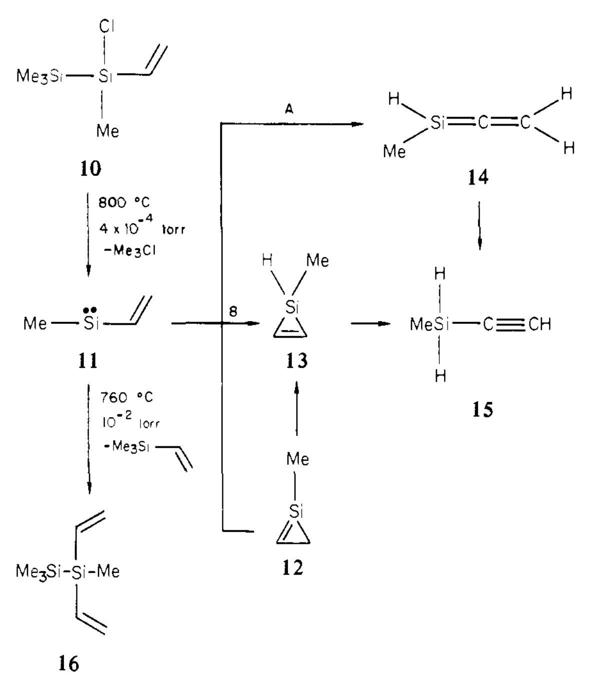
vinyltetramethyldisilane (**10**) by reaction of 1,1-dichlorotetramethyldisilane and 1 equiv of vinylmagnesium chloride in THF [**10**: 42% by NMR, 17% GC isolated; NMR δ 0.17 (s, 9H), 0.5 (s, 3H), 6.08 (m, 3H); mass spectrum, m/e 180 (0.9%), 178 (2.4), 165 (2.2), 163 (4.6), 155 (38), 85 (69), 73 (1 00); calcd for $C_6H_{15}Si_2Cl$ m/e 178.0401, measured m/e 178.0401].



FVP of **10** [800 °C 4 × 10^{-4} torr)] afforded two products of α elimination, trimethylchlorosilane (30%) and trimethylvinylsilane (11.5%), along with a surprising third major product, ethynylmethylsilane [**15**: 11.9% (39% based on Me_3SiCl); NMR of SiMe obscured by impurity absorbtions, δ 2.27 (t, 1H, J = 1 Hz, collapses to s with $h\nu$ at δ 4.05, C≡CH), 4.05 (d of q, 2H, J = 4.5 and 1 Hz, $h\nu$ at δ 2.27 collapses to q; mass spectrum, m/e 70 (27%), 69 (24), 68 (7), 55 (100), 54 (17), 53 (42); both NMR and mass spectrum matched those of an authentic sample of **15** prepared from LAH reduction of dichloroethynylsilane]. Ethynylsilane (**15**) was also observed (by NMR spectrometry among the products from the FVP [760 °C (10^{-2} torr)] of 1,1-divinyltetramethyldisilane (**16**). The major product of this pyrolysis is trimethyl vinylsilane arising from α elimination to afford vinylsilylene **11**. Thus, it seems likely that ethynylsilane (**15**) arises from isomerization of silylene **11**. It is reasonable to suggest that the isomerization is initiated by intramolecular π addition to form 1-silacyclopropene **12** (the known carbene mechanism)[10] followed by (disallowed) hydrogen migration to silicon.

Indeed, the formation of silylacetylenes from the gas-phase copyrolyses of silylene precursors and terminal acetylenes has previously been argued to involve rearrangement of intermediate silacyclopropenes.[4,11] Two other routes are possible: (A) α-C–H insertion to form silaallene **14** followed by 1,3-hydrogen migration; (B) β-C–H insertion to directly form silirene **13**. Neither of these paths has ever been observed for vinylcarbenes.[12] Thus, it is likely, but not demanded, that the isomerization of **11** to **15** involves the intermediacy of silirene **12** and represents another silylene to silene rearrangement. Labeling experiments and alternant methods for generation of **11** must now be performed to clear up the admittedly speculative route for the **11** to **15** isomerization.

Currently we are attempting extensions of these rearrangements, including the obvious cyclopropenylsilylene to silacyclobutadiene isomerization.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 80631-65-8; **3**, 80631-66-9; **5**, 80631-67-0; **6**, 80631-68-1; *cis*-**7**, 74045-33-3; *trans*-**7**, 74045-45-7; **8**, 80631-69-2; **10**, 80631-70-5; **12**, 80631-71-6; **15**, 16689-89-7; **16**, 70745-07-2; 1-methylcyclobutene, 1489-60-7; 1,1-dichlorotetramethyldisilane, 4518-99-4; trimethylmethoxysilane, 1825-61-2; cyclopropyllithium, 3002-94-6; 2,3-dimethylbutadiene, 513-81-5; vinyl chloride, 75-01-4; trimethylchlorosilane, 75-77-4; trimethylvinylsilane, 754-05-2.

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(10) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; pp 328-332.

(11) Haas, C. H.; Ring, M. A. *Inorg. Chem.* **1975**, *14*, 2553.

(12) See ref 10. The π-addition mechanism is obvious from the fact that cyclopropenes are best formed from β,β-disubstituted vinylcarbenes.

Cyclotrisilane $(R_2Si)_3$ and Disilene $(R_2Si{=}SiR_2)$ Systems: Synthesis and Characterization

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Received December 7, 1981

Recent renewed activities in cyclopolysilane chemistry[1] concern the nature of silicon–silicon bonding in small ring systems.[1,2] Thus, the degree of electron delocalization in the yet unknown cyclotrisilane (trisilacyclopropane) system (**1**) attracts special interest.[3] Its physical and chemical properties would be unique in many ways. While a large number of cyclopolysilanes $(CR_2Si)_n$ with $n \geq 4$ are available through the reaction of a dichlorosilane with an appropriate electron donor,[1,4] the thus far unsuccessful construction of this smallest ring system has been attributed (tacitly) to the expected high instability and/or reactivity owing to the ring strain intrinsic to **1**.[5] Apparently, the careful selection of both the silicon substituents (R's) and the electron donor is of vital importance in the synthesis. Using an approach similar, in principle, to that adopted earlier in the synthesis of an isolable cyclobutadiene derivative,[6] we have now achieved the first synthesis of a crystalline derivative, hexa-2,6-dimethylphenylcyclotrisilane (**1a**). We present herein not only unequivocal evidence for the structure of this new compound, but also we describe its remarkable reaction, a near-quantitative photochemical conversion into the corresponding disilene (Si═Si) derivative (**2**),[7,8] yet an-

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† To whom correspondence should be addressed at the Massachusetts Institute of Technology.

‡ Institut de Chimie Physique, Universite de Fribourg Suisse.

(1) For the synthesis of peralkylpolycyclosilanes, see: (a) Watanabe, H.; Muraoka, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45. (b) Watanabe, H.; Muraoka, T.; Kohara, Y.; Nagai, Y. *Chem. Lett.* **1980**, 735. (c) Carlson, C. W.; Matsumura, K.; West, R. *J. Organomet. Chem.* **1980**, *194*, C5. (d) Biernbaum, M.; West, R. *Ibid.* **1977**, *131*, 179 and references quoted therein. (e) For a review of perarylpolycyclosilanes, see: Gilman, H.; Schwebke, G. L. *Adv. Organomet. Chem.* **1964**, *1*, 89.

(2) For the properties of peralkylpolycyclosilanes, see: (a) West, R.; Carberry, E.; *Science* **1975**, *189*, 179. (b) Brough, L. F.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139 and the preceding articles of this series.

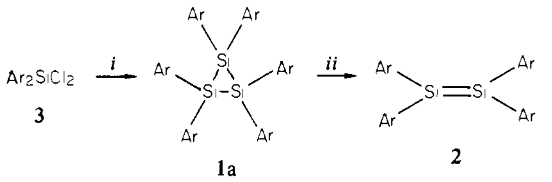
(3) The system is mentioned from time to time in the literature. For instance, see: Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

(4) The method was originated by: Kipping, F. S. *Proc. Chem. Soc.* **1911**, *27*, 143.

(5) Even cyclotetrasilanes $(R_2Si)_4$ react readily with oxygen if the substituents are small, e.g., R = CH_3. See: Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.

(6) (a) Masamune, S.; Nakamura, N.; Suda, M. Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. (b) Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *Ibid.* **1975**, *97*, 1973. (c) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.

Scheme I[a]



Ar: 2,6-dimethylphenyl

[a] (*i*) Lithium naphthalenide. (*ii*) $h\nu$ (253.7 nm); room temperature.

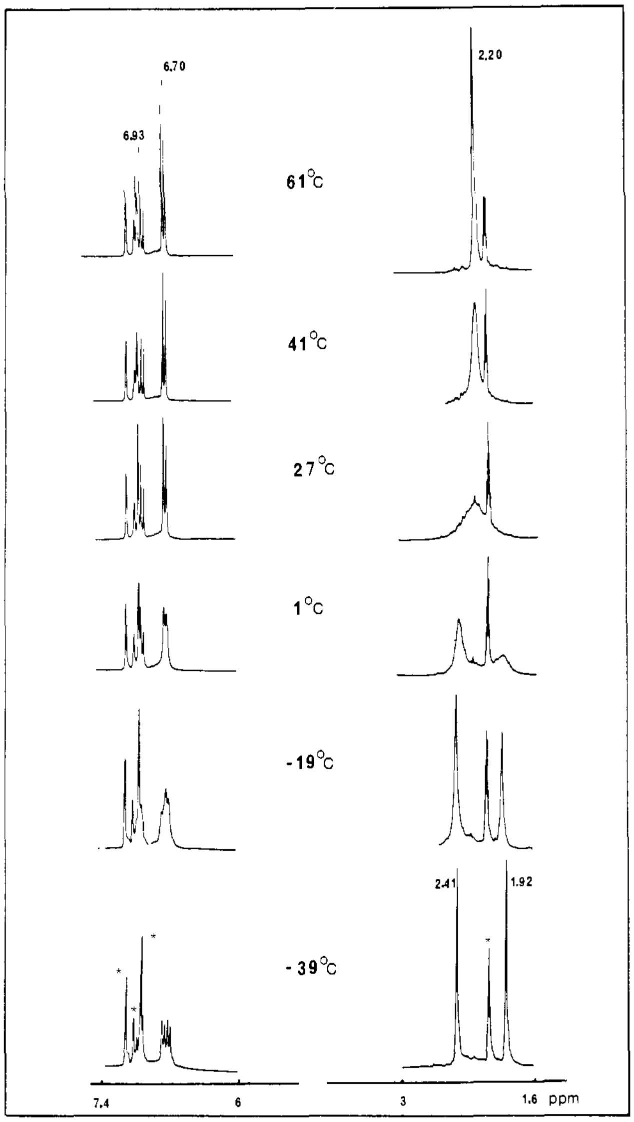


Figure 1. Temperature-dependent ^1H NMR spectra of **1a**. The signals due to the partially deuterated toluene used as solvent are indicated by asterisks.

other new system that has also been sought after for many years (see Scheme I).

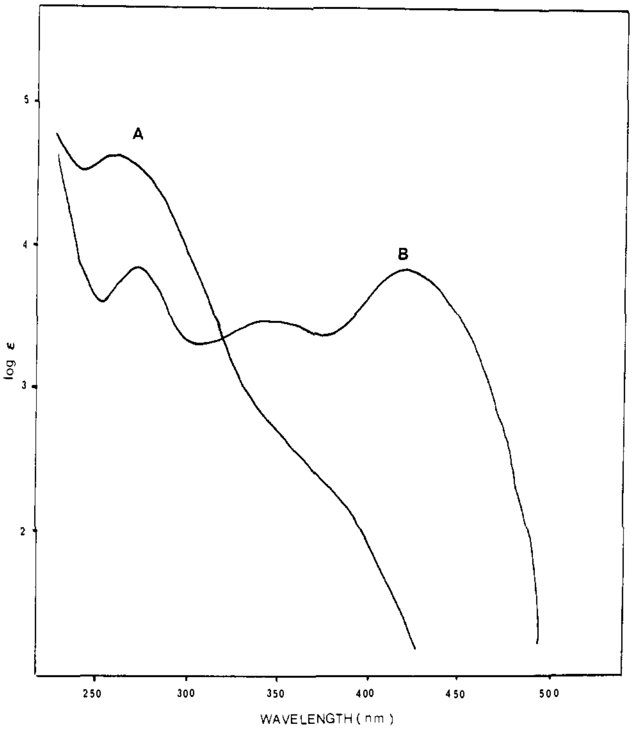


Figure 2. Ultraviolet and visible spectra of **1a** (A) and **2** (B) in cyclohexane.

Synthesis and Spectra Properties of 1a. A solution of bis(2,6-dimethylphenyl)dichlorosilane (**3**)[9] (7.9 g, 25 mmol) in dimethoxyethane (DME) (50 mL) was added dropwise to a cold (−78 °C), dark green solution of lithium naphthalenide prepared from lithium (30% dispersion, 3.6 g, 0.154 g-atom) and naphthalene (**4**) (10 g, 78 mmol) in DME (100 mL).[7b,10] The mixture was stirred for 1 h at −78 °C and then was allowed to warm to room temperature. The usual workup including flash chromatography provided two major products, A and B, in addition to recovered **4**. Compound A, mp 227 °C, R_f 0.55 (30:1 petroleum ether–ether) obtained in 29% yield is readily identified as tetrakis-1,1,2,2-(2,6-dimethylphenyl)disilane on the basis of its spectral data.[11] The other product, B, mp 272–273 °C (recrystallized from 1:4 benzene–petroleum ether) R_f 0.48 (same as above), 10% yield, exhibits physical properties fully consistent with the trimeric structure, $(C_{16}H_{18}Si)_3$: mass spectrum, field desorption mass spectrum, calcd *m/e* 714.3533, found *m/e* 714.3601 (M^+, 100%),[12] electron impact mass spectrum, found *m/e* 714 (M^+, 8%), 476 $[(M - C_{16}H_{18}Si)^+$, 24], 371 $[(M - C_{24}H_{27}Si)^+$, 25], 343 (7), 238 ($C_{16}H_{18}Si$, 49), 133 (C_8H_9Si, 100); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 26.4, 127.48, 128.22, 140.99, 144.50. ^1H NMR spectra show that both the aromatic and aliphatic proton signals (1:2 ratio) are temperature dependent (see Figure 1), indicating hindered rotation of the aromatic rings along the axis of the carbon–silicon bond.

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(7) This disilene species has been postulated as a reaction intermediate. (a) Review: Gaspar, P. P. "Reactive Intermediates"; Jones, M., Moss, R. S., Eds. Wiley: New York, **1978**; Vol. 1, Chapter 7. (b) Roark, D. N.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1972**, *94*, 5837. (c) Barton, T. J.; Kilgour, J. A. *Ibid.* **1976**, *98*, 7746. (d) Wulff, W. D.; Goure, W. F.; Barton, T. J. *Ibid.* **1978**, *100*, 6236. (e) Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *Ibid.* **1979**, *101*, 486. (f) Sakurai, H.; Nakadaira, Y.; Kobayashi, T. *Ibid.* **1979**, *101*, 487. (g) Nakadaira, Y.; Otsuka, T.; Sakurai, H. *Tetrahedron Lett.* **1981**, *22*, 2417. (h) Rich, J. D.; Drahnak, T. J.; West, R.; Michl, J. *J. Organomet. Chem.* **1981**, *212*, C1. (i) Chen, Y.-S.; Cohen, B. H.; Gaspar, P. P. *Ibid.* **1980**, *195*, C1.

(8) For theoretical treatments of disilene, see: (a) Curtis, M. D. *J. Organomet. Chem.* **1973**, *60*, 63. (b) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311. (c) Daudel, R.; Kari, R. E.; Poirier, R. A.; Goddard, J. D.; Csizmadia, I. G. *J. Mol. Struct.* **1978**, *50*, 115. (d) Roelandt, F. F.; van de Vondel, D. F.; van der Kelen, G. P. *J. Organomet. Chem.* **1979**, *165*, 151. (e) Snyder, L. C.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1979**, *101*, 5222.

(9) Prepared according to the procedure reported by: Gilman, H.; Smart, G. N. R. *J. Org. Chem.* **1950**, *15*, 720.

(10) Compare: (a) Sh, T. R.; Andrianov, K. A.; Nogaideli, A. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1396 (*Chem. Abstr.* **1965**, *63*, 16378). (b) Andrianov, K. A.; Nogaideli, A. I.; Sh, T. R. *Ibid.* **1965**, 2228 (*Chem. Abstr.* **1967**, *66*, 8039).

(11) ^1H NMR (270 MHz, $CDCl_3$): δ 2.19 (s, 24H, Me), 5.55 (s, 2H, Si-H), 6.85 [d, 8H, J = 7.32 Hz, Ar-H(3,5)], 7.1 [t, 4H, J = 7.32 Hz, Ar-H(4)]. IR ($CHCl_3$) 2140 (ν_{Si-H}) cm^{-1}. Field desorption mass spectrum calcd *m/e* for $C_{32}H_{38}Si_2$ 478, found *m/e* 478 (M, 100%), M + 1 (45%), M + 2 (16%), (M + 3, 4.9%); electron impact mass spectrum, calcd *m/e* 478.2512, found *m/e* 478.2519.

(12) (M + 1, 70%), (M + 2, 41), (M + 3, 14), 476 (M-C_{16}lH_{18}Si, 5.7).

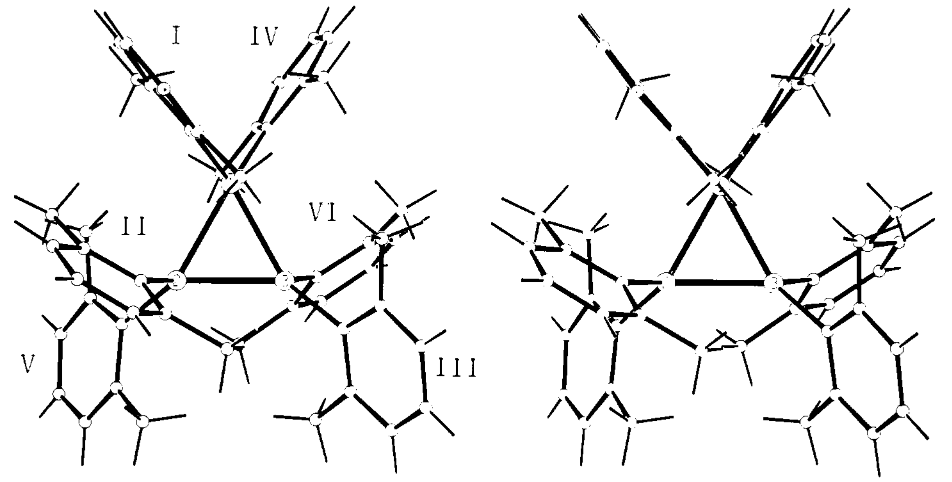

Figure 3.

The unique ultraviolet spectrum of **1a** in cyclohexane [λ_{max} 260 nm (log ϵ 4.61)] (see Figure 2) is typical of the cyclopolysilane system.[1c,2a] The final proof for this assignment is provided below.

Crystallographic Analysis of 1a. The crystals were monoclinic, space group $P2_1/n$, with a = 20.384 (4) Å, b = 11.395 (2) Å, c = 19.696 (6) Å, β = 118.84 (2)°, and d_{calcd} = 1.185 g cm^{-3} for Z = 4 ($C_{48}H_{54}Si_3$, M 715.21). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.05 × 0.12 × 0.5 mm; the data were corrected for absorption (μ = 12.9 cm^{-1}). A total of 3744 independent reflections were measured for $\theta < 48°$, of which 2644 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[13] and was refined by full-matrix least-squares analysis. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The orientations of the hydrogen atoms of the methyl groups are based on peaks found on a difference map and thus only represent the probable orientation about the C_{Me}–C_{Ph} bond. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.049 and R_w = 0.047 for the observed reflections. The final difference map has no peaks greater than ±0.3 Å^{-3}.

In the skeletal drawing shown in Figure 3, in which the silicon atoms and phenyl rings are labeled 1–3 and I–VI, respectively, the plane of the silicon triangle is parallel to the plane of the paper. The three silicon atoms form an isosceles triangle with Si(1) at the apex [bond angles: Si(2)–Si(1)–Si(3), 58.7°; Si(1)–Si(2)–Si(3), 60.7°; Si(1)–Si(3)–Si(2), 60.6°]. As is evident from the drawing, an approximate 2-fold axis of molecular symmetry passes through Si(1) and the midpoint of the Si(2)–Si(3) bond. The unique Si(2)–Si(3) bond (2.375 Å) is 0.05 Å shorter than the two equivalent bonds, Si(1)–Si(2) and Si(1)–Si(3) (2.422 and 2.425 Å), which form the sides of the triangle. The Si–C bond lengths range from 1.90 to 1.93 Å.

As a result of the molecular symmetry, the following pairs of phenyl rings are equivalent: I and IV; II and VI; III and V (see Figure 3). The two phenyl rings (I and VI) at Si(1) are almost perpendicular to the plane of the three silicons, while the other four phenyl rings are inclined 15–30° away from a perpendicular conformation. The dihedral angles between the plane of three silicon atoms and the best plane through each of the phenyl rings are 88.9, 75.1, 54.2, 83.1, 58.9, and 74.3°, respectively, for rings I–VI.

The interatomic distances and bond angles in this conformation indicate some crowding of several pairs of the methyl groups attached on phenyl rings III and V, I and V, I and III, and IV and VI. Indeed, the closest H–H approach observed for the first pair is 1.95 Å, and the others are in the range 2.12–2.16 Å, the distances being shorter than a van der Waals contact of 2.2–2.3 Å expected for H atoms. Therefore, this steric congestion is, at least, in part responsible for the extraordinarily long Si–Si bond lengths (perhaps the longest ever observed),[14] and the nonequivalence of the methyl groups manifested in the solution ^1H NMR spectra below room temperature (Figure 1) is quite natural.

Synthesis and Characterization of 2. While **1a**, unexpectedly, is stable to oxygen, moisture, and heat to its melting point, it reacts readily with halogens and alkali metals and is labile to ultraviolet light.[3] Thus, the proton signals (vide supra) of **1a** [3 mg in degassed cyclohexane-d_{12} (0.4 mL)] are cleanly replaced with a new set of signals, (270 MHz) δ 2.26 (s, 24H, Me), 6.82 [d, 8H, J = 7.94 Hz, Ar-H(3,5)], 6.98 [t, 4H, J = 7.94 Hz, Ar-H(4)], upon irradiation with a low-pressure mercury lamp (spiral, 125 W) for 5 min at room temperature. The solution becomes intensely yellow and yields yellow crystals **2**, mp 216–217.5 °C, upon cooling to 0 °C. Compound **2** exhibits the following spectral properties: UV (cyclohexane) λ_{max} 272 nm (log ϵ 3.85), ~340 nm (3.44), 422 nm (3.8) (Figure 2);[15,16] electron impact mass spectrum, calcd m/e for $C_{32}H_{36}Si_2$ 476.2356, found 476.2365 (M^+).[16,17] The chemical reactivity of **2** is high, as expected:[16] it is extremely sensitive to air and moisture and reacts with bromine to yield the corresponding dibromo derivative; mp 259–263 °C with sintering prior to melting, field desorption mass spectrum, calcd and found m/e for $C_{32}H_{36}Si_2Br_2$ 632, 634, 636 (1:2:1).[18] All of these physical and chemical properties leave no doubt that **2** indeed possesses the disilene structure.

It is extremely gratifying that this cyclotrisilane route to **2** has proven to be highly efficient and free from side reactions. The chemical behavior of **1a** and **2** undoubtedly will provide significant information for the mechanistic elucidation of many reactions in which **1** or **2** has, in the past, been invoked as an intermediate.[7,19]

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(13) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368.

(14) The Si–Si bond lengths are 2.331 (3) Å in $(SiH_2)_2$ (a) (Beagley, B.; Conrad, A. R.; Freeman, J. M.; Moneghan, J. J.; Norton, B. G. *J. Mol. Struct.* **1972**, *11*, 371), 2.338 (4) Å in $(Me_2Si)_6$ (b) (Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1566), 2.378 Å in (t-BuMeSi)$_4$ with the trans, trans, trans geometry (c) (Hurt, C. J.; Calabrese, J. C.; West, R. *J. Organomet. Chem.* **1975**, *91*, 273), 2.340 (9) Å in $Me_3Si(Me_2Si)_4SiMe_3$ (d) (Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401), and 2.365 Å in R_2HSi–$SiHR_2$ (R = cyclohexyl) (e) (Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795). Also see: Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605. The C–Si bond lengths are: 1.935 (4) (axial), 1.913 (4) Å (equatorial) in b, 1.918 (3) (axial) and 1.893 (4) Å (equatorial) in c, 1.877 (3) Å in d, and 1.886 Å in e.

(15) The error in intensity is approximately 10%.

(16) Compound **2** can be handled in a drybox (O_2 concentration less than 5 ppm) without any observable deterioration in purity.

(17) Octaphenylcyclotetrasilane shows its *distinct* parent peak in an electron impact mass spectrum: m/e calcd for $C_{48}H_{40}Si_4$ 728, found m/e 728 (M^+, 1.5%), 468 (36.8), 259 (100), 181 (74), 105 (62).

(18) Identical with the product obtained from tetrakis-1,1,2,2-(2,6-dimethylphenyl)disilane reacted with 2 equiv of bromine.

Acknowledgment. We thank Dr. W. A. Gilbert for his graphic analysis of **1a** and the National Science Foundation and Hoffmann-La Roche (unrestricted grant awarded to S. Masamune) for financial support. S. Murakami is on leave from Yoshitomi Pharmaceutical Industries, Ltd., Japan. High-resolution mass spectra were provided by the facility, supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann), from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: Listings of final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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(19) **Note Added in Proof:** After the submission of this paper a report on the synthesis of a disilene derivative appeared: West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. Also see: *Chem. Eng. News* **1981**, *Dec. 21*, 8.

Total Synthesis of Racemic Chorismic Acid

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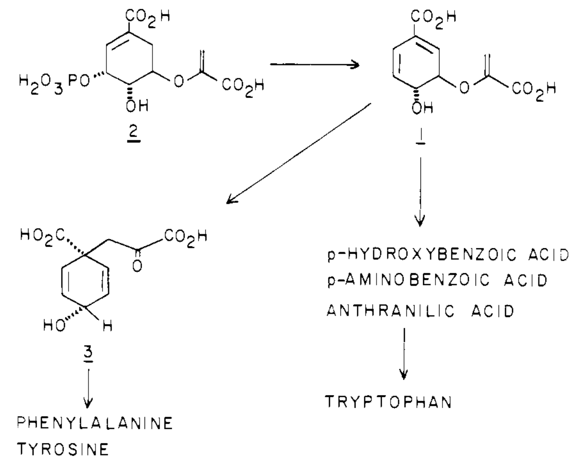
Received December 23, 1981

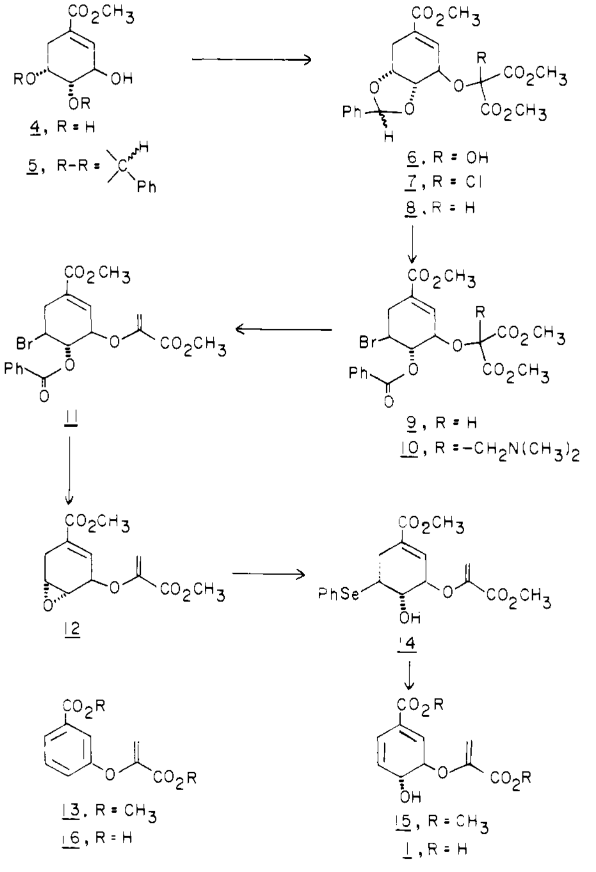
Chorismic acid (**1**) occupies the unique position of being the last common intermediate in the biosynthesis of aromatic substances through the shikimate pathway in bacteria, fungi, and higher plants.[1] Despite intensive efforts by numerous research groups, unambiguous confirmation of a branch-point intermediate beyond 5-enolpyruvylshikimic acid 3-phosphate (**2**) and establishment of the structure of this intermediate remained a mystery until Gibson and co-workers developed a mutant of *A. aerogenes* from which **1** was isolated (initially as the barium salt and later as the stable dicarboxylic acid),[2-4] and the structure and absolute stereochemistry were established.[5] Gibson and collaborators, in particular, and others capitalized on this discovery to elucidate detailed information on the biosynthetic pathway from **1** to the aromatic substances indicated in Scheme I and to numerous other aromatic derivatives.[1] The chorismic pathway remains an area of intensive study, and the rearrangement of **1** to prephenic acid (**3**), presumably a Claisen rearrangement,[6-9] is most unusual as an enzyme-catalyzed transformation.

The important biosynthetic role and the unique structure of **1** have attracted considerable attention. Disodium prephenate (free-acid unstable) recently has yielded to total synthesis;[10,11] but, although known for nearly 2 decades, **1** previously has not yielded to total synthesis.[12] Described below is our total synthesis of racemic **1**.

Scheme I



Scheme II



Starting material for the synthesis (Scheme II) was methyl 4-*epi*-shikimate (**4**).[13] Protection of the C_4 and C_5 hydroxyl groups was effected by reaction of **4** with benzaldehyde (catalyzed by TsOH; toluene, reflux) to give a 3:2 mixture of benzylidine acetals, **5**,[16] in 72% yield. Functionalization of the C_3 hydroxyl group of

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(1) For detailed reviews, see: (a) Weiss, U.; Edwards, J. M. "The Biosynthesis of Aromatic Compounds"; Wiley: New York, 1980. (b) Haslam, E. "The Shikimate Pathway"; Halstead Press, Wiley: New York, 1974.

(2) Gibson, M. I.; Gibson, F. *Biochem. Biophys. Acta* **1962**, *65*, 160-163.

(3) Gibson, F.; Jackman, L. M. *Nature* **1963**, *198*, 388-389.

(4) Gibson, F. *Methods Enzymol.* **1970**, *17A*, 362-364 and references cited therein.

(5) Edwards, J. M.; Jackman, L. M. *Aust. J. Chem.* **1965**, *18*, 1227-1239.

(6) Andrews, P. R.; Haddon, R. C. *Aust. J. Chem.* **1979**, *32*, 1921-1929.

(7) Görisch, H. *Biochemistry* **1978**, *18*, 3700-3705.

(8) Andrews, P. R.; Cain, E. N.; Rizzardo, E.; Smith, G. D. *Biochemistry* **1977**, *16*, 4848-4852.

(9) Andrews, P. R.; Smith, G. D.; Young, I. G. *Biochemistry* **1973**, *12*, 3492-3498.

(10) Danishefsky, S.; Hirama, M. *J. Am. Chem. Soc.* **1977**, *99*, 7740-7741; Danishefsky, S.; Hirama, M.; Fritsch, N. Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7013-7018.

(11) Gramlich, W.; Plieninger, H. *Tetrahedron Lett.* **1978**, 3619-3622. *Chem. Ber.* **1979**, *112*, 1550-1570, 1571-1584.

(12) A synthesis of norchorismic acid, where the C_3 substituent is $-OCH_2CO_2H$ rather than the enolpyruvyl moiety, has been reported: Ikota, N.; Ganem, B. *J. Chem. Soc., Chem. Commun.* **1978**, ,869-870.

(13) Although preparation of **4** and **4**-*epi*shikimic acid is described in the literature,[14,15] we found an alternate procedure to **4** from methyl 2,5-dihydrobenzoate to be more practical. Epoxidation (CH_3CO_3H) and treatment with base afforded methyl 3-hydroxy-2,3-dihydrobenzoate, which underwent syn epoxidation (*m*-CPBA) at C_4-C_5. Solvolysis of the epoxide with acetic acid and treatment with CH_3O^-/CH_3OH gave pure **4** in ~20% overall yield after recrystallization. Details will be presented in a full paper.

(14) Grewe, R.; Kersten, S. *Chem. Ber.* **1967**, *100*, 2546-2553.

(15) Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1973**, *95*, 7821-7828.

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