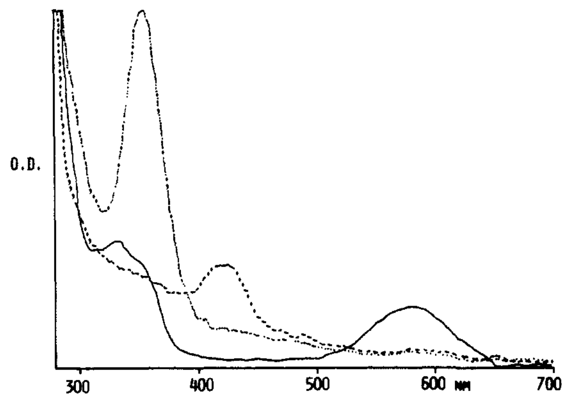


Figure 1. Reaction of Mes$_2$Si: with CO in rigid matrix: (—), after photolysis at 77 K, showing silylene absorptions; (···), after annealing, band at 354 is assigned to CO complex; (---), further warming, showing disilene spectrum.

Table I

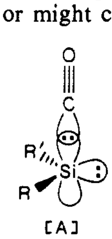
R, R′	RR′Si:	RR′Si:CO	RR′Si=SiRR′
mes, mes	580, 330	354, 284	420
mes, t-Bu	505, 290	338, 290	330
Me, Me	454	345	not obsd
mes, OAr	398	328	380, 342

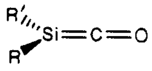
warming the new band disappeared as absorptions for the disilenes **4a** and **4b** grew in.

With precursors **1c** and **1d**, photolysis in 3-MP gave not only the absorption bands for silylenes **2c**,**2d** but also an absorption attributed to the complex **3c**,**3d**. On standing for several hours the complex band grew more intense, while the silylene band decreased. Annealing of the matrix led to complete disappearance of the silylene band and a simultaneous large increase of the absorption band near 350 nm attributed to the complex. Further warming gave the stable disilene **4c** from **3c**. In the dimethylsilylene case further warming gave products with no absorption longer than 300 nm.

Photolysis of **1a–d** was also carried out in a 4:1 2-methylbutane:3-methylpentane mixture, which forms a soft matrix at 77 K.[8] Under these conditions only the absorption bands attributed to the silylene–CO complex were observed. Annealing of the matrix led again to the disilenes **4a–c** but not **4d**.

Carbon monoxide might react with silylenes to give a nonplanar complex (A) or might combine to form a silaketene (B). Silylene–CO complexes **3a–c** behave similarly to other acid–base complexes of silylenes **2a–c** with donor molecules in that they produce disilenes (**4a–c**) when the matrix is melted.[1,4] These results are consistent with formulation of the CO adducts as acid–base complexes (A) rather than silaketenes (B), which would not be expected to dissociate readily. Recent theoretical calculations also indicate that A is more stable than B.[9]


[A]


[B]

Weak absorption bands at longer wavelength were also observed in matrices containing large amounts of **3b**, **3c**, and **3d**, at 425 (sh), 610, and 590 nm, respectively (Figure 2). Observation of these additional bands was easier in the soft matrices, where photogeneration of the silylene–CO complex was most efficient. These bands also disappear upon melting of the matrix, but at present it is not certain whether they arise from the silylene–CO complexes **3b–d** or from some other species generated simultaneously.[10]

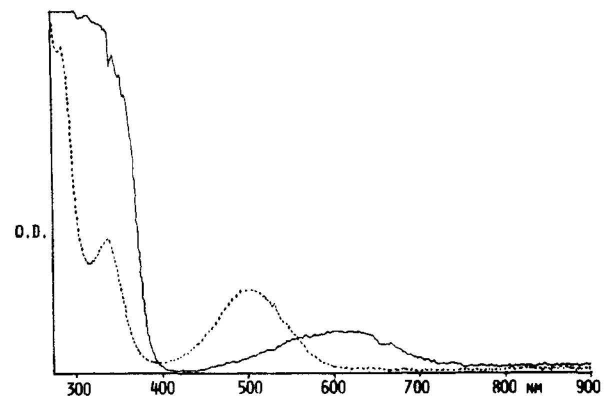


Figure 2. Interaction of Mes(tBu)Si: with CO at 77 K: (---), irradiation in 3-MP; band at 505 is due to silylene, band at 338 is assigned to CO complex; (—), irradiation in soft matrix showing bands at 338 and 610.

Formation of the CO complexes **3c** and **3d** from silylenes **2c** and **2d** in 3-MP at 77 K requires that CO migrate through the rigid 3-MP matrix at this temperature. Silylene complexes **3a** and **3b** however were observed in 3-MP only when the matrix is annealed. Tentatively, we suggest that conformational effects prevent the formation of the complexes from **2a** and **2b** in the rigid matrix. Warming of the matrix may allow relaxation of the silylenes to conformations which can react with CO to give the observed complexes.

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF under Contract no. F49620-86-0010 and National Science Foundation Grant no. CHE-8318820-02.

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(8) Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, *209*.

(9) Hamilton, T. P.; Schaefer, H. F., submitted to *J. Chem. Phys.*

(10) The long wavelength absorptions might possibly be due to $R_2Si{:}O{\equiv}C$ complexes in which the carbonyl oxygen serves as the electron donor. Complexes between the ketone, tetramethylindanone, and silylenes have been reported to absorb near 600 nm (see ref 4). The long wavelength band was not observed for **3a**, probably because of the difficulty in generating high concentrations of silylene **2a** in hydrocarbon matrices.

Synthesis of Homocub-4(5)-ene: Confirmation of a Computational Prediction

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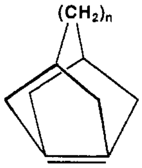
Received June 6, 1988

We have reported the synthesis of the $n = 1$[1] and $n = 2$[2] members of a homologous series of pyramidalized alkenes (**1**),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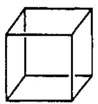
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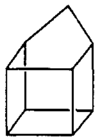
3

and we have also published the synthesis and X-ray crystal structure of the 10-methylselenonium derivative of the $n = 3$ hydrocarbon.[3] More recently, we have reported the results of

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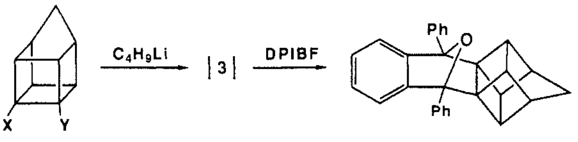
(1) Renzoni, G. E.; Yin, T.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 7121.

(2) Renzoni, G. E.; Yin, T.-K.; Miyake, F.; Borden, W. T. *Tetrahedron* **1986**, *42*, 1581. Yin, T.-K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544.

(3) Hrovat, D. A.; Miyake, F.; Trammell, G., Gilbert, K. E., Mitchell, J.; Clardy, J.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5524.

ab initio molecular orbital calculations of the olefin strain energies (OSE) of these and several other pyramidalized alkenes.[4] The calculations predict that cubene (**2**) should have only a slightly larger OSE than **1**, $n = 1$, which led us to conjecture that **2** should be preparable by the same type reaction that we used to generate **1**, $n = 1$.[4] In the following communications Eaton and Maggini report experiments that confirm this prediction.[5] In this communication we report our successful generation of homocub-4(5)-ene (**3**) by an analogous route.

Our choice of **3** as a molecule with which to test our prediction was based on the existence of a published route to a promising precursor (**4**),[6] coupled with the expectation that the additional methylene bridge in homocubene would not substantially decrease the OSE from that computed for cubene. This surmise was tested by ab initio calculations on **3** and its hydrogenation product, homocubane. At the 6-31G* TCSCF level of theory the hydrogenation energy of **3** was actually computed to exceed that of **2**[4] by 7.4 kcal/mol.[7]



4, X=Br, Y=CO_2H
5, X=Y=Br
6, X=Br, Y=I
7, X=C_4H_9, Y=I

8

In order to prepare a vicinal dihalide for dehalogenation to **3**, bromoacid **4** was subjected to a modified Hunsdiecker reaction.[8] Irradiation of 107 mg of **4** in 2.5 mL of CH_2Cl_2 containing 60 mg of HgO, 49 mg of $MgSO_4$, and 96 mg of Br_2 with a 60-W incandescent lamp afforded dibromide **5**[9] in 50% yield. However, attempts to dehalogenate **5** by reaction with *n*-butyllithium in THF at −78 °C[1] led only to recovered starting material.

In order to prepare a dihalide that might prove more reactive toward dehalogenation, the modified Hunsdiecker reaction was repeated, but with iodine in place of bromine. Bromoiodide **6**[9] was obtained in 90% yield and subjected to dehalogenation with 1.1 equiv of *n*-butyllithium in THF at −78 °C in the presence of diphenylisobenzofuran (DPIBF). After warming the reaction mixture to room temperature and adding water, a CH_2Cl_2 solution of maleic anhydride was added to quench the unreacted DPIBF. The DPIBF adduct of maleic anhydride and unreacted maleic anhydride were precipitated from the solution by addition of pentane,[10] and the pentane soluble fraction was evaporated to afford an adduct of **3** with DPIBF in 50% yield.

The crude adduct was purified by recrystallization from pentane at −30 °C to give white crystals, mp 157–8 °C. The exact mass (calcd for $C_{29}H_{22}O$ 386.1671, found 386.1669), ^1H NMR ($CDCl_3$) [δ 1.54 (d, 1 H, $J = 11.0$ Hz), 1.63 (d, 1 H, $J = 11.0$ Hz), 2.59 (m, 2 H), 3.15 (m, 2 H), 3.48 (m, 2 H), 6.86 (m, 2 H), 7.13 (m, 2 H), 7.38 (m, 2 H), 7.45 (m, 4 H), 7.59 (m, 4 H)], and proton decoupled ^{13}C NMR ($CDCl_3$) [δ 40.58, 41.46, 41.54, 42.19, 50.56, 91.00, 119.72, 126.72, 127.61, 127.92, 128.30, 136.50, 144.62] of the adduct were wholly consistent with the formulation of its structure as **8**.

When DPIBF was omitted from the reaction mixture and **6** was treated with excess *n*-butyllithium, the product **7**[9] of formal replacement of the bromine in **6** with an *n*-butyl group was the major product. The same product **7** was formed, but in smaller amounts, when DPIBF was present to trap homocub-4(5)-ene (**3**).

That formation of **7** does not occur simply by exchange of the bromine in **6** with *n*-butyllithium is indicated by the unreactivity of dibromide **5** toward *n*-butyllithium, the expectation that the iodine would be more reactive than the bromine in **6** toward this reagent, and the isolation of **8** when DPIBF is present in the reaction mixture as an olefin-trapping reagent. The route by which **7** is generated presumably involves formation of homocub-4(5)-ene (**3**), addition of *n*-butyllithium to the pyramidalized double bond in **3**, and reaction of the resulting tertiary alkyllithium with either the *n*-butyliodide produced in the first step of the reaction sequence or with unreacted **6**. A similar mechanism has been invoked by Wiberg in order to explain the formation of 1-bromo-4-*n*-butylbicyclo[2.2.0]hexane from the reaction of 1-bromo-4-chlorobicyclo[2.2.0]hexane with *n*-butyllithium.[11] Alkyllithium addition to the double bond of **2** also accounts for the products observed by Eaton and Maggini.[5,12]

The results reported herein provide confirmation of the theoretical prediction that, as in the case of **1**, $n = 1$,[1] a highly pyramidalized double bond can be introduced into the (homo)cubane skeleton by dehalogenation of a vicinal dihalide with *n*-butyllithium. Like bicyclo[2.2.0]hex-1(4)-ene,[11] both cubene (**2**)[5] and homocub-4(5)-ene (**3**) react with alkyllithium reagents, and these alkenes can be trapped as Diels–Alder adducts with dienes. Additional chemistry of **3** and its direct spectroscopic observation are both under investigation.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. 3, 116531-30-7; **4**, 106684-70-2; **5**, 116503-52-7; **6**, 116503-53-8; **7**, 116503-54-9; **8**, 116503-55-0; DPIBF, 5471-63-6.

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(4) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

(5) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, following communications in this issue. We thank Professor Eaton for informing us of his results and for agreeing to simultaneous publication.

(6) Klunder, A. J. H.; Ariaans, G. J. A.; v. d. Loop, A. A. R. M.; Zwanenberg, B. *Tetrahedron* **1986**, *42*, 1903.

(7) The 6-31G* TCSCF energy calculated for homocubene and the SCF energy for homocubane at their 3-21G SCF optimized geometries were, respectively, −345.2380 and −346.5021 hartrees.

(8) Cristol, S. J.; Firth, W. C., Jr. *J. Org. Chem.* **1961**, *26*, 280. Meyers, A. I.; Fleming, M. P. *J. Org. Chem.* **1979**, *44*, 3405.

(9) All new compounds gave spectroscopic and analytical data that were consistent with the assigned structures.

(10) We found that the adduct rearranged on attempted chromatographic separation of it from this mixture.

(11) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E.; Dailey, W. P.; Burgmaier, G. J.; Bailey, W. F.; Warner, P. *Tetrahedron* **1986**, *42*, 1895.

(12) The difference between the type of addition product obtained by Eaton and Maggini[5] and that (**7**) isolated by us is attributable to their use of excess *tert*-butyllithium for generating **2**. Under these reaction conditions, iodocubane derivatives, analogous to **7**, would not be expected to be formed.

Cubene (1,2-Dehydrocubane)

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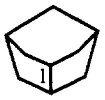
Received June 3, 1988

In recent years we have developed excellent methodology for the synthesis of variously substituted cubanes.[1] This allows us to start with the cubane system, already an extraordinary structure[2] and move outward in our continuing exploration of the limits of bonding in organic compounds.[3] We report now on the synthesis and trapping of 1,2-dehydrocubane (**1**), colloquially "cubene", the most highly pyramidalized olefin yet known.[4]


1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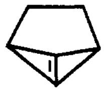
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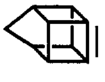
4

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(1) (a) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. (b) Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *Ibid.* **1987**, *109*, 948. (c) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055. (d) Eaton, P. E.; Cunkle, G. T. *Ibid.* **1986**, *27*, 6055.

(2) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

(3) Eaton, P. E.; Hormann, R. E. *J. Am. Chem. Soc.* **1987**, *109*, 1268. (b) Eaton, P. E.; Hoffmann, K.-L. *Ibid.* **1987**, *109*, 5285.

(4) Pyramidalization is a deviation from planarity. For an olefinic carbon the pyramidalization angle is that between the plane defined by that carbon and its two substituents with the line passing through both olefinic carbons.