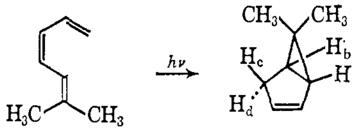


8a **9**

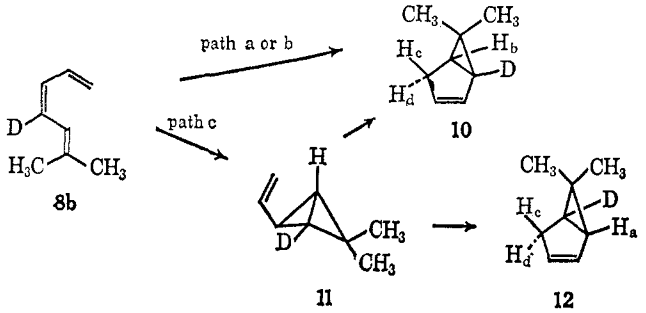
ment was based on analogy with previously studied cyclization reactions and the following physical evidence.

The infrared spectrum of **9** showed maxima at 3020 (m), 2910 (s), 1440 (m), 1370 (m), and 940 (m) cm^{-1}. The mass spectrum showed its parent peak at m/e 108, and the ultraviolet spectrum showed $\lambda_{max}^{cyclohexane}$ 211 mμ (ϵ 4030). The 100-Mc nmr spectrum of **9**[13] allowed the identification of *endo-* and *exo*-methyl groups at τ 9.3 and 9.0, respectively, H_b as a triplet ($J_{ab} = J_{bd} = 7$ cps) at 8.86, H_a as an unresolved multiplet at 8.45, H_c as a doublet ($J_{cd} = 18$ cps, $J_{bc} = 0$ cps) at 8.1, H_d as a doublet of doublets ($J_{cd} = 18$ cps, $J_{bd} = 7$ cps) centered at 7.60, and the olefinic protons as an unresolved multiplet at 4.55. Thus, a good, unidirectional example of the desired photocyclization was available for the key labeling experiment.

The synthesis of **8b** was carried out in a manner analogous to that of **8a**. Reduction of methyl β-methylcrotonate with lithium aluminum deuteride afforded **6b**. Manganese dioxide oxidation of **6b** gave **7b**, whose infrared spectrum showed pertinent maxima at 2100 (m) and 1670 (s) cm^{-1}. The nmr spectrum had resonances at τ 8.30 and 8.10 (allylic methyl doublets) and a broad singlet at 4.50 (olefinic proton). The aldehydic proton signal, at τ 0.75 in **7a**, was absent. The mass spectrum showed its parent peak at m/e 85 with a strong peak at 83.[11,14]

Treatment of **7b** with the appropriate Wittig reagent afforded **8b**. The infrared spectrum showed pertinent maxima at 2250 (w), 2200 (w), and 2100 (w) cm^{-1}. The nmr spectrum showed a broad allylic methyl signal at τ 8.25 and olefinic protons from 3.1 to 5.1. The mass spectrum had its parent peak at m/e 109.[14]

Photoisomerization of **8b** *via* paths a or b should now lead to **10**, while preliminary cyclization to **11** should lead to equivalent amounts of **10** and **12** (neglecting small kinetic isotope effects).



Irradiation of **8b** followed by glpc isolation of the product afforded labeled 6,6-dimethylbicyclo[3.1.0]hex-2-ene whose mass spectrum showed its parent peak at m/e 109.[14] The product was shown to be **10** rather than a mixture of **10** and **12** on the basis of its 100-Mc nmr spectrum. The nmr spectrum of **10** showed, as expected, H_b as a doublet ($J_{bd} = 7$ cps) at τ 8.86, H_c as a doublet ($J_{cd} = 18$ cps, $J_{bc} = 0$ cps) at 8.1, and H_d as a doublet of doublets ($J_{cd} = 18$ cps, $J_{bd} = 7$ cps) at 7.60. There was no resonance at τ 8.45 corresponding to H_a in **9**.

The theoretical spectrum for a path c product mixture would show H_b as a doublet ($J_{bd} = 7$ cps) at τ 8.86 (from **10**), H_a as a diffuse singlet at 8.45 (from **12**), and H_d as a doublet ($J_{cd} = 18$ cps) at 7.60 superimposed on a doublet of doublets ($J_{cd} = 18$ cps, $J_{bd} = 7$ cps) from both **10** and **12**.

These data suggest that, at least in simple cases, 2-vinylbicyclo[1.1.0]butanes are not intermediates in the photoisomerization of 1,3,5-hexatrienes or 1,3-cyclohexadienes to bicyclo[3.1.0]hexenes.[15]

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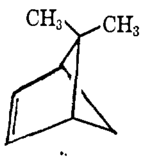
[13] For data on the nmr spectra of bicyclo[3.1.0]hexenes see: W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964); H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965); K. J. Crowley, *Tetrahedron Letters*, 2863 (1965).

[14] A low-voltage mass spectrum indicated that this product was >95% d_1.

[15] By similar arguments it can also be shown that the bicyclo[2.1.1]hexene (i) is not an intermediate in this transformation.



i

[16] National Institutes of Health Postdoctoral Fellow, 1965–1967.

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Received February 10, 1967

Stereochemistry of Asymmetric Silicon. Optically Active Functionally Substituted Disilanes[1]

Sir:

We wish to report the resolution of the first optically active functionally substituted disilanes[2] and the first stereospecific reactions of asymmetric silicon in a disilane in which the silicon–silicon bond remains intact.[3]

Diastereomeric phenylmethyl-(−)-menthoxychlorosilanes, bp 110° (0.1 torr), prepared from phenylmethyldichlorosilane and (−)-menthol,[4] were allowed to couple with triphenylsilyllithium,[5] yielding (±)-1,2,2,2-

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[1] Preliminary studies carried out at The Pennsylvania State University.

[2] For previous work with optically inactive functionally substituted disilanes see: (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 355–356; (b) V. Bazant and V. Chavalovsky, "Organosilicon Compounds," Vol. 1, Academic Press Inc., New York, N. Y., 1965, pp 152–162; (c) A. D. Petrov, B. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, "Synthesis of Organosilicon Monomers," Consultants Bureau, New York, N. Y., 1965, pp 292–293, 374, 483; (d) H. Gilman and R. A. Tomasi, *Chem. Ind.* (London), 954 (1963); (e) H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, 254 (1961); (f) J. V. Urenovitch and A. G. MacDiarmid, *J. Chem. Soc.*, 1091 (1963); (g) U. Stolberg, *Ber.*, **96**, 2798 (1963); (h) J. E. Drake and J. Simpson, *Inorg. Nucl. Chem. Letters*, **2**, 219 (1966); (i) U. Wannagat, G. Schreiner, O. Brandstaetter, and M. Peach, *Monatsh. Chem.*, **96**, 1902 (1965); (j) J. V. Urenovitch and R. West, *J. Organometal. Chem.* (Amsterdam), **3**, 138 (1965); (k) M. Kumada and M. Ishikawa, *ibid.*, **1**, 153 (1963); (l) M. Kumada, K. Naka, and M. Ishikawa, *ibid.*, **2**, 136 (1964); (m) M. Kumada, M. Ishikawa, and S. Maedo, *ibid.*, **2**, 478 (1964).

[3] A nonfunctionally substituted optically active disilane and the stereochemistry of the lithium cleavage of its silicon–silicon bond have been reported previously: L. H. Sommer and R. Mason, *J. Am. Chem. Soc.*, **87**, 1619 (1965).

[4] For a discussion of the partial alcoholysis of polyhalogen silanes, see ref 2a, p 288.

[5] Prepared *via* the modified procedure of H. Gilman, *et al.* See H. Gilman and H. J. S. Winkler "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

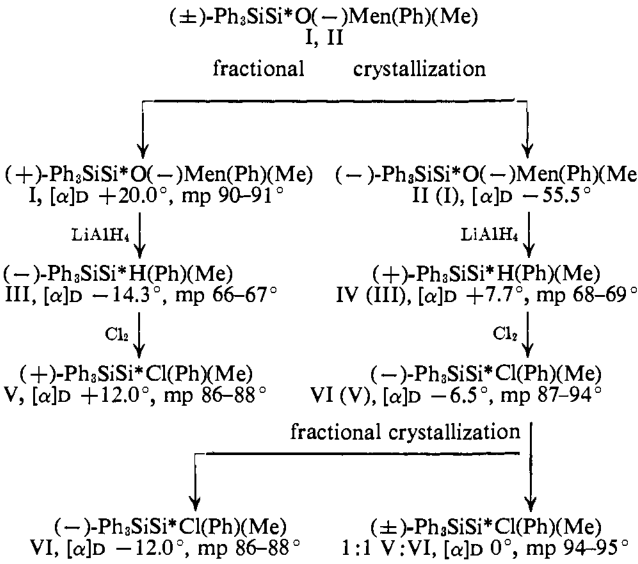
Table I. Stereochemistry for Optically Active $Ph_3SiSi^*X(Ph)(Me)$

Reactant X	Reagent	Solvent	Product X	Minimum stereospecificity	Ref
(−)-H	Cl_2	CCl_4	(+)-Cl	95% retn	7, *a*
(−)-H	Br_2	CCl_4	(+)-Br	73% retn	7, *a*
(+)-Cl	H_2O	Et_2O	(−)-OH	87% invn	*a*
(+)-Cl	MeOH–Et_3N	Pentane	(−)-OMe	90% invn	*a*
(+)-Cl	$LiAlH_4$	Et_2O	(+)-H	95% invn	*a*
(+)-Br	H_2O	Et_2O	(−)-OH	74% invn	*a*
(+)-Br	MeOH–Et_3N	Pentane	(−)-OMe	70% invn	*b*
(+)-Br	$LiAlH_4$	Et_2O	(+)-H	73% invn	*b*
(−)-OH	$LiAlH_4$	Et_2O	(+)-H	87% retn	*a*
(−)-OMe	$LiAlH_4$	Et_2O	(+)-H	90% retn	*a*

[a] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964). [b] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967).

tetraphenyl-1-methyl-1-(−)-menthoxydisilanes (I and II), bp 200° (0.2 torr). Resolution of the syrupy mixture of diastereomers I and II was achieved *via* fractional crystallization, giving (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane (I), mp 90–91°, $[\alpha]_D$ +20.0° (*c* 2.0, pentane), and in lesser optical purity the other diastereomer II (containing some I), $[\alpha]_D$ −55.5° (*c* 1.0, pentane).

Scheme I



In the manner outlined in Scheme I, the diastereomeric relationship of I and II and the enantiomeric relationship of their derivatives have been clearly established. Where phase behavior permitted, recrystallization to constant melting point and rotation was taken as indication of optical purity. The $LiAlH_4$ reduction of I (or II) affords in high yield (−)-1,2,2,2-tetraphenyl-1-methyldisilane (III) (or the corresponding (+) enantiomer IV). Since the melting points (hence, relative solubilities) of III and IV differ only slightly in the racemic and optically active forms, fractional crystallization is futile.[6] However, the 1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilanes (V and VI), prepared *via* chlorination[7] of III and IV, respectively, display in the optically active and racemic modifications different crystalline forms which may be separated mechanically by tweezers after repeated fractional crystallization.[8] Thus identical melting points, infrared spectra, and equal but opposite in sign specific rotations of V and VI prove their enantiomeric relationship.

Assignments of stereochemistry for reactions of the new optically active system are given in Table I. These results are internally consistent and are in complete harmony with previous stereochemical principles which have been found to apply to monosilanes $R_1R_2R_3Si^*X$, where R_1 = Ph, R_2 = Me, and R_3 = α-naphthyl, neopentyl, benzhydryl, or ethyl.[9] References to previous parallel studies with optically active monosilanes are provided by Table I. Relative configurations assigned in Table II are derived from the stereochemical assignments in Table I. Satisfactory infrared spectra and analyses were obtained for all new compounds.

Table II. Enantiomers Having the (−)-$Ph_3SiSi^*H(Ph)(Me)$ Configuration

Compd	$[\alpha]_D$, deg (solvent)	Concn, g/100 ml
(−)-H	−14.3 (pentane)	4.2
(+)-Cl	+12.0 (ether)	4.1
(+)-Br	+ 9.8 (ether)	4.2
(+)-OH	+ 9.8 (ether)	4.2
(+)-OMe	+27.0 (pentane)	4.0

It is of considerable fundamental interest to note that, thus far, replacement of an organic R group in $R_1R_2R_3Si^*X$ by Ph_3Si has not resulted in significant differences in functional group stereochemistry. However, we are continuing to investigate the possibility that substantial differences in the polar and conjugative effects of Ph_3Si,[10] as compared to organic R groups, may affect the stereochemistry of the $Ph_3SiSi^*X(Ph)(Me)$ system.

Acknowledgment. We are grateful for initial support of this work by the Dow Corning Corporation

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(6) This phase behavior differs from that of the α-naphthylphenylmethylsilanes. See L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 42.

(7) The substitution of the hydride H of the disilanes is favored over the cleavage of the Si–Si bond. The newly introduced negative substituent then protects the Si–Si bond against further attack by halogen. See ref 2g.

(8) Starting with 100% racemic $Ph_3SiSi^*Cl(Ph)(Me)$, crystals of the optically active form have not been obtained.

(9) See ref 6, Chapters 3, 4, and 11.

(10) Disilanes have absorptions in the ultraviolet attributed to the silicon–silicon bond acting as a chromophore, probably through the use of vacant d orbitals of the silicon atom. Certain substituents possessing π-electron systems are apparently able to conjugate with the silicon–silicon bond through overlap of d and π orbitals: H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.* (Amsterdam), **2**, 369 (1964).

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Photosensitized Decarbonylation of Furans

Sir:

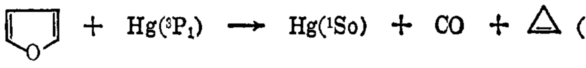
The photochemistry of furans appears to have attracted very little attention. We wish to report that the photosensitized decomposition of furan and two substituted furans in the vapor phase leads to decarbonylation as the principal process.

Irradiation of a mixture of furan (5–150 mm) and mercury vapor at room temperature with the mercury resonance radiation at 2537 A gave rise to carbon monoxide and a C_3H_4 (mol wt, 40 (mass spectrometry)) fraction. By means of infrared analysis, it was observed that this fraction contained very little propyne (3429, 2150, and 1260 cm^{-1}) or allene (1980 cm^{-1})[1] but was made up principally of a third compound with an absorption at 1645 cm^{-1} and an intense band at 998 cm^{-1}. The nmr spectrum of this material (CCl_4 solution at room temperature; $SiMe_4$ as internal reference) showed a triplet at τ 9.04 ($J \sim 1.5$ cps) and another triplet of equal intensity at τ 3.05. The material polymerized readily at room temperature. These data agree well with those reported for cyclopropene by Wiberg and co-workers.[2,3] A vapor sample of this material when condensed with a vapor sample of 1,3-cyclopentadiene was observed to give a product whose infrared spectrum agreed with the spectrum that has been reported for the adduct of cyclopropene and 1,3-cyclopentadiene.[3]

Similarly, the decomposition of 2-methylfuran in the vapor phase by mercury ($^3P_1$) atoms gave carbon monoxide and a C_4H_6 fraction, which was found to consist of a mixture of 1,3-butadiene (45 parts) and 3-methylcyclopropene (55 parts). The latter had an infrared absorption at 1630 cm^{-1} and nmr absorptions at τ 9.04, 8.58, and 3.05 whose intensities were in the ratio of 3:1:2. These data agree with the properties of 3-methylcyclopropene that have been reported by Closs, *et al.*[4]

Mercury-photosensitized decomposition of 2,3-benzofuran in the gas phase also gave carbon monoxide. The only other product that was observed was a polymer.

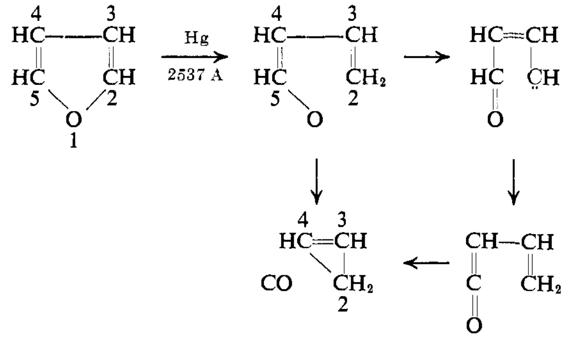
In quantitative studies, it was found that the yield of carbon monoxide was nearly equal to the amount of furan that disappeared. The yield of cyclopropene was even at best only one-half of this value, which is not surprising in view of the instability of this compound at room temperature. The principal photochemical reaction appears to be


(1)

It is possible to write two equations similar to (1) for the formation of allene and propyne. However, it should be noted that reaction 1 requires the migration of only one proton from one carbon to another, whereas the formation of allene or propyne will require the migration of two protons.[5]

The quantum yields for the formation of CO (in the sensitized reaction) from furan (5–15 mm), 2-methylfuran (12 mm), and benzofuran (2 mm) were 0.41, 0.29, and 0.03, respectively. The dependence of the quantum yield on the pressure was studied in the case of furan. Over a 20-fold increase in pressure, the quantum yield decreased by less than a factor of 2. In view of the ready availability of furan and the high quantum yield of reaction 1, the use of this method for the synthesis of cyclopropene is being investigated.[6]

With the data that are available, it is not possible to suggest a unique mechanism for the decarbonylation process. However, certain possibilities can be ruled out. An initial valence tautomerization of furan seems unlikely since irradiation of furan in the condensed phase gave neither carbon monoxide nor an isomer of furan.[7] The most likely pathways are those that follow the initial break of a C–O bond.



It is undoubtedly the C_3–C_4 bond that ends as the double bond in cyclopropene, as 2-methylfuran gives 3-methylcyclopropene rather than 1-methylcyclopropene. The initial break in 2-methylfuran is not likely to be between oxygen and C_2 because a stable acetyl group would then be formed. The elimination of CO from 2,3-benzofuran would also suggest an initial break at the substituted side of the furan ring.

The timing of the initial rupture of the C–O bond cannot be established at present. A concerted mechanism as well as a mechanism which involves a transient vinylketene intermediate are two distinct possibilities. Experiments to distinguish between these two are currently being undertaken.

Acknowledgment. The author wishes to thank Mr. Hershel W. Amburn and Miss Marianne J. Carlson for the nmr spectra, and Dr. Harold Shechter for many helpful discussions.

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(1) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp 337, 339.

(2) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(3) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(4) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3797 (1963).

(5) Propyne is reported to be a product of the pyrolysis of cyclopropene,[3] but allene was not reported to be formed.

(6) The principal requirement seems to be the use of a fast flow system to sweep the cyclopropene from the irradiation zone as quickly as it is formed.

(7) We assume that, if a valence tautomer is formed, it is likely to be stable enough to be detected only in the condensed phase.