

cuprates,^{4-6,8} which suggests that the long Cu-C distance seen in $[\text{Cu}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$, 2.027 (7) Å,⁷ may be due to disorder problems involving its isomorphism with $[\text{Li}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$ (see ref 7 for details). The lattices of **2** and **3** also contain THF and toluene. The sandwich structures of the $[\text{Li}(12\text{-crown-4})_2]^+$ cations are very similar to those previously described by us.¹¹ In all three $[\text{Li}(12\text{-crown-4})_2]^+$ cations, the average Li-O distance is 2.37 Å, with a range of 2.21-2.56 Å. Various types of disorder are common in the crown ether rings, and two of these occur in the ring of **1** and in one of the two rings of **3**. Details for **2** and **3** are presented in the supplementary material.¹²

In summary, our results show that monomeric cuprates with commonly used organic substituents are readily obtained simply by adding crown ethers which coordinate lithium. These monomeric compounds are somewhat less soluble than their oligomeric counterparts due to their greater ionic character. Nonetheless they are sufficiently soluble in THF for mechanistic study. Investigations on these organocuprates and other lithium/transition-metal anionic complexes¹³ are continuing.

Acknowledgment. We thank the Research Corporation, the Committee on Research of the University of California, and the National Science Foundation (CHE-8116355) for generous financial support.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates for $[\text{Li}(12\text{-crown-4})_2][\text{CuPh}_2]\cdot\text{THF}$ and $[\text{Li}(12\text{-crown-4})_2][\text{Cu}(\text{Br})\text{CH}(\text{SiMe}_3)_2]\cdot\text{PhMe}$ (14 pages). Ordering information is given on any current masthead page.

(11) Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1984**, *106*, 819-821. Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174. Power, P. P.; Xu, X. *J. Chem. Soc., Chem. Commun.* **1984**, 358.

(12) Details of the structure of **1** and the treatment of the crown ether disorder problem will be submitted for publication to *Acta Crystallographica* by Professor H. Hope.

(13) Olmstead, M. M.; Power, P. P., unpublished work.

Photoisomerization of a Highly Substituted Silene

A. G. Brook,* K. D. Safa, Paul D. Lickiss, and Kim M. Baines

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Canada M5S1A1

Received November 30, 1984

The successful isolation of remarkably stable solid silenes $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{R}$ ($\text{R} = \text{C}_{10}\text{H}_{15} = 1\text{-adamantyl}$ or $\text{R} = \text{CET}_3$)¹ has led us to investigate the effects that the various substituents have on the stability and chemistry of silenes. In the course of this study a remarkable silene-to-silene photochemical rearrangement was observed when one of the silyl groups on silicon in the above silene was replaced by *tert*-butyl.²

Photolysis³ of $(\text{Me}_3\text{Si})_2\text{-}t\text{-BuSiCOC}_{10}\text{H}_{15}$ (**1**)^{4,5} (prepared by coupling of $(\text{Me}_3\text{Si})_2\text{-}t\text{-BuSiLi}$ ⁶ with adamantoyl chloride in 55% yield) in methanol gave two diastereomeric methanol adducts of

(1) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(2) The silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{C}_{10}\text{H}_{15}$ does not rearrange photochemically under similar conditions.

(3) Photolysis employed one to four 100-W Par 38 mercury flood or spot lamps, $\lambda > 360$ nm, usually for 2-24 h.

(4) All new compounds had IR, ¹H, ¹³C, and ²⁹Si NMR, and mass spectral data consistent with the assigned structure. All NMR spectra were run in C₆D₆ unless otherwise noted.

(5) Properties of **1**: mp 87-88 °C; IR 1625 cm⁻¹ (C=O); ¹H NMR 0.30 (18 H, s, Me₃Si), 1.17 (9 H, s, Me₃C), 1.5-2.1 ppm (15 H, m, C₁₀H₁₅); ¹³C NMR 2.13 (Me₃Si), 22.13 (Me₃C), 31.72 (Me₃C), 28.42 (d), 37.04 (t), 37.08 (t), 51.46 (s) (all C₁₀H₁₅ H coupled), 246.53 ppm (C=O); ²⁹Si NMR -15.48 (Me₃Si), -32.24 (Si) ppm.

(6) By cleavage of $(\text{Me}_3\text{Si})_2\text{Si-}t\text{-Bu}$ (from the reaction of *t*-BuSiCl₃, Li, and Me₃SiCl) with MeLi in THF under reflux over 22 h.

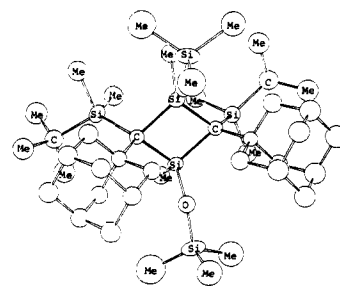
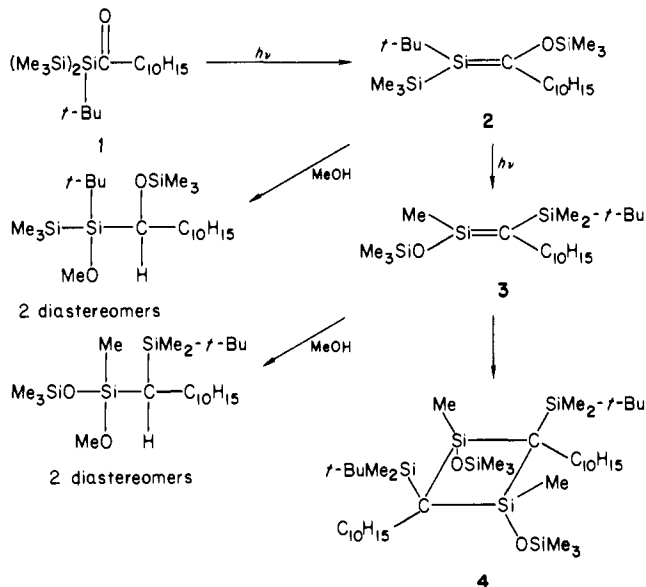


Figure 1. Crystal structure of dimer **4**.

Scheme I



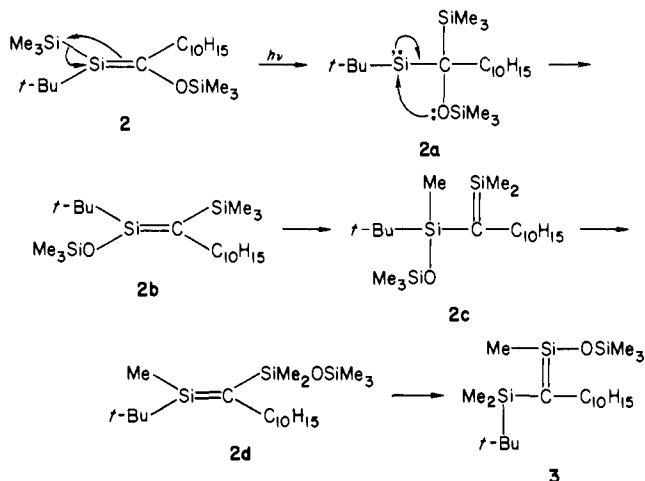
the anticipated silene **2** in about 3:1 proportions. When photolyzed in C₆D₆, NMR signals attributable to the silene **2** were seen to develop⁷ as the acylsilane concentration diminished, but on further irradiation to convert all the acylsilane to silene **2** a new species **3** was formed at the expense of **2**. After prolonged photolysis (but not in the dark where no change occurred) a clean set of NMR signals resulted, attributable to a new silene **3**,⁸ whose structure appeared to have little relationship to that of its precursor **2**. In particular, the ²⁹Si and ¹³C NMR signals due to the sp² hybridized silicon and carbon of **3** were strongly shifted downfield (from 73.7 to 126.5 ppm) and upfield (from 195.6 to 118.1 ppm), respectively, relative to **2**. In addition one of the ²⁹Si NMR signals observed for **3** was upfield of Me₄Si, indicating the probable absence of silicon-silicon bonds in **3**. The new silene (which gave new adducts if treated with methanol) was relatively stable, surviving for time periods varying from a few days to a few weeks before spontaneously disappearing with the simultaneous formation of two dimers, the major one as a precipitate. The spectral properties of the major dimer⁹ were consistent with its being a head-to-tail

(7) Properties of **2**: ¹H NMR 0.33, 0.39 (each 9 H, s, Me₃Si), 1.33 (9 H, s, Me₃C), ca. 1.5-2.2 ppm (C₁₀H₁₅, overlapped); ¹³C NMR 2.13 (Me₃Si, accidental overlap with starting material), 4.47 (Me₃Si), 28.34 (Me₃C), 31.54 (Me₃C), 37.33 (t), 42.34 (t), 29.35 (d), 43.46 (s) (C₁₀H₁₅, DEPT), 195.59 ppm (C=Si); ²⁹Si NMR -13.17 (Me₃Si), 12.25 (Me₃SiO), 73.69 (Si=C) ppm.

(8) Properties of **3**: ¹H NMR 0.19 (9 H, s, Me₃SiO), 0.42 (3 H, s, MeSi), 0.61 (6 H, s, Me₂Si), 1.08 (Me₃C), 1.6-2.2 ppm (C₁₀H₁₅); ¹³C NMR 2.75 (Me₃Si), 4.77 (MeSi), 6.99 (Me₂Si), 21.13 (Me₃C), 28.45 (Me₂C), 30.47 (d), 37.19 (t), 49.03 (t), 39.65 (s), (C₁₀H₁₅, DEPT), 118.07 ppm (C=Si); ²⁹Si NMR (INEPT, H coupled) 6.33 (decet, Me₃SiO), 8.55 (sept, Me₂Si), 126.53 (q, Si=C) ppm.

(9) Properties of **4**: mp 220-222 °C; ¹H NMR (C₆H₆) 0.27 (9 H, s, SiMe₃), 0.43 (6 H, s, SiMe₂), 0.71 (3 H, s, MeSi), 1.14 (9 H, s, CMe₃), 1.54-2.51 ppm (15 H, m, C₁₀H₁₅); ¹³C NMR (CDCl₃), 2.96 (Me₃Si), 8.13 (MeSi), 12.57 (Me₂Si), 24.57 (Me₃C), 30.79 (Me₂C), 30.19 (d), 36.55 (t), 44.49 (t), 45.57 (s), (C₁₀H₁₅, DEPT), 50.74 ppm (C ring); ²⁹Si NMR (CDCl₃, INEPT, H coupled), 3.87 (m, Me₂Si), 4.26 (q, MeSi), 7.82 (decet (8 seen), Me₃Si) ppm; MS, *m/e* 788 (M⁺).

Scheme II



dimer (unlike the head-to-head dimers normally formed from silenes derived from the photolysis of acylpolysilanes^{10,11}) and this was confirmed by an X-ray structure determination¹² which showed the 1,3-disilacyclobutane structure **4** (see Figure 1). INEPT¹³ ²⁹Si studies and DEPT¹⁴ ¹³C studies confirmed that the photoisomeric silene observed in solution, i.e., **3**, had properties consistent with its being the monomeric precursor to **4** (see Scheme I). Dimer **4** did not undergo photolysis under the reaction conditions.

The pathway by which the remarkable rearrangement **2** → **3** occurs is under investigation. From the kinetics, it is clear that the disappearance of the acylsilane is a clean first-order reaction, and the silene-to-silene rearrangement is part of a consecutive series of photochemical transformations. However, the nature of the photochemical processes are not yet known, the study being complicated by the facts that more than one photochemical reaction is occurring and that silenes are known to react with ketones, dienes, and many other reagents commonly used to probe the multiplicities of photochemical intermediates.

A complex pathway involving rearrangements for which at least some precedents are known can be proposed as a working hypothesis (Scheme II). Photochemical silene-to-silylene rearrangements have been observed¹⁵ and thus **2** could form the silylene **2a** which might reasonably be expected to collapse to the isomeric silene **2b**. Recent studies by Wiberg clearly indicate that methyl groups on the sp² hybridized silicon of silenes readily undergo 1,3-silicon-to-silicon migrations^{16,17} so that **2b** could isomerize to **2c**. The essentially thermoneutral rearrangement of **2c** → **2d** followed by a second 1,3-methyl migration would yield the observed silene **3**. This scheme involves an uncomfortably large number of sequential migrations but we are unable to propose a simpler process at this time which involves steps for which some precedents are known. This complex chemistry is not an isolated case since photolysis of a related acylsilane, where phenyl replaces *tert*-butyl, undergoes related but different rearrangements. As part of our continuing investigations we are attempting to intercept intermediate species, such as those proposed, but obviously in such

a complex system this is a nontrivial task.

Acknowledgment. We are indebted to Dr. J. Sawyer for the crystal structure and to the Natural Science and Engineering Research Council of Canada for financial support and for a scholarship to K.M.B.

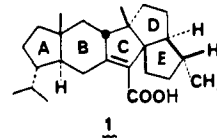
Total Synthesis of (±)-Retigeranic Acid

E. J. Corey,* Manoj C. Desai, and Thomas A. Engler

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

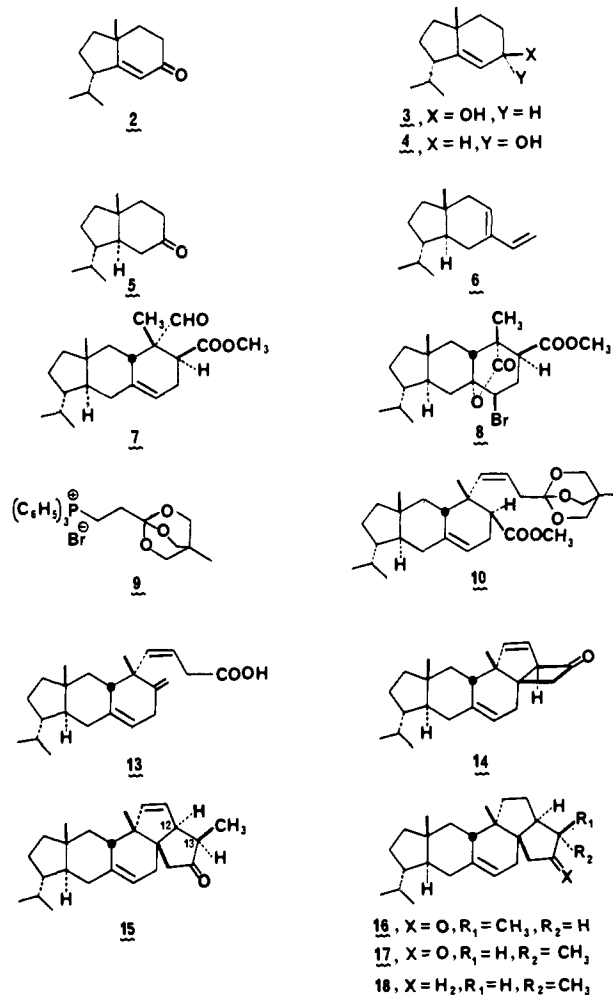
Received February 25, 1985

Retigeranic acid is a sesterterpene monocarboxylic acid of novel structure which has been obtained from various lichens found in the Himalayas.^{1,2} X-ray crystallographic analysis of the *p*-bromoanilide revealed the structure and absolute configuration shown in **1**.² We describe herein the first total synthesis of **1** as



the racemate.³ The synthesis confirms the X-ray assignment of structure and stereochemistry.

The starting point for the synthesis was the hydrindenone **2**,



(10) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

(11) Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y.-M.; Lee, J.-S.; Picard, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 6750.

(12) Full details of the X-ray structure will be published separately by A. G. Brook, J. Sawyer and P. D. Lickiss.

(13) Doddrell, D. M.; Pegg, D. T.; Brooks, W. M.; Bendall, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 727.

(14) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.

(15) Reisenauer, H. P.; Mihm, G.; Maier, G., *Angew. Chem.* **1982**, *94*, 864.

(16) Wiberg, N. *J. Organometal. Chem.* **1984**, *273*, 141.

(17) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

(1) (a) Rao, P. S.; Sarma, K. G.; Seshardri, T. R. *Curr. Sci.* **1965**, *34*, 9; (b) *Ibid.* **1966**, *35*, 147.

(2) Kaneda, M.; Takahashi, R.; Iitaka, Y.; Shibata, S. *Tetrahedron Lett.* **1972**, 4609.

(3) For purposes of the present discussion the ring designations shown in formula **1** have been adopted.