β-Trimethylsilyl Cyclopropylcarbenes

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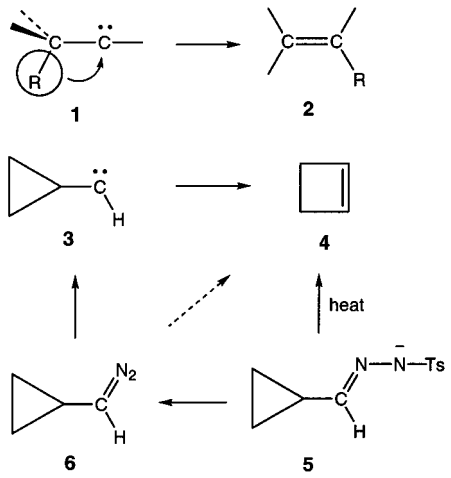
Received July 24, 2000

Thermal decomposition of the in situ generated lithium salt of the tosylhydrazone derivative of cyclopropyl trimethylsilylmethyl ketone gave 1-cyclopropyl-1-trimethylsilylethylene, a product of exclusive silyl migration. Thermal decomposition of the sodium salts of tosylhydrazone derivatives of 1-trimethylsilylcyclopropyl alkyl ketones also gave methylenecyclopropane products derived from trimethylsilyl migration. These reactions were interpreted in terms of rapid trimethylsilyl migration to carbene-like centers that compete effectively with ring expansion processes of cyclopropylcarbenes. Computational studies (B3LYP/6-31G*) suggest that cyclopropyl stabilization of carbenes is more effective than *β*-trimethylsilyl stabilization. However, *β*-trimethylsilyl stabilized conformations are easily attained, and these conformations can lead to silyl migrations. There are two minimum energy conformations of methyl-1-trimethylsilylcyclopropylcarbene, **27**, and the rotational barrier to interconversion of these conformations (5.4 kcal/mol) is substantially lower than in the parent cyclopropylcarbene (15 kcal/mol). The onset of a stabilizing interaction in the transition state between the carbene vacant orbital with the adjacent Si−C *σ*-orbital is proposed. Computational studies also show a very small (2.0 kcal/mol) barrier for trimethylsilyl migration in trimethylsilylmethyl cyclopropylcarbene, **11**.

Introduction

Singlet carbenes **1** are prone to intramolecular rearrangement via 1,2-shifts to the carbenic center.[1] The chemistry of cyclopropylcarbene **3** is no exception and is characterized by a remarkably facile ring expansion to give cyclobutene, **4**. This chemistry of **3** was first described by Shechter and Friedman[2] and was based on the pyrolysis of the tosylhydrazone salt **5**. Thermal decomposition of **5** gave cyclobutene as the major product, presumably via the intermediacy of the diazocompound **6** and the cyclopropylcarbene **3**. However, the intermediacy of carbene **3** and analogous cyclopropylcarbenes has recently been questioned in the formation of cyclobutene derivatives. Jones and Shevlin[3] have shown that cyclopropylmethylcarbene generated by alternative methods gives vinylcyclopropane (and not 1-methylcyclobutene) as the major product. Platz[4] has shown that a substituted cyclopropylcarbene is effectively trapped by alkene or amines (in preference to ring expansion). These studies led to the suggestion that cyclobutene products may not arise from free carbenes such as **3**. Instead some energetic nitrogen-containing intermediate may be a direct source of the ring expanded product.



We[5] and others[6] have been interested in the chemistry of carbenes containing silicon in adjacent and more remote positions relative to the carbenic center. Our previous studies have shown that the trimethylsilyl group undergoes very facile migration to carbenic centers. The alkene **8** derived from silyl migration is the major product formed from carbene **7**,[5a] while the silyl migration product **10** is formed exclusively from **9**.[5b] With these results in mind, we wanted to determine the fate of cyclopropyl carbenes with silicon in the *β*-position as in **11** and **12**. Will silyl migration compete successfully with the rapid ring expansion process usually seen in cyclopropyl carbenes? Reported here are the results of these studies.

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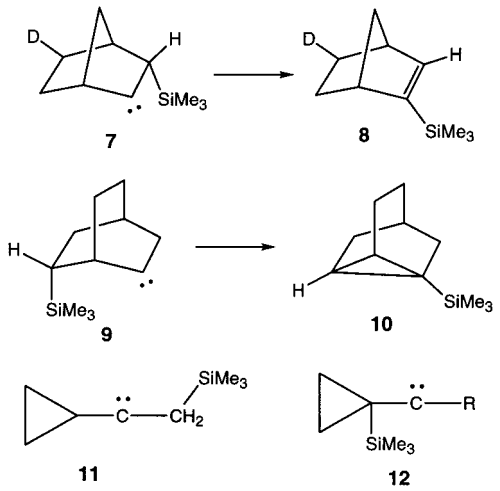
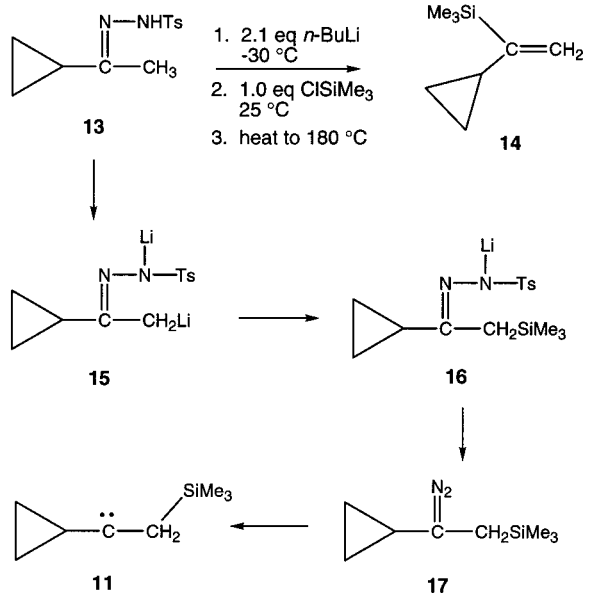
10.1021/jo001112b CCC: $20.00 © 2001 American Chemical Society
Published on Web 01/24/2001

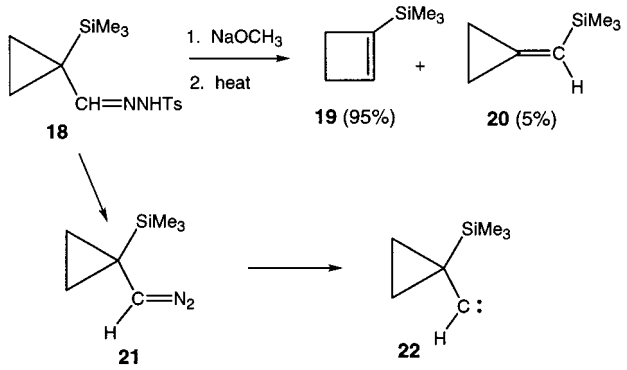


Results and Discussion

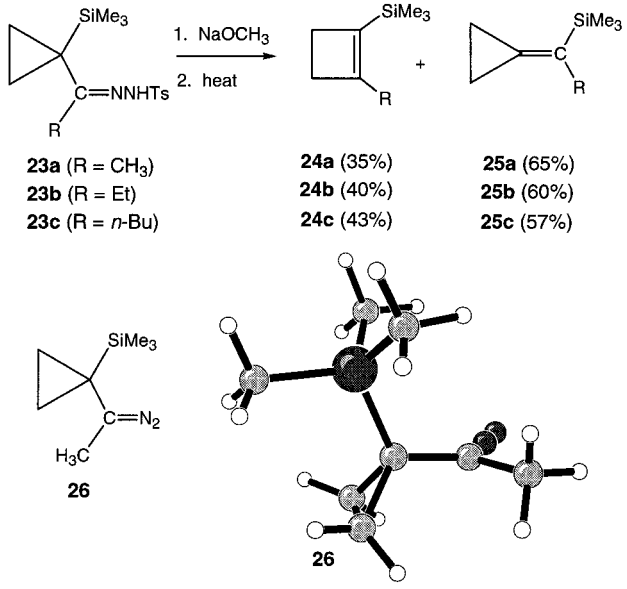
Tosylhydrazone Salt Pyrolyses. The approach used to generate carbenes in this study was the thermal decomposition of tosylhydrazone salts.[7] Tosylhydrazones are usually derived from the corresponding aldehydes or ketones. However, since cyclopropyl trimethylsilylmethyl ketone is not readily available, an alternative approach was used to generate the tosylhydrazone salt precursor to carbene **11**. The tosylhydrazone derivative of cyclopropyl methyl ketone, **13**, was doubly deprotonated with 2 equiv of *n*-BuLi at −78 to −30 °C. Silylation with 1 equiv of $ClSiMe_3$ led to the lithium salt **16**, which was dried and then pyrolyzed under vacuum at up to 180 °C. The sole product formed from this series of reactions was the alkene **14**. No propargyltrimethylsilane, a product of carbene fragmentation, was observed. The product **14** does not arise via the Shapiro reaction[8] since the dilithio derivative **15** does not eliminate LiTs and molecular nitrogen at −30 °C. Additionally, the dry salt **16** was extracted with hexane prior to pyrolysis to remove any trace of **14** (hexane soluble) that might have arisen from the Shapiro reaction. These transformations are consistent with the intermediacy of the carbene **11**, which undergoes exclusive trimethylsilyl migration to the carbene center. This trimethylsilyl migration is substantially faster than either ring expansion or hydrogen atom migration.



Attention was next focused on the carbene **12**. 1-Trimethylsilylcyclopropanecarboxaldehyde[9] was converted to the corresponding tosylhydrazone **18**. Deprotonation with $NaOCH_3$ followed by vacuum pyrolysis of the dry sodium salt led to a product mixture (56% yield) containing 95% of the cyclobutene **19** as well as 5% of the methylenecyclopropane **20**. Again, no fragmentation product, trimethylsilylacetylene, was observed. The chemistry of the diazocompound **21** is therefore beginning to deviate from that of the parent diazocompound **6**. Formation of the small amount of methylenecyclopropane **20** suggests that silicon migration can begin to compete with ring expansion in a carbene-like transition state[10] or in the carbene **22**.



1-Trimethylsilylcyclopropylmethyl ketone[11] was converted in fashion similar to the tosylhydrazone **23a**, and the dry sodium salt was pyrolyzed under vacuum. The



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(10) As in refs 3 and 4, concerted loss of molecular nitrogen and rearrangement remains a possibility.

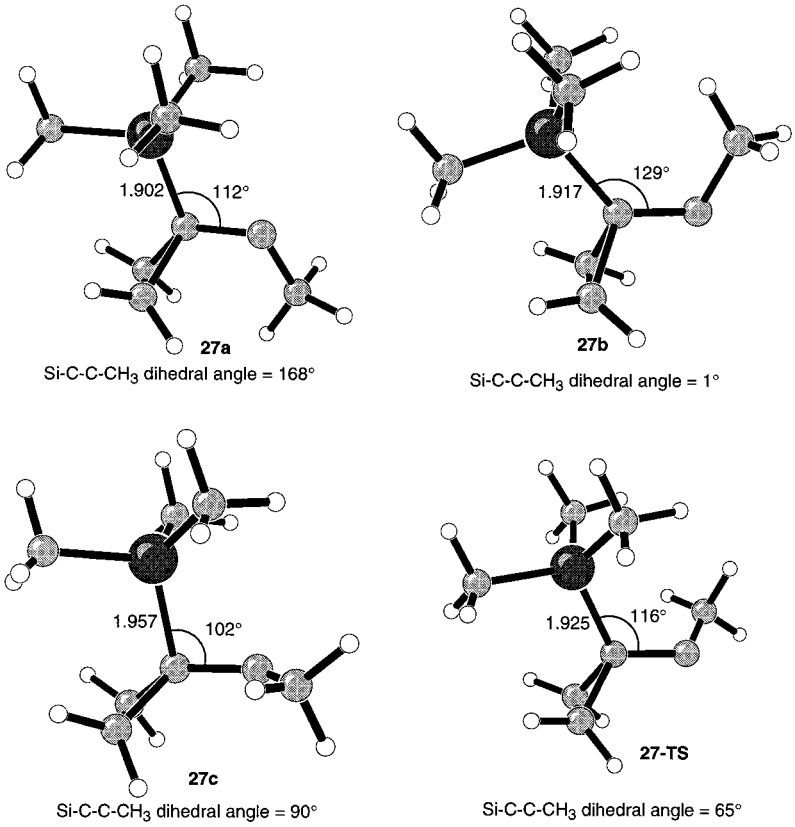

Figure 1. B3LYP/6-31G* structures of carbenes **27a**, **27b**, the 90° constrained form **27c**, and the transition state **27-TS** for interconversion of **27a** and **27b**.

behavior was significantly different from that of the salt **5** in that the methylenecyclopropane **25a** was the major product (65%) and only 35% of the ring expanded cyclobutene **24a** was formed. Analogous behavior is seen in the tosylhydrazones **23b** and **23c** derived from 1-trimethylsilylcyclopropyl ethyl ketone and 1-trimethylsilylcyclopropyl *n*-butyl ketone. Silyl migration very successfully competes with the ring expansion process in all of these systems.

Computational Studies. Ab initio molecular orbital computational studies can offer some insights into the behavior of the diazocompound **26** as well as the carbene **27** derived from **26**. Recently, density functional computational methods have been applied to carbene intermediates,[12−17] and this method has been used in the present studies. Geometries were optimized at the B3LYP/6-31G* level, and single point energies were also calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level. The B3LYP/6-31G* calculated structure of **26** shows a conformation where the Si−C−C−N dihedral angle is approximately 90° (87°). Analogous to the parent cyclopropylcarbene **3**,[18] there are two minimum energy conformations of the carbene **27** as shown in Figure 1. Conformation **27a** has the trimethylsilyl group *anti* to the methyl group and the vacant orbital on the carbene aligned essentially in conjugation with the cyclopropane ring. The second minimum energy conformation (**27b**) has the trimethylsilyl and methyl groups in a *syn*-orientation. This *syn*-conformation **27b** is 0.53 kcal/mol lower energy than **27a** at the B3LYP/6-311+G**//B3LYP/6-31G* level. Conjugation of the vacant carbene orbital with the cyclopropane ring therefore appears to be more important than conjugation with the filled C−Si σ-orbital.

To evaluate the importance of the interaction of the carbene vacant orbital with the C−Si σ-orbital, the energy of conformation **27c** was calculated. Conformation **27c** is not an energy minimum, and this structure was arrived at by constraining the Si−C−C−CH_3 dihedral angle to 90°.[19] This conformation **27c** is only 3.6 kcal/mol higher in energy than **27a** and corresponds to a loss of cyclopropyl stabilization of the carbene. By way of contrast, the analogous constrained conformation (H−C−C−H dihedral angle = 90°) of the parent cyclopropylcarbene **3** is 15.1 kcal/mol higher energy than the *anti*-conformation of **3**.[20] These findings are completely in line with a stabilizing interaction of the carbene center

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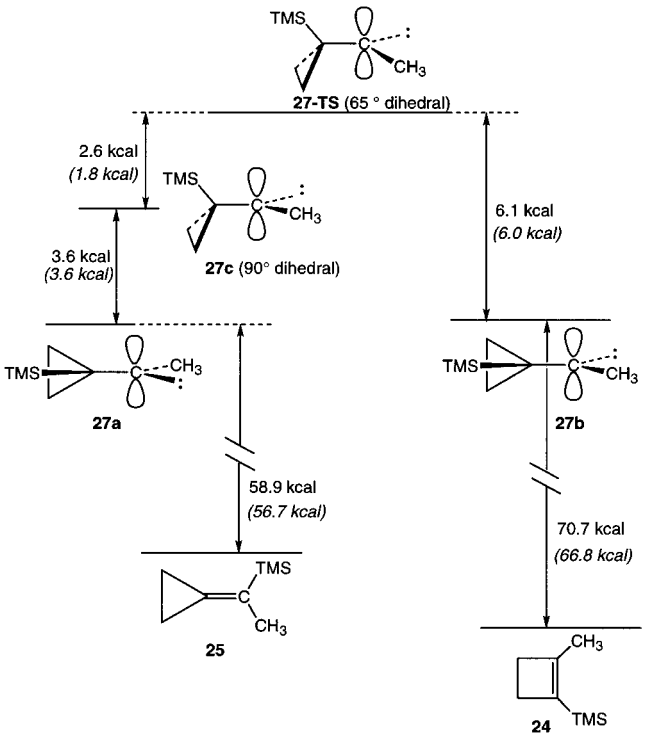


Figure 2. B3LYP/6-31G* energy levels of carbene **27** and the rearrangement products **24** and **25**. B3LYP/6-3111+G**// B3LYP/6-31G* energy levels are shown in parentheses.

in **27c** with the conjugating adjacent silicon−carbon bond. In support of this suggestion, the bond from silicon to the cyclopropyl carbon increases from 1.902 Å in **27a** to 1.957 Å in **27c**. The Si−C−C bond angle also decreases to 102° in **27c**. When the Si−C−C−CH_3 dihedral angle in **27c** is not constrained, attempted geometry optimization leads to $SiMe_3$ migration and formation of methylenecyclopropane **25** without barrier.

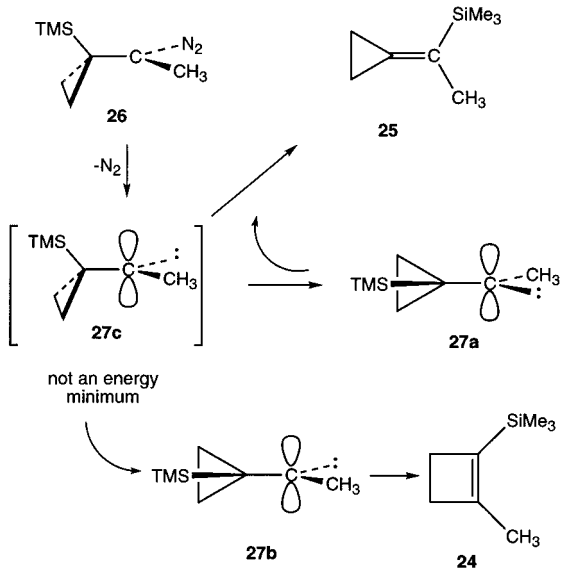
The transition state for interconversion of **27a** and **27b** was located on the energy surface and corresponds to **27-TS**. This transition state has one imaginary frequency and hence corresponds to an energy maximum, which lies 5.4 kcal/mol above **27a**. The Si−C−C−CH_3 dihedral angle of 65° indicates minimal carbene stabilization from the cyclopropyl ring but the beginnings of stabilization by the adjacent silicon. In line with this interpretation is the lengthening of the Si−C bond to 1.925 Å. However, maximal interaction with the adjacent Si−C bond, as in **27c**, has not been achieved. The energy levels of these carbene conformations are shown in Figure 2.

The computational profile of carbene **22**(α-H) (Figure 3) is analogous to that of carbene **27**(α-CH_3). There are two minima (**22a** and **22b**) with **22b** being lower in energy by 1.0 kcal/mol at the B3LYP/6-311+G**//B3LYP/6-31G* level. The transition state (**22-TS**) for interconversion of these conformations lies 6.5 kcal/mol above **22a**. The Si−C bond length of 1.938 Å is again indicative of some stabilization of this transition state by the beginning of an interaction of the carbene vacant orbital with the Si−C bond.

(20) Our calculated rotational barrier for conversion of *anti*-**3** to *syn*-**3** is 15.1 kcal/mol at the B3LYP/6-31G* level. This transition state is very close in structure (H−C−C−H dihedral = 96°) and energy to the 90° constrained structure. A previous barrier to rotation of 13.1 kcal/mol for conversion of *anti*-**3** to *syn*-**3** (single point MP4SDQ/6-31G* approximated value) has been reported.[18c,d]

The question arises as to which carbene conformation is generated in pyrolysis of diazocompound **26**. In principle, loss of molecular nitrogen from **26**, without extensive reorganization, would give a conformation **27c** with the carbene vacant orbital aligned with the C−Si σ-bond. While this carbene conformation is not an energy minimum, it is a favorable conformation for $SiMe_3$ migration. The possibility therefore exists that loss of N_2 from **26** is concerted with silicon migration, i.e., a carbene as a discrete intermediate may not be involved in the formation of methylenecyclopropane **25**.

Consider next the possibility of formation of carbene **27** as a discrete intermediate. Carbene **27a** cannot ring expand since the TMS and methyl groups are *anti*. Carbene **27a** is also in an unfavorable conformation for silicon migration. However, upon bond rotation, **27a** passes through a conformation close to **27c**, where $SiMe_3$ migration should be facile. Conformation **27a** can therefore lead to the silyl migration product **25**. On the other hand, conformation **27b** is the conformation that can ring expand to give **24**. However, analogous to the proposal of Jones, Shevlin,[3] and Platz,[4] the discrete intermediacy of carbene **27b** in formation of **24** remains open to question. These suggestions are summarized in the following scheme.



An explanation for the smaller amount of silyl migration (5%) in the products derived from diazocompound **21** would be desirable. The large amount of ring expanded product **19** might well arise from a concerted loss of N_2/ring expansion process, as suggested for the parent diazocompound **6**.[3,4] This possibility cannot be ruled out with current information, but there is no obvious reason (such as steric effects) why α-CH_3 substitution in diazocompound **26** should change the behavior. Another possibility involves a subtle conformational difference between diazocompounds **21** and **26**. The calculated minimum energy structure of **21** has a Si−C−C−H dihedral angle of 77°. Loss of molecular nitrogen from **21**, along with a 77° bond rotation, would lead preferentially to the *syn*-carbene **22b**. A larger rotation would be required to generate the *anti*-conformation of **22a**. The *syn*-conformation **22b** is the conformation that leads to the ring expanded product **19** (95%). Diazocompound **26**

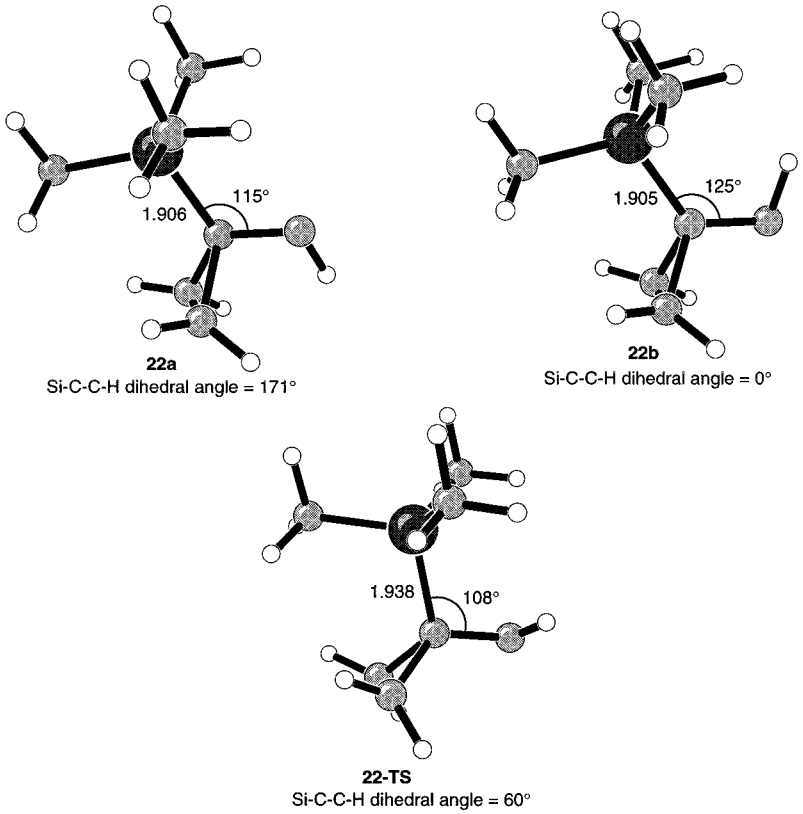


Figure 3. B3LYP/6-31G* structures of carbenes **22a**, **22b**, and the transition state **27-TS** for interconversion of **22a** and **22b**.

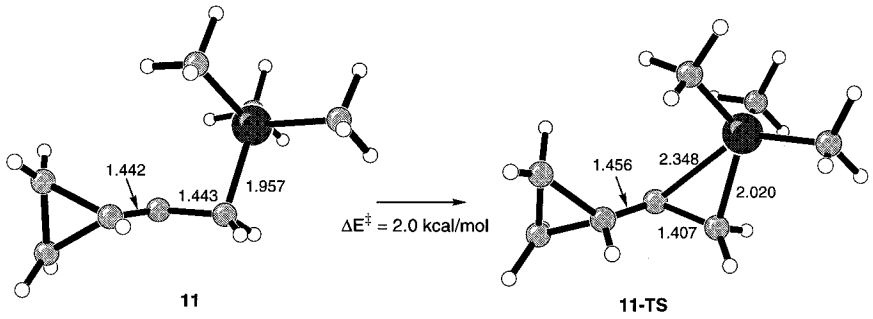
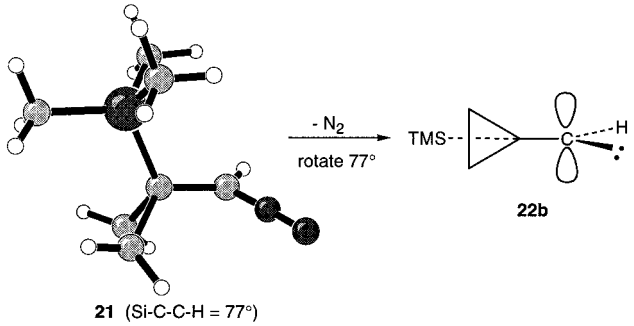


Figure 4. B3LYP/6-31G* structures of carbenes **11** and the transition state for silyl migration **11-TS**.

differs in that the 87° Si−C−C−CH_3 dihedral angle could lead to either carbene **27a** or **27b** with comparable facility.



The B3LYP/6-31G* calculated structure of carbene **11** is shown in Figure 4. This carbene appears to be stabilized simultaneously by the cyclopropyl group as well as the β-trimethylsilyl group. A manifestation of this β-silyl stabilization is the Si−C bond length of 1.957 Å, as well as the Si−C−C−C dihedral angle of 106°. Although this angle is not exactly 90°, it still permits a substantial interaction of the Si−C bond with the carbene vacant orbital. The total energy of **11** is also in line with this suggestion. Carbene **11** is 11.1 kcal/mol more stable than the isomeric carbene **27b**, where only cyclopropyl stabilization is important. Finally, the transition state for migration of the trimethylsilyl group (**11-TS**) has been located, and it lies only 2.0 kcal/mol above **11**. This is significantly smaller than previously calculated barriers for hydrogen migration to typical carbene centers.[14,21] This remarkably small calculated barrier to silyl rearrangement is consistent with the experimentally observed exclusive formation of alkene **14** from **11**. The β-trimethylsilyl group not only stabilizes carbene **11**, but this interaction leads to facile trimethylsilyl migration.

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Conclusions

Thermal decomposition of the tosylhydrazone salt **16**, a potential precursor to carbene **11**, gives the product from 1,2-silyl migration exclusively. The potential ring expansion, fragmentation, or 1,2-hydrogen migration processes do *not* compete with the facile 1,2-silyl migration. 1-Trimethylsilylcyclopropylcarbenes (or transition states having carbenic character) rearrange to form cyclobutenes along with varying amounts of methylenecyclopropanes derived from silyl migration. The methylenecyclopropane products are significant in that methylenecyclopropanes are *not* observed in the rearrangement of the parent systems, which do not contain trimethylsilyl groups. 1,2-Silyl migration to carbene like centers again successfully competes with the ring expansion process.

Computational studies (B3LYP/6-31G*) show two minimum energy conformations for 1-trimethylsilylcyclopropylcarbenes **22** and **26** with the cyclopropyl ring conjugated with the carbene vacant orbital. The 90° rotated conformation, which is presumably the optimal orientation for silyl interaction with the carbene vacant orbital, was *not* an energy minimum. Rotational barriers of 6.5 and 5.4 kcal/mol for interconversion of conformations of **22** and **26** have been calculated. These barriers are significantly lower than the 15.1 kcal/mol barrier for interconversion of the parent cyclopropylcarbene conformers. It is suggested that one carbene conformer leads to cyclobutene (ring expansion), while the other conformer, upon rotation, can lead to methylenecyclopropanes (silyl migration). When in competition, cyclopropyl stabilization wins out over β-trimethylsilyl stabilization of carbenes. However the ready availability of silyl stabilized carbene conformations allows for facile silyl migration to cyclopropyl carbenic centers.

Experimental Section

Preparation of Lithium Salt 16. A solution of 1.272 g of tosylhydrazone **13**[2] (5.04 mmol) in 8 mL of THF was cooled to −78 °C, and 6.3 mL of 1.6 M *n*-butyllithium (10.1 mmol) was added. The mixture was then warmed to −20 °C over 30 min and then recooled to −50 °C. Trimethylsilyl chloride (561 mg; 5.16 mmol) was added at −50 °C, and the mixture was then gradually warmed to room temperature. After 3 h the solvent was removed using a rotary evaporator to give 1.87 g of the crude lithium salt **16**. The salt **16** was washed with about 10 mL of hexanes, and the hexanes were decanted using a pipet. After evacuation using a rotary evaporator, the last traces of hexanes were removed at a pressure of 0.1 mm.

Preparation of Tosylhydrazone 18. A suspension of 271 mg of *p*-toluenesulfonyl hydrazide (1.46 mmol) in 2 mL of methanol was stirred as a solution of 208 mg of 1-trimethylsilylcyclopropane carboxaldehyde[9] (1.46 mmol) in 0.5 mL of methanol was added at room temperature. The reaction mixture became homogeneous and was kept at room temperature for 4.5 h. ^{1}H NMR analysis of an aliquot showed that the reaction had gone to completion. The tosylhydrazone **18** did not crystallize, even upon standing in methanol in the freezer for 5 days. The solution of **18** in methanol was converted directly to the sodium salt by reaction with sodium methoxide. ^{1}H NMR of **18** ($CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 7.8 Hz, 2 H), 6.67 (s, 1 H), 2.43 (s, 3 H), 0.78−0.74 (m, 2 H), 0.71−0.67 (m, 2 H), −0.070 (s, 9 H).

Preparation of Tosylhydrazone 23a. A suspension of 167 mg of *p*-toluenesulfonyl hydrazide (0.897 mmol) in 1 mL of methanol was stirred as a solution of 135 mg of 1-trimethylsilylcyclopropyl methyl ketone[11] (0.866 mmol) in 0.5 mL of methanol was added at room temperature. The mixture became homogeneous, and after 20 h the mixture was cooled in a freezer. The tosylhydrazone **23a** (271 mg, 97% yield), mp 116−119 °C, was collected. ^{1}H NMR of **23a** ($CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 2.42 (s, 3 H), 1.60 (s, 3 H), 0.73−0.69 (m, 2 H), 0.62−0.59 (m, 2 H), −0.14 (s, 9 H). Anal. Calcd for $C_{15}H_{24}N_2O_2SSi$: C, 55.52; H, 7.45. Found: C, 55.56; H, 7.46.

Preparation of 1-Trimethylsilylcyclopropyl Ethyl Ketone. Ethyllithium was prepared by dropwise addition of a solution of 2.18 g of ethyl bromide (20.0 mmol) in 5 mL of ether to a mixture of 367 mg of lithium wire (containing 1% sodium) (52.8 mmol) in 15 mL of ether at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for an additional 15 min. The ethyllithium solution was then added dropwise to a solution of 1.181 g of 1-trimethylsilylcyclopropyl carboxylic acid[22] (7.459 mmol) in 15 mL of ether at 0 °C. The reaction mixture was then stirred at room temperature for 8 h, quenched with 25 mL of saturated NH_4Cl solution, and extracted with ether. The ether extract was washed with saturated NaCl solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the ether solvent was removed using a rotary evaporator. The residue was chromatographed on 11 g of silica gel. Elution with 10% ether in hexanes gave 436 mg (34% yield) of 1-trimethylsilylcyclopropyl ethyl ketone. ^{1}H NMR ($CDCl_3$) δ 2.24 (q, J = 7.2 Hz, 2 H), 1.09 (d of d, J = 4.2, 6.4 Hz, 2 H), 1.00 (t, J = 7.2 Hz, 3 H), 0.78 (d of d, J = 3.7, 5.9 Hz, 2 H), 0.049 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 212.7 (quat), 31.4 (t, J = 125 Hz), 20.8 (quat), 11.2 (t, J = 163 Hz), 8.3 (q, J = 127 Hz), −2.2 (q, J = 119 Hz). HRMS (EI) calcd for $C_9H_{18}OSi$ 170.1127, found 170.1091.

Preparation of Tosylhydrazone 23b. A suspension of 446 mg of *p*-toluenesulfonyl hydrazide in 0.5 mL of methanol was stirred as a solution of 400 mg of 1-trimethylsilylcyclopropyl ethyl ketone prepared above in 2.5 mL of methanol was added at room temperature. The mixture became homogeneous, and after 18 h the mixture was cooled in a freezer. Crystallization of the tosylhydrazone **23b** occurred, and the excess methanol solvent was decanted. The remaining solid was washed with a minimal amount of cold hexanes. The solid was dried for several hours on the rotary evaporator to give 454 mg of tosylhydrazone **23b** (57% yield), mp 68−70 °C. ^{1}H NMR ($CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.1 Hz, 2 H), 2.42 (s, 3 H), 1.93 (q, J = 7.8 Hz, 2 H), 0.97 (t, J = 7.8 Hz, 3 H), 0.74−0.68 (m, 2 H), 0.64−0.58 (m, 2 H), −0.15 (s, 9 H). Anal. Calcd for $C_{16}H_{26}N_2O_2SSi$: C, 56.76; H, 7.74. Found: C, 57.19; H, 7.60.

Preparation of 1-Trimethylsilylcyclopropyl *n*-Butyl Ketone. A solution containing 510 mg of 1-trimethylsilylcyclopropyl carboxylic acid (3.228 mmol) in 12 mL of ether was stirred at 0 °C, and 5.0 mL of 1.6 M *n*-butyllithium (8.0 mmol) was added under nitrogen. The mixture was then warmed to room temperature for 20 h, recooled to 0 °C, and then quenched with 15 mL of saturated NH_4Cl solution. The ether phase was separated, washed with saturated NaCl solution, and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the ether was removed using a rotary evaporator and the residue was chromatographed on 11 g of silica gel. Elution with 5% ether in hexanes gave 346 mg (54% yield) of 1-trimethylsilylcyclopropyl *n*-butyl ketone. ^{1}H NMR ($CDCl_3$) δ 2.19 (t, J = 7.3 Hz, 2 H), 1.58−1.42 (m, 2 H), 1.34−1.20 (m, 2 H), 1.08 (d of d, J = 3.6, 5.7 Hz, 2 H), 0.88 (t, J = 7.3 Hz, 3 H), 0.78 (d of d, J = 4.0, 6.1 Hz, 2 H), 0.048 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 212.4 (quat), 37.8 (t, J = 124 Hz), 26.5 (t, J = 125 Hz), 22.4 (t, J = 120 Hz), 21.0 (quat), 14.0 (q. J = 125 Hz), 11.1 (t, J = 162 Hz), −2.2 (q, J = 120 Hz). HRMS (EI) calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1450.

Preparation of Tosylhydrazone 23c. A suspension of 249 mg of *p*-toluenesulfonyl hydrazide in 0.5 mL of methanol was stirred at room temperature as a solution of 262 mg of 1-trimethylsilylcyclopropyl *n*-butyl ketone in 2.5 mL of methanol was added. The mixture was stirred at room temperature for 17 h, and some of the methanol was then removed using a rotary evaporator. The mixture was cooled in a freezer, and the excess methanol was decanted from the solid that formed.

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The last traces of methanol were removed using a rotary evaporator to give 470 mg (97% yield) of tosylhydrazone **23c**, mp 79−80 °C. ^{1}H NMR ($CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2 H), 7.78 (br s, 1 H), 7.30 (d, J = 8.1 Hz, 2 H), 2.42 (s, 3 H), 1.87 (m, 2 H), 1.34−1.18 (m, 4 H), 0.82 (t, J = 7.1 Hz, 3 H), 0.68 (m, 2 H), 0.57 (m, 2 H), −0.15 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 164.6 (s), 143.8 (s), 135.6 (s), 129.5 (d, J = 162 Hz), 128.2 (d, J = 165 Hz), 27.7 (t, J = 129 Hz), 27.4 (t, J = 127 Hz), 23.1 (t, J = 126 Hz), 21.6 (q, J = 128 Hz), 14.4 (s), 13.7 (q, J = 125 Hz), 8.5 (t, J = 163 Hz), −2.4 (q, J = 119 Hz).

Pyrolyses of Tosylhydrazone Salts. General Procedure.[7] The tosylhydrazones **18** or **23** (1.00 equiv) were placed in a flask, and 1.06 equiv of $NaOCH_3$ (approx 0.6 M in methanol) was added with stirring. After the tosylhydrazone dissolved, the methanol solvent was removed using a rotary evaporator. The solid salt was further dried by evacuation at 15 mm and at 0.05 mm. The flask containing the dry salt was then fitted with a short path distillation head and a receiver flask and placed in an oil bath. The temperature of the oil bath was gradually raised to 80 °C, and then the receiver flask was cooled in a dry ice/acetone bath. The temperature of the oil was then raised gradually to 180 °C while maintaining the system under vacuum. During this time the pressure rose to approximately 2 mm and then decreased back to 0.05 mm. The products of these pyrolyses collected in the cold receiver flask. Structures were determined by standard spectroscopic techniques. Product ratios were determined by ^{1}H NMR spectroscopy. Pure samples of products were isolated by preparative gas chromatography. The following procedures are representative.

Pyrolysis of the Lithium Salt 16. The dry salt **16** was prepared as described previously. Vacuum pyrolysis of 760 mg of **16**, as described above, gave 206 mg (64% yield) of the vinylcyclopropane **14** as the exclusive product. ^{1}H NMR ($CDCl_3$) δ 5.34 (d of d, J = 1.3, 2.6 Hz, 1 H), 5.17 (d of d, J = 0.7, 2.6 Hz, 1 H), 1.41 (m, 1 H), 0.64 (d of d of d, J = 4.0, 6.0, 8.2 Hz, 2 H), 0.44−0.41 (m, 2 H), 0.13 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 153.77 (quat), 119.67 (t, J = 151 Hz), 15.26 (d, J = 156 Hz), 6.48 (t, J = 161 Hz), −1.54 (q, J = 119 Hz). HRMS (EI) calcd for $C_8H_{16}Si$ 140.1021, found 140.1005.

Pyrolysis of the Sodium Salt of 18. The tosylhydrazone **18** prepared above (1.46 mmol) was reacted with 2.6 mL of 0.58 M $NaOCH_3$ in methanol (1.50 mmol). After removal of the solvent and pyrolysis as described above, 103 mg (56% yield) of a mixture containing 95% **19**[23] and 5% **20**[24] was collected. Structural assignments were made by comparison with reported spectral data. A sample of **20** was isolated by preparative gas chromatography. ^{1}H NMR of **20** ($CDCl_3$) δ 5.97 (quintet, J = 2.0 Hz, 1 H), 1.16−0.96 (m, 4 H), 0.11 (s, 9 H). These observed signals are in accord with the literature spectral data for **20**. ^{1}H NMR of **19** ($CDCl_3$) δ 6.47 (t, J = 0.9 Hz, 1 H), 2.66 (t of d, J = 1.2, 3.6 Hz, 2 H), 2.54−2.52 (m, 2 H), 0.047 (s, 9 H). ^{13}C NMR of **19** ($CDCl_3$) δ 156.10 (quat), 147.63 (d, J = 166 Hz), 32.15 (t, J = 136 Hz), 31.83 (t, J = 137 Hz), −2.23 (q, J = 119 Hz).

Pyrolysis of the Sodium Salt of 23a. Vacuum pyrolysis of the dry sodium salt of **23a** (R = CH_3) gave a 63% yield of a mixture containing 65% of **25a** and 35% of **24a**. The cyclobutene **24a**[23] is a known compound with reported spectral data. Thus, spectral data for **25a** and **24a** were extracted from the spectrum of the product mixture. ^{1}H NMR of **25a** ($CDCl_3$) δ 1.86 (quintet, J = 1.8 Hz, 3 H), 1.14−1.10 (m, 2 H), 0.93−0.89 (m, 2 H), 0.11 (s, 9 H). ^{13}C NMR of **25a** ($CDCl_3$) δ 131.64 (quat), 123.35 (quat), 19.66 (q, J = 126 Hz), 3.98 (t, J = 160 Hz), 0.40 (t, J = 160 Hz), −1.56 (q, J = 119 Hz). ^{1}H NMR of **24a** ($CDCl_3$) δ 2.54 (m, 2 H), 2.27 (m, 2 H), 1.74 (m, 3 H), 0.067 (s, 9 H). ^{13}C NMR of **24a** ($CDCl_3$) δ 157.76 (quat), 144.24 (quat), 34.10 (t, J = 134 Hz), 27.46 (t, J = 137 Hz), 18.14 (q, J = 125 Hz), −1.30 (q, J = 118 Hz).

An attempt to isolate a pure sample of cyclobutene **24a** by preparative gas chromatography led to complete thermal rearrangement to 2-methyl-3-trimethylsilyl-1,3-butadiene. ^{1}H NMR of 2-methyl-3-trimethylsilyl-1,3-butadiene ($CDCl_3$) δ 5.74 (d, J = 2.6 Hz, 1 H), 5.43 (d, J = 2.6 Hz, 1 H), 4.95 (d, J = 1.3 Hz, 1 H), 4.90 (d, J = 1.1 Hz, 1 H), 1.88 (bs, 3 H), 0.17 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 152.71, 146.37, 125.10, 113.75, 22.14, −0.41.

Pyrolysis of the Sodium Salt of 23b. Vacuum pyrolysis of the dry sodium salt of **23b** (R = Et) gave an 80% yield of a mixture, containing 60% of **25b** and 40% of **24b** as determined by ^{1}H NMR spectroscopy. The cyclobutene **24b** completely rearranged to 2-ethyl-3-trimethylsilyl-1,3-butadiene during preparative gas chromatography. ^{1}H NMR of 2-ethyl-3-trimethylsilyl-1,3-butadiene ($CDCl_3$) δ 5.69 (d, J = 3.0 Hz, 1 H), 5.40 (d, J = 3.0 Hz, 1 H), 4.84 (d, J = 0.9 Hz, 1 H), 4.78 (d, J = 0.8 Hz, 1 H), 2.19 (q, J = 7.5 Hz, 2 H), 1.02 (t, J = 7.5 Hz, 3 H), 0.14 (s, 9 H). ^{13}C NMR of 2-ethyl-3-trimethylsilyl-1,3-butadiene ($CDCl_3$) δ 153.43 (quat), 153.40 (quat), 124.86 (d of d, J = 155, 158 Hz), 109.84 (t, J = 156 Hz), 28.47 (t, J = 126 Hz), 12.68 (q, J = 127 Hz), −0.65 (q, J = 119 Hz). ^{1}H NMR of **25b** ($CDCl_3$) δ 2.26 (q of quintets, J = 1.3, 7.5 Hz, 2 H), 1.08−1.05 (m, 2 H), 1.05 (t, J = 7.5 Hz, 3 H), 0.99−0.96 (m, 2 H), 0.12 (s, 9 H). ^{13}C NMR of **25b** ($CDCl_3$) δ 130.97 (quat), 129.38 (quat), 27.65 (t, J = 123 Hz), 14.37 (q, J = 126 Hz), 2.76 (t, J = 160 Hz), 1.00 (t, J = 161 Hz), −0.88 (q, J = 119 Hz). HRMS (EI) calcd for $C_9H_{18}Si$ 154.1178, found 154.1159.

Pyrolysis of the Sodium Salt of 23c. Vacuum pyrolysis of the dry sodium salt of **23c** (R = *n*-Bu) gave a 91% yield of a mixture containing 57% of **25c** and 43% of **24c** as determined by ^{1}H NMR spectroscopy. The cyclobutene **24c** completely rearranged to 2-*n*-butyl-3-trimethylsilyl-1,3-butadiene during preparative gas chromatography. ^{1}H NMR of 2-*n*-butyl-3-trimethylsilyl-1,3-butadiene ($CDCl_3$) δ 5.68 (d, J = 3.0 Hz, 1 H), 5.40 (d, J = 3.1 Hz, 1 H), 4.82 (d, J = 1.2 Hz, 1 H), 4.78 (d, J = 2.0 Hz, 1 H), 2.17 (t, J = 7.3, 2 H), 1.42−1.24 (m, 4 H), 0.89 (t, J = 7.3 Hz, 3 H), 0.14 (s, 9 H). HRMS (EI) calcd for $C_{11}H_{22}Si$ 182.1491, found 182.1462. ^{1}H NMR of **25c** ($CDCl_3$) δ 2.24 (t of quintets, J = 1.3, 7.5 Hz, 2 H), 1.42 (quintet, J = 7.5 Hz, 2 H), 1.29 (sextet, J = 7.5 Hz, 2 H), 1.10−1.07 (m, 2 H), 0.96−0.93 (m, 2 H), 0.90 (t, J = 7.5 Hz, 3 H), 0.11 (s, 9 H). ^{13}C NMR of **25c** ($CDCl_3$) δ 131.67 (quat), 128.00 (quat), 34.46 (t, J = 125 Hz), 31.94 (t, J = 125 Hz), 22.74 (t, J = 124 Hz), 14.09 (q, J = 124 Hz), 3.25 (t, J = 158 Hz), 1.13 (t, J = 159 Hz), −0.82 (q, J = 119 Hz). HRMS (EI) calcd for $C_{11}H_{22}Si$ 182.1491, found 182.1476.

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 94 and Gaussian 98 series of programs.[25] Energy minima were characterized via frequency calculations which showed no imaginary frequencies. Electronic energies are presented without zero point vibrational energies. Transition states showed one imaginary frequency.

Acknowledgment is made to the National Science Foundation for support of this research.

Supporting Information Available: Structures and energies of diazocompounds **21** and **26**, carbenes **11**, **22**, and **27**, carbene rearrangement transition states **11-TS**, **22-TS**, and **27-TS**, and spectral data for **23c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001112B

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