclized to the spiroselenurane 3[1b,7a] by treatment of the corresponding selenide dibromide with triethylamine. Compound 3 was assigned the indicated structure on the basis of the following evidence:



2, mp 106° **3**, mp 123° dec

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(1) (a) We use the name "selenurane" (in analogy with sulfurane) for tetrasubstituted selenium(IV) compounds. The name selenane, used by J. I. Musher,[3a] is not acceptable since it is the established systematic name for selenacyclohexane. (b) The *Chemical Abstracts* name for 3 is 3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzooxaselenole].

(2) Dialkoxyselenuranes,[4a] diacyloxyselenuranes,[4b,c] and related sulfur compounds[5,6] have been reported.

(3) For a discussion of bonding in high-valent metalloid compounds, see: (a) J. I. Musher, *Ann. N. Y. Acad. Sci.*, **192**, 52 (1972); (b) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

(4) (a) R. Paetzold and U. Lindner, *Z. Anorg. Allg. Chem.*, **350**, 295 (1967); (b) D. G. Foster, *Recl. Trav. Chim. Pays-Bas*, **54**, 447 (1935); (c) R. Lesser and R. Weiss, *Chem. Ber.*, **47**, 2510 (1914).

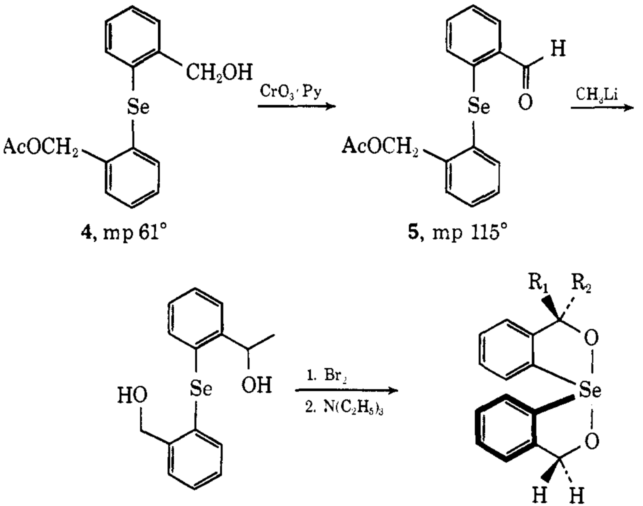
(5) (a) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997 (1972); (b) E. F. Perozzi and J. C. Martin, *ibid.*, **94**, 5519 (1972).

(6) I. Kapovits and A. Kalman, *Chem. Commun.*, 649 (1971).

(7) (a) Elemental analysis, nmr spectra (CCl_4), and infrared spectra were consistent with the structures assigned. (b) High temperature nmr spectra were measured using hexachlorobutadiene as solvent.

the infrared spectrum does not show hydroxy or selenoxide[8] absorption. The nmr spectrum, in addition to an aromatic multiplet,[9] has two methyl singlets, at δ 1.51 and 1.57. The compound is stable to hydrolysis, nonpolar, soluble in pentane, and can be chromatographed on silica gel using pentane as eluent.[10] The diastereotopic methyl groups are consistent with a chiral trigonal-bipyramidal[11] structure, and they remain diastereotopic[7b] up to 200°, so that enantiomer interconversion through pseudorotational[12] or other processes has a free energy of activation greater than 27 kcal/mol.

That the high configurational stability of **3** is not entirely due to steric hindrance by the gem-dimethyl groups or the geometric constraints imposed by the spiro structure is shown by the following results. Lithium aluminum hydride reduction of the diester **1** followed by partial acetylation of the diol[7a] gave the hydroxyacetate **4**,[7a] which was oxidized to the aldehyde **5**[7a] using a modified Collins procedure.[13] Treatment of **5** with methyllithium gave the diol **6** which could be brominated and cyclized to a 74:26 mixture of diastereomeric spiroselenuranes **7a** and **7b** (nmr, C_6D_6, **7a**: δ 1.54, d, J = 6.5 Hz, CH_3; 5.30, s, CH_2; 5.42, q, J = 6.5 Hz, CH; 6.7–7.2, m, Ar H; 8.21, m, *o*-Ar H;[9] **7b**: 1.40, d, CH_3; 8.5, m, *o*-Ar H;[9] other peaks obscured by the major isomer). Two crystallizations of this mixture from ether gave 98:2 ratio of the two isomers. Isomerization back to the equilibrium mixture occurred with a half-life of 220 min in benzene-d_6 at 120°. The minimum free energy of activation for configurational inversion at selenium in **7** is thus 30.9 kcal/mol. We have not established whether the isomerization of **7a** to **7b** is an intramolecular rearrangement, or a water or otherwise catalyzed reaction,[14] nor, in fact, can we say with certainty that isomerization is occurring at selenium rather than at carbon. These matters are under investigation.

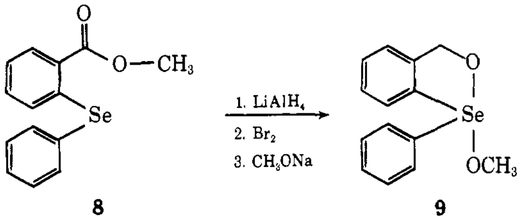


4, mp 61° **5**, mp 115°

6

7a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$

Monocyclic dialkoxyselenuranes also show substantial resistance to configurational isomerization. Methyl 2-phenylselenobenzoate[4c] (**8**) gives the alcohol on reduction. The corresponding dibromide could be converted to the extremely water-sensitive selenurane **9** by treatment with sodium methoxide in methanol–ether under anhydrous conditions (nmr: δ 4.62, 5.01, AB q, J = 14 Hz, 2 H; 3.36, s, 3 H; 7.0–7.3 m, Ar H, 6 H; 7.8, m, *o*-Ar H,[9] 2 H; 8.15, m, *o*-Ar H,[9] 1 H). The protons of the diastereotopic methylene group remain nonequivalent[7b] up to 140°, at which temperature **9** rapidly decomposes. Thus, here also the barrier to configurational isomerization at selenium is at least 20.7 kcal/mol.



8 **9**

These results are consistent with what is known about isomerization of pentacoordinate compounds. The main factors governing the stability of isomeric trigonal bipyramidal phosphoranes are the following:[15] small rings prefer to span apical–equatorial postions, and electronegative groups prefer apical positions. If the reasonable assumption is made that these apply to the chalcogens also, a high barrier to enantiomer (or diastereomer) interconversion through a series of pseudorotations would be predicted for compounds **3**, **7**, and **9**, since both rules have to be violated for such isomerizations to occur. In addition, it may well be that the energy requirement for placing a lone pair of electrons in an apical position is prohibitive,[3] thus preventing all Berry pseudorotations except those involving the lone pair site as pivot.

No well-documented case of pseudorotation in sulfuranes or selenuranes has been reported: SeF_4,[16] SF_4,[16] $PhOSF_3$,[17] and $PhSF_3$[18] all show intermolecular fluorine exchange or distinct apical and equatorial fluorines in the nmr spectrum. The spiro systems **10**[19] and **11**[5b] have nonequivalent fluorines at room temperature, as does an acyclic analog of **11**.[5a] The re-

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(8) R. Paetzold and G. Bochmann, *Spectrochim. Acta, Part A*, **26**, 391 (1970).

(9) In all selenuranes of this type, protons ortho to the selenium were strongly downfield shifted to the region δ 7.5–8.5.

(10) Rapid elution is necessary for this chromatography, otherwise **3** behaves as a very polar substance, requiring ether or ether–methanol to be removed. We believe that the selenurane is hydrolyzed to a monocyclic or acyclic compound on the silica gel, with the formation (reversibly) of highly polar selenoxide and hydroxide functions.

(11) Distorted trigonal bipyramidal structures (with one equatorial site vacant) have invariably been found for tetracoordinate selenium(IV) and sulfur(IV) compounds. For example: (a) selenium tetrafluoride: I. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectrosc.*, **28**, 454 (1968); (b) diphenylselenide dichloride: J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.*, **64**, 508 (1942); (c) dialkoxydiphenylsulfurane: I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **94**, 5011 (1972).

(12) I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie, *Accounts Chem. Res.*, **4**, 288 (1971), and references therein.

(13) R. Radcliffe and R. Rodehurst, *J. Org. Chem.*, **35**, 4000 (1970).

(14) Isomerization rates (nmr integration) follow first-order kinetics and are reasonably reproducible, but the rate in pyridine containing 10% deuterium oxide is at least 25 times as fast as in dry pyridine. Thus, the isomerization in benzene could conceivably involve catalysis by trace amounts of water.

(15) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970).

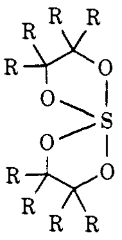
(16) E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959); J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 1016 (1963).

(17) J. I. Darragh and D. W. A. Sharp, *Angew. Chem., Int. Ed. Engl.*, **9**, 73 (1970).

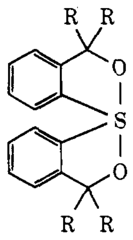
(18) W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3058 (1962).

(19) M. Allan, A. F. Janzen, and C. J. Willis, *Can. J. Chem.*, **46**, 3671 (1968).

markable compound, tetrakispentafluorophenylsulfurane, recently reported by Sheppard[20] may be an exception, since it showed only one pentafluorophenyl group in the nmr spectrum, but here also an intermolecular mechanism could be operative.



10, R = CF$_3$



11, R = CF$_3$

Conceptually, sulfuranes and selenuranes have an isomerization pathway open to them which is not available to phosphoranes, *i.e.*, the possibility of lone pair inversion through a square planar transition state. Clearly, the relatively high configurational stability of the selenuranes reported here suggests that such a pathway is no more, and perhaps less energetically accessible than the intermediates required for isomerization *via* Berry pseudorotation.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(20) W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 5597 (1971).

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Received August 24, 1972

Isomerization of Cyclopropane. A Molecular Orbital Study on Alternative Mechanisms

Sir:

Recently the mechanism of the stereoisomerization of cyclopropane was investigated with EHT[1] and with *ab initio* methods.[2,3] In these studies the attention was focused on trimethylene biradical-like transition states characterized by one long C–C distance.

During our MO studies on carbene insertion reactions,[4] we found that alternative mechanisms involving transition states with two long and one short C–C bonds or with three C–C bonds of about equal length are feasible according to the calculated activation energies. The results of these calculations are presented in this preliminary communication.

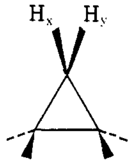
The method used in this study is our modified[5] CNDO[6] procedure. In general it yields satisfactory heats of atomization together with reasonable equilibrium geometries for hydrocarbons,[5] hydrocarbon radicals,[7] and carbocations.[8] The ability of the method to allow a complete minimization of the energy of a molecular system with respect to its geometrical parameters is essential for the calculation of reaction coordinates.

As MO theoretical calculations have shown,[4,9] insertion reactions of carbenes proceed *via* a concerted two-step mechanism. In the first step, the empty orbital of the carbene attacks a bonding orbital of the substrate forming a three center bond as in I. (I corresponds to the prototype reaction CH$_2$ + H$_2$.[4b]) In the second phase of the reaction the lone pair of the carbene combines with the antibonding substrate orbital leading to the final product orbitals. The addition of methylene to double bonds[10] proceeds analogously.[9b,10]

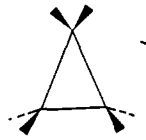
We found that in the methylene adduct I the original H$_2$ has a low rotational barrier about the axis perpendicular to the H–H bond. Thus, a mechanism for the thermal enantiomerization process at a tetragonal C atom *via* II as the transition state is conceivable.

I

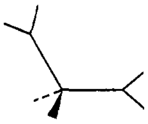
II



III



IV



V

According to our calculations this mechanism describes the minimum energy path for the interchange of two H atoms in methane. Analogous mechanisms are conceivable for the cis–trans isomerization of cyclopropane. We have investigated three different mechanisms for the interchange of two hydrogens at the same C atom of cyclopropane characterized by the structures of the corresponding transition states.

1. The transition state III can be described as an adduct of cyclopropylidene and H$_2$. III is characterized by three C–C bonds of comparable length (C1–C2 = 1.50 Å; C2–C3 = 1.51 Å; C–C in cyclopropane: 1.51 Å[5]). The three-center bond in III leads to a short H$_x$–H$_y$ distance (0.82 Å as compared with the calculated value for H$_2$ of 0.73 Å) and to stretched C–H$_x$ and C–H$_y$ bonds (1.36 Å). Energetically III comes out to be 73 kcal/mol above cyclopropane. A different and probably less favorable[1,11] transition state with an intact cyclopropane ring was proposed previously.[12]

2. The transition state IV can be described as an adduct of methylene and ethylene. In IV, the three carbon atoms participate in the three-center bond. Thus, two stretched and one shortened C–C bonds (1.61 and 1.42 Å, respectively) are obtained. The mechanism involving IV entails an activation energy of 67 kcal/mol.

A transition state which is analogous to IV but with the restriction of the CCC plane to be a symmetry plane was also considered by Salem, *et al.*,[2b] but found

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(1) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(2) (a) J. A. Horsley, Y. Lean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972); (b) Y. Lean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser and R. M. Stevens, "Proceedings of the 23rd IUPAC Congress, Boston 1971," Butterworths, Washington, D. C., 1971.

(3) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 638 (1972).

(4) (a) H. Kollmar and H. O. Smith, *Angew. Chem.*, **84**, 680 (1972); (b) H. Kollmar, *Tetrahedron*, in press.

(5) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

(6) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).

(7) H. Kollmar, *Chem. Phys. Lett.*, **8**, 533 (1971).

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(9) (a) R. C. Dobson, O. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6189 (1971); (b) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972).

(10) R. Hoffmann, R. Gleiter, and F. B. Mallory, *ibid.*, **92**, 1460 (1970).

(11) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(12) F. T. Smith, *ibid.*, **29**, 235 (1958).