Table I. Properties of Selected $AlPO_4$ Molecular Sieves

| | adsorption properties[a] | | | |
|---|---|---|---|---|
| | | | intracrystalline pore vol, $cm^3/g$ | |
| structure[c] | pore size, nm | ring[b] size | $O_2$ | $H_2O$ |
| $AlPO_4$-5 determined, novel[d] | 0.8 | 12 | 0.18 | 0.3 |
| $AlPO_4$-11 unknown | 0.61 | 10 or puckered 12 | 0.11 | 0.16 |
| $AlPO_4$-14 unknown | 0.41 | 8 | 0.19 | 0.28 |
| $AlPO_4$-16 unknown | 0.3 | 6 | 0 | 0.3 |
| $AlPO_4$-17 erionite/ offretite type | 0.46 | 8 | 0.20 | 0.28 |
| $AlPO_4$-18 unknown | 0.46 | 8 | 0.27 | 0.35 |
| $AlPO_4$-20 sodalite type | 0.3 | 6 | 0 | 0.24 |
| $AlPO_4$-31 unknown | 0.8 | 12 | 0.09 | 0.17 |
| $AlPO_4$-33 unknown | 0.41 | 8 | 0.23 | 0.23 |

[a] Determined by standard McBain–Bakr gravimetric techniques after calcination (500–600 °C in air) to remove R; pore size determined from measurements on molecules of varying size (kinetic diameter from ref 1); pore volumes near saturation, $O_2$ at −183 °C, $H_2O$ at ambient temperature. [b] Number of tetrahedral atoms (Al or P) in ring that controls pore size; when structure not known, estimated from adsorption measurements. [c] Structures distinguished by their characteristic X-ray powder diffraction patterns. [d] See text.

In the two-dimensional layer structures the organic R is presumed to be intercalated between $AlPO_4$ layers. The layer structures undergo crystallographic collapse and structural rearrangement to dense phases when the interlayer organic species is removed by thermal treatment.

In contrast, many of the three-dimensional aluminophosphates exhibit excellent thermal stability. Most remain crystalline after the 400–600 °C calcination necessary to remove the organic template and free the intracrystalline void volume for adsorption or catalysis. Indeed, many retain their structure after calcination at 1000 °C. Several materials tested for hydrothermal stability show virtually no structural loss when treated with 16% steam at 600 °C.

The aluminophosphate molecular sieves exhibit intracrystalline pore volumes ($H_2O$) from 0.04 to 0.35 $cm^3/g$ and adsorption pore sizes from 0.3 to 0.8 nm, spanning the entire range of pore volumes and pore sizes known in zeolites and silica molecular sieves. The uniform pore dimensions defined by the crystal structure enable the use of these new materials for size- and shape-selective separations and catalysis. Properties of selected $AlPO_4$ molecular sieves are given in Table I.

Some of the aluminophosphate molecular sieves are small pore materials. $AlPO_4$-20, like its zeolite analogue sodalite, is a small-pore molecular sieve that admits only water. $AlPO_4$-14 and $AlPO_4$-33 adsorb xenon (0.40 nm) but not *n*-butane (0.43 nm). $AlPO_4$-17 and $AlPO_4$-18 have a slightly larger pore size of 0.46 nm, adsorbing *n*-paraffins but excluding isoparaffins.

$AlPO_4$-11, whose structure has not yet been determined, is intermediate in pore size. It adsorbs molecules as large as cyclohexane (0.60 nm) but not 2,2-dimethylpropane (0.62 nm). This pore size is similar to that of silicalite[2] and indicates that the $AlPO_4$-11 structure contains voids bounded by 10-rings or puckered 12-rings.

Large-pore structures include $AlPO_4$-5, known to have 12-ring channels which allow adsorption of molecules at least as large as 2,2-dimethylpropane (0.62 nm). $AlPO_4$-31, with unknown structure, has a pore size like that of $AlPO_4$-5 and must also contain 12-ring pores.

Nearly all of the aluminophosphate molecular sieves with pore sizes from 0.4 to 0.8 nm (8-, 10-, or 12-rings) exhibit a characteristic adsorption pore volume for oxygen (and in some cases hydrocarbons) that is only 50–80% that of the water pore volume. This requires that their framework structures contain both large-pore voids and voids accessible through small pores (6-rings) which admit only water. In the case of the known $AlPO_4$-5 structure, the excess water volume is associated with small voids outlined by columns of twisted chains of 4-rings and 6-rings parallel to the *c* axis.[4]

Zeolites are hydrophilic due to the interaction of the dipole of the water molecule with the electrostatic fields of the anionic aluminosilicate framework and the balancing nonframework cations. The molecular sieve silicalite, with a neutral $SiO_2$ framework and no extra-framework cations, is hydrophobic. In contrast, the neutral aluminophosphate frameworks with no extra-framework cations are moderately hydrophilic, apparently due to the difference in electronegativity between aluminum (1.5) and phosphorus (2.1). They exhibit less affinity for $H_2O$ than the hydrophilic zeolites such as type A and type X zeolites yet substantially more than hydrophobic silicalite.

The aluminophosphate materials have interesting properties for potential use in adsorptive and catalytic applications, due to both their unique surface selectivity characteristics and novel structures. The discovery of this new family opens the door to a new era in molecular sieve materials.

**Acknowledgment.** We dedicate this paper to the late Donald W. Breck, a pioneer in the discovery of new molecular sieve materials, whose encouragement and chemical and structural insights supported us throughout the course of this work. We thank R. L. Patton for many fruitful discussions and critical review of the manuscript, P. A. Burtis and R. T. Gajek for their excellent technical assistance, and Union Carbide Corp. for permission to publish this article.

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## An Unusual Ground-State Di-π-methane Rearrangement in the Thermal Isomerization of Homoazulene

Lawrence T. Scott* and Ihsan Erden

*Department of Chemistry*
*University of Nevada, Reno, Nevada 89557*

*Received November 16, 1981*

Homoazulene (**1**, 1,5-methano[10]annulene), a nonbenzenoid aromatic hydrocarbon with an extraordinarily twisted π system, has recently become available in sufficient quantity to permit extensive physical and chemical investigations.[1] Preliminary spectral analysis reveals a distinct resemblance between the electronic properties of **1** and those of azulene.[2] Our interest in the thermal rearrangements of azulene[3] and aromatic compounds in general[4] has prompted us to examine the behavior of **1** at elevated temperatures. Some unusual transformations have been discovered, including one which appears to represent the first example of a ground-state di-π-methane rearrangement (Scheme II).

Flash vacuum pyrolyses (FVP) were conducted in a 10-cm vertical quartz tube (12-mm i.d.) at ca. 0.01 torr. At 300 °C, homoazulene passed through unchanged. Such thermal stability was not anticipated. At 435 °C, five isomeric products were formed in high overall yield (reaction 1), although a small amount of **1** still survived even at this temperature. Phenylcyclopentadienes **2** and **3** have been reported previously and interconvert by 1,5-hydrogen shifts at temperatures well below 435 °C.[5] Their presence in the pyrolysate was obvious from the $^1H$ NMR spectrum; however, further confirmation was obtained by GC

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(1) (a) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I., *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 274–279. (b) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216–5220. (c) For an earlier synthesis, see: Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239–3240. (d) For a discussion of the geometry of **1**, see: Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907.

(2) Scott, L. T., unpublished results. See also ref 1b.

(3) Scott, L. T.; Kirms, M. A.; Minton, M. A. *Croat. Chem. Acta* **1980**, *53*, 643–647; Scott, L. T.; Kirms, M. A.; Minton, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875–5879.

(4) Scott. L. T. *Acc. Chem. Res.*, in press.

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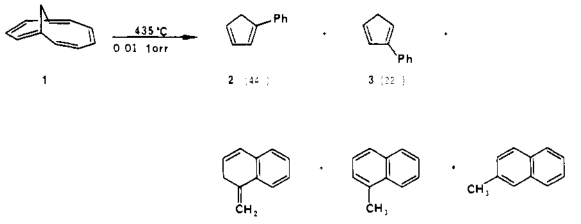


**1** **2** (44%) **3** (22%) **4** (19%) **5** (10%) **6** (5%) (1)

comparison with an authentic sample. Treatment of the mixture with tetracyanoethylene (TCNE) gave the corresponding Diels–Alder adducts of **2** and **3**.[6] $^1$H NMR spectra of the pyrolysate also contained peaks characteristic of 1-methylene-1,2-dihydronaphthalene (**4**), an unusual hydrocarbon first prepared 3 years ago in our laboratory.[7] One drop of trifluoroacetic acid added to the NMR tube instantly isomerized all of **4** to **5**. The methylnaphthalenes (**5** and **6**) were identified by $^1$H NMR spectroscopy and GC comparison with authentic samples. FVP of **1** at 550 °C gave **2**, **3**, **5**, and **6** but no **4** and no residual homoazulene.

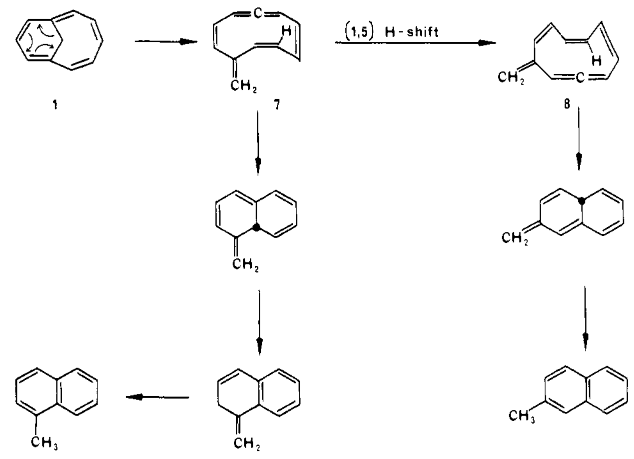
The formation of **4**, **5**, and **6** is most reasonably explained by the mechanism depicted in Scheme I. Thus, homoazulene contains a cyclohexadiene ring which can open by an allowed electrocyclic process to give the 10-membered ring allene **7**. Reclosure by an alternative mode followed by a 1,5-hydrogen shift would then yield **4**. Further prototropic isomerization to **5** is impeded by orbital symmetry restrictions[7] and apparently occurs to a significant extent only at 550 °C. Symmetry-allowed 1,5 shift of a hydrogen in **7** would generate the isomeric allene **8**, a plausible precursor for the minor product **6**. None of these intermediates has been isolated, of course, but the pathways appear entirely reasonable.

This scheme accounts only for products **4**, **5**, and **6**, which comprise less than 40% of the total; the dominant mode of rearrangement generates a five-membered ring. Bond formation between the bridgehead carbon atoms of **1** to produce the novel diradical **9** represents one obvious pathway to a five-membered ring.[8] This intermediate, however, should then rearrange via **10** to **11**, a known compound[9] (Scheme II).

Since the bicyclic pentaene **11** was not found among the thermal rearrangement products of **1**, an authentic sample was prepared[9] and subjected to FVP at 435 °C. Under these conditions, it does not survive but rearranges quantitatively to phenylcyclopentadienes **2** and **3**, plus a small amount of $\alpha$-methylnaphthalene (**5**). Other bicyclo[6.3.0]undecapentaenes, isomeric with **11**, also rearrange thermally to phenylcyclopentadienes, presumably via spiro[4.6]undecapentaene.[10] We consider this good evidence for the mechanistic pathway in Scheme II.

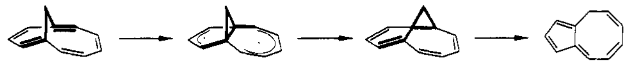
The transformation **1** → **10** constitutes a di-$\pi$-methane rearrangement[11] (see bold lines in Scheme II). Such processes are ordinarily associated with the chemistry of electronically excited states,[11] since kinetic and thermodynamic factors oppose the corresponding ground-state rearrangement in most cases. Transannular bond formation in **1**, however, relieves all twisting of the $\pi$ system and yields an intermediate (**9**) stabilized by extensive delocalization of electrons.[8] Electrocyclic opening of **10** to **11** overcomes the normal problem of endothermicity. Thus, homoazulene appears ideally constructed to undergo a ground-state di-$\pi$-methane rearrangement, although temperatures in the range of 435 °C and above are still required.

Scheme I



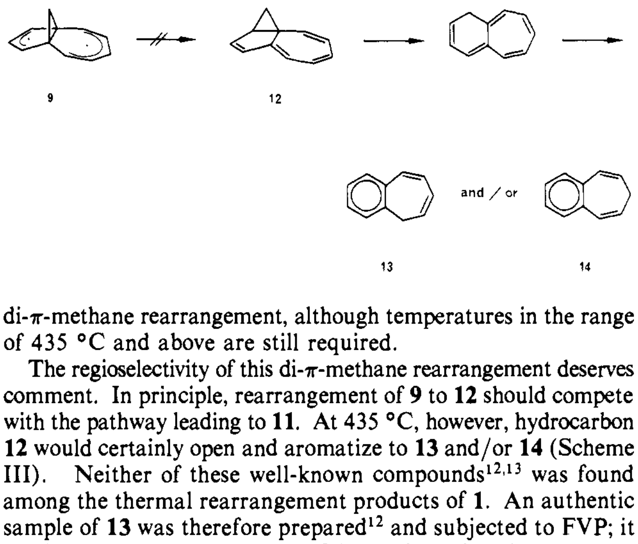
**1** **7** **8** **5** **4** **6**

Scheme II



**1** **9** **10** **11**

Scheme III



**9** **12** **13** **14**

The regioselectivity of this di-$\pi$-methane rearrangement deserves comment. In principle, rearrangement of **9** to **12** should compete with the pathway leading to **11**. At 435 °C, however, hydrocarbon **12** would certainly open and aromatize to **13** and/or **14** (Scheme III). Neither of these well-known compounds[12,13] was found among the thermal rearrangement products of **1**. An authentic sample of **13** was therefore prepared[12] and subjected to FVP; it survived unchanged even at 550 °C. Hydrocarbon **14** reportedly isomerizes to **13** at high temperatures.[13] The absence of both benzotropylidenes (**13** and **14**) from the FVP products of **1** requires that intermediate **9**, if involved, rearrange exclusively as in Scheme II and not as in Scheme III. We presently have no explanation to offer for this regioselectivity.

Finally, it should be mentioned that a trace of azulene is also found in the FVP of **1**. The rich visible spectrum of azulene clearly distinguishes the parent $C_{10}H_8$ hydrocarbon from its methyl-substituted derivatives which would be isomeric with **1** ($C_{11}H_{10}$). Loss of $CH_2$ from intermediate **9** could account for the formation of azulene. The analogous fragmentation of certain 1,6-methano[10]annulenes to give naphthalene and a carbene is well-known.[14]

We conclude that homoazulene (**1**) rearranges thermally by two competing pathways. The dominant pathway (ca. 75%) involves an unusual ground-state di-$\pi$-methane rearrangement which leads regioselectively to **11** (Scheme II); compound **11** then continues on to **2**, **3**, and **5**. The minor pathway (ca. 25%) begins

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(6) Mp 122–124 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$) $\delta$ 7.40 (s, rel area 10), 7.30 (s, 5), 6.9–6.5 (m, 5), 4.36 (br s, 1), 4.00 (br s, 3), 2.85–2.15 (m, 6); IR (KBr) 3080, 2940, 2905, 2250, 1495, 1446, 1340, 1265, 1210, 1030, 915 cm$^{-1}$.

(7) Scott, L. T.; Brunsvold, W. R. *J. Org. Chem.* **1979**, *44*, 641.

(8) Intermediate **9** could also be formulated as a zwitterion with twofold homoaromatic character.

(9) Scott, L. T.; Brunsvold, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 6535–6536.

(10) (a) A freshly prepared sample of bicyclo[6.3.0]undeca-1(8),2,4,6,9-pentaene[10b] was converted exclusively to phenylcyclopentadienes **2** and **3** (2:1) upon FVP at 435 °C. (b) Schönleber, D. *Chem. Ber.* **1969**, *102*, 1799–1801. (c) Dürr, H.; Scheppers, G. *Ibid.* **1970**, *103*, 380–388. (d) Dürr, H.; Kober, H. *Tetrahedron Lett.* **1972**, *1255*–1258.

(11) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

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(13) Gruber, G. W.; Pomerantz, M. *Tetrahedron Lett.* **1970**, 3755–3758.

(14) Rautenstrauch, V.; Scholl, H.-J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 288–289.

with an electrocyclic ring opening to **7** which gives rise to **4**, **5**, and **6** (Scheme I). All the observed products are readily accomodated by these two mechanisms.

**Acknowledgment.** We thank the National Science Foundation, the National Institutes of Health (CA 23488), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

**Registry No.** **1**, 65754-71-4; **2**, 2327-56-2; **2** TCNE adduct, 80485-39-8; **3**, 1961-93-9; **3** TCNE adduct, 80502-01-8; 4, 68367-49-7; **5**, 90-12-0; **6**, 91-57-6; **11**, 276-32-4; **13**, 264-08-4; bicyclo[6.3.0]undeca-1-(8),2,4,6,9-pentaene, 276-33-5.

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## Silylene to Silene Thermal Rearrangement. Generation and Rearrangement of Cyclopropylsilylene and Vinylsilylene

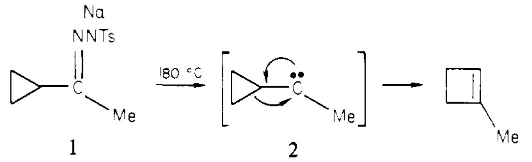
Thomas J. Barton,* Gary T. Burns, William F. Goure, and William D. Wulff

*Department of Chemistry*
*Iowa State University*
*Ames, Iowa 50011*

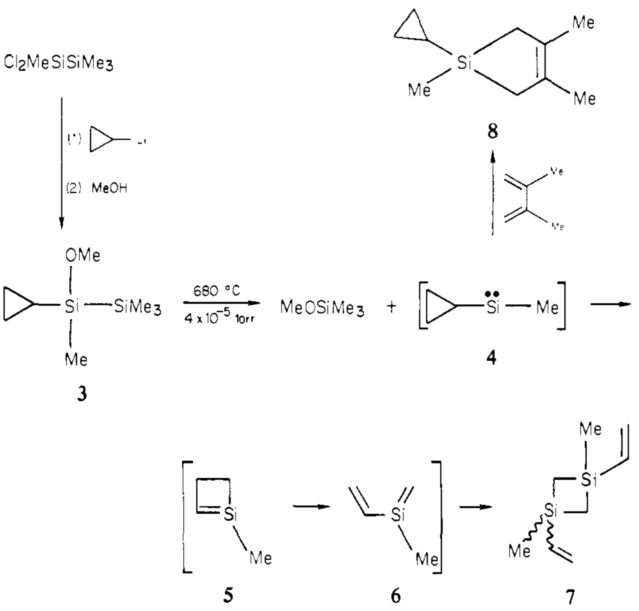
*Received October 26, 1981*

Although the isomerization of carbenes to olefins is a long-established reaction and there are now several documented examples of facile rearrangement of silylcarbenes to silenes ($R_2Si{=}CR'_2$),[1] there exists only a single report[2] of the rearrangement of a silylene ($R_2Si$:) to a silene.[3] Thus, the photochemically induced isomerization of $Me_2Si$: to $MeHSi{=}CH_2$[2] is the sole example of a reaction which recent calculations reveal to be essentially thermoneutral.[6]

In an attempt to gain the first definitive evidence for a thermally induced silylene to silene rearrangement, it was decided to generate cyclopropylmethylsilylene (**4**), as thermally generated cyclopropylcarbene (**2**) is known to undergo facile rearrangement via ring expansion. For example, thermolysis of the sodium salt of cyclopropyl methyl ketone tosylhydrazone (**1**) affords 1-methylcyclobutene in 92% yield.[7]



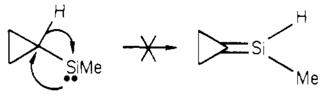
Synthesis of the desired thermal precursor of silylene **4** was accomplished by reaction of 1,1-dichlorotetramethyldisilane and cyclopropyllithium[8] ($Et_2O$, 0 °C, 160 min) followed by quenching with an equimolar mixture of methanol and pyridine. After distillation [72–75 °C (20 torr)], separation of 1-cyclopropyl-1-methoxytetramethyldisilane (**3**) from 1,1-dicyclopropyltetramethyldisilane was achieved by preparative gas chromatography (GC) [**3**: 30% yield; NMR ($CCl_4$) $\delta$ 0.00 (s, 3H), 0.10 (s, 9H), −0.40 to 0.70 (m, 5H), 3.38 (s, 3H); mass spectrum, *m/e* 188 (14%), 173 (76, 133 (67), 115 (84, 73 (100); calcd for $C_8H_{20}OSi_2$ *m/e* 188.1053, measured *m/e* 188.1055; 30% yield]. Flash vacuum pyrolysis (FVP) of **3** was conducted through a quartz-packed horizontal 36-cm tube at 680 °C ($4 \times 10^{-5}$ torr) with 88% mass balance. The two major products were isolated by preparative GC: trimethylmethoxysilane (99%) and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane (**7**) (42%) as an equal mixture of cis and trans isomers [**7**, NMR ($CCl_4$) $\delta$ 0.14 (apparent t, 4H), 0.28 (s, 3H), 0.30 (s, 3H), 5.35–6.57 (vinyl m, 6H); mass spectrum, *m/e* 168 (24%), 153 (64), 140 (100), 127 (68), 126 (20), 125 (64), 113 (46), 99 (41), 85 (30), 83 (18), 73 (27), 71 (31), 69 (27), 59 (65); calcd for $C_8H_{16}Si_2$ *m/e* 168.0788, measured *m/e* 168.0791].



The most economical mechanistic rationalization for the formation of **7** is $\alpha$ elimination of $Me_3SiOMe$ to form silylene **4**, ring expansion of **4** to 1-methyl-1-silacyclobutene (**5**), ring opening of **5** to vinylsilene **6**, and the usual head-to-tail silene dimerization of **6**. Thus, the conversion of **4** to **5** represents the first example of a thermal silylene to silene rearrangement. Also, the isomerization of **5** to **6** represents the first example of a silene to silene rearrangement.

Evidence that silylene **4** is indeed involved in this remarkably efficient sequence was obtained from the cothermolysis of **3** and 2,3-dimethylbutadiene (500 °C, vertical quartz-packed 36-cm tube, 55-mL/min $N_2$ flow) to afford 4-cyclopropyl-1,2,4-trimethyl-4-silacyclopentene (**8**), the expected product of addition of **4** to the diene [**8**: 43% yield; NMR ($CCl_4$) $\delta$ -0.44 to 0.70 (m, 5H), 0.07 (s, 3H), 1.20 (br s, 4H), 1.63 (br s, 6H); mass spectrum, *m/e* 166 (56%), 151 (23), 125 (100), 124 (83), 123 (77), 109 (90), 97 (31), 95 (26), 85 (28), 83 (45), 69 (42), 67 (22), 59 (96), 58 (28); calcd for $C_{10}H_{18}Si$ *m/e* 166.1178, measured *m/e* 166.1179].

It is of interest to note that silylene **4** eschews the opportunity for 1,2-hydrogen migration to silicon to form cyclopropylidenesilane **9**. Molecular orbital calculations have revealed that the



silicon–carbon double bond should be significantly strengthened by d–$\sigma$ hyperconjugation in the silicon analogue of methylenecyclopropane.[9]

Another carbene that is known to undergo facile rearrangement is vinylcarbene which isomerizes to cyclopropene through intramolecular $\pi$ addition.[10] Thus, we constructed 1-chloro-1-

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(2) Drahnek, T. J.; Michl, J.; West, R. *J. Am. Chem.* **1981**, *103*, 1843.

(3) Gaspar[4] has made the interesting suggestion that the origin of 1,3-dimethyl-1,3-disilacyclobutane from generation of $Me_2Si$: above 600 °C could "in principle" arise from $Me_2Si$: rearranging to $MeHSi{=}CH_2$ followed by dimerization. However, this mechanism is not demanded.[5]

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(5) Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

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