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# Rearrangement Kinetics of Spiropentylchlorocarbene, [3]Triangulylchlorocarbene, and Related Species

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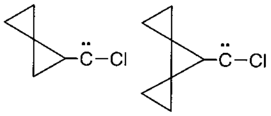
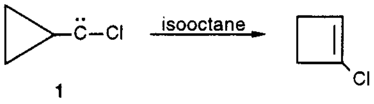
## ABSTRACT



**Absolute rate constants were measured for the 1,2-$CH_2$, 1,2-cyclopropyl, and 1,2-$CMe_2$ rearrangements of spiropentylchlorocarbene (5), [3]-triangulylchlorocarbene (6), and tetramethylcyclopropylchlorocarbene (7). The factors responsible for the observed relative migratory aptitudes (cyclopropyl > $CH_2$ > $CMe_2$) were analyzed with the aid of electronic structure calculations.**

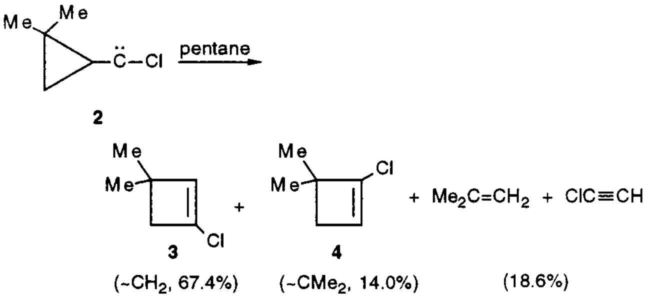
The ring expansion of cyclopropylcarbene to cyclobutene[1] is a classic case of the 1,2-C migration commonly encountered in carbene chemistry.[2] A particularly well-characterized example is the rearrangement of cyclopropylchlorocarbene (**1**) to 1-chlorocyclobutene (Scheme 1),[3,4] for which $k_{re} = 0.9 \times 10^6\ s^{-1}$ at 20 °C.[3a,b] The attendent activation parameters are $E_a = 3.0 \pm 0.4$ kcal/mol, log $A = 8.2 \pm 0.2\ s^{-1}$, $\Delta G^‡ \approx 9$ kcal/mol, $\Delta H^‡ \approx 2-3$ kcal/mol, and $\Delta S^‡ \approx -20$ to $-24$ eu.[3b] The unfavorable entropy of activation may reflect the unusual motions required of the migrating group during the rearrangement.[3,5]

**Scheme 1**



In 1993, we described the intramolecularly competitive "$CH_2$" and "$CMe_2$" rearrangements of 2,2-dimethylcyclopropylchlorocarbene (**2**), which afforded isomeric cyclobutenes **3** and **4**, respectively, accompanied by 19% of a 1:1 mixture of isobutene and chloroacetylene formed by fragmentation; Scheme 2.[6] Additional experiments showed that the fragmentation (and some rearrangement to **3** and **4**) occurred not in carbene **2** but in its electronically excited diazirine precursor. Correction for rearrangement in the excited state gave the **3**/**4** product ratio resulting only from carbene **2** as 5.2:1, i.e., $CH_2$ migration was ~5 times faster

**Scheme 2**



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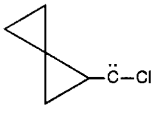
[1] Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.

[2] Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; pp 59f. (b) Regitz, M., Ed. *Methoden Org. Chem. (Houben-Weyl), 4th ed.* 1989, *E19b*. (c) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 12. (d) Jones, M., Jr., Moss, R. A., Eds. *Carbenes*; Wiley: New York, 1973; Vol. 1, Chapter 1.

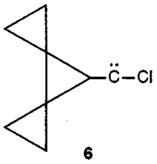
10.1021/ol010023y CCC: $20.00

than $CMe_2$ migration.[6] The associated rate constants were determined by laser flash photolysis (LFP) as $1.3 \times 10^6$ $s^{-1}$ (**2** → **3**) and $2.5 \times 10^5$ $s^{-1}$ (**2** → **4**). Computational studies based on density functional theory gave structures and energies for **2** and for the transition states of its rearrangements to **3** and **4**. It was concluded that steric problems associated with the $CMe_2$ migration to **4** led to the 5-fold kinetic advantage enjoyed by the $CH_2$ migration to **3**; $\Delta\Delta G^{\ddagger}$ was computed at 1.4 kcal/mol, corresponding to a predicted 10-fold preference for $CH_2$ migration.[6]

What would be the effect of "mutating" the *gem*-dimethyl unit of **2** into a cyclopropyl ring, as in spirocyclopentylchlorocarbene, **5**? How would the steric and electronic alterations accompanying this mutation play out in the kinetics and products of **5**? In the course of answering these questions, we extended our studies to the unbranched[3]-triangulylchlorocarbene, **6**,[7] as well as its tetramethylated "open" analogue, 2,2,3,3-tetramethylcyclopropylchlorocarbene, **7**. Both **5** and **6** have previously been generated (possibly as carbenoids) by the action of BuLi or hexamethyldisilazane sodium salt (respectively) on $RCHCl_2$ precursors,[8,9] but these methods are not suited to LFP kinetics measurements.



**5**



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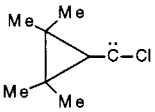
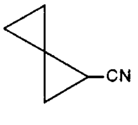


**7**

The diazirine precursors of carbenes **5**–**7** required prior syntheses of nitriles **8**–**10**, which were accomplished by the $Rh_2(OAc)_4$ or $Pd(OAc)_2$ catalyzed additions of "CHCN" (from diazoacetonitrile,[10] 6 h addition time, $CH_2Cl_2$, 0 °C) to methylenecyclopropane,[11] bicyclopropylidene,[12] or tetramethylethylene, respectively. The nitriles were each converted with $MeAl(Cl)NH_2$ to the corresponding amidinium hydrochlorides (**11**),[13] which were characterized by $^1H$ NMR and elemental analysis. The amidines, in DMSO solution, were then oxidized to the 3-chloro-3-alkyldiazirines, **12**, with 12% aqueous NaOCl solution ("pool chlorine," saturated with NaCl, 80 min, 0 °C, ~50% yields).[14] Each diazirine displayed appropriate $^1H$ NMR and UV spectra ($\lambda_{max}$ 346 nm, pentane).



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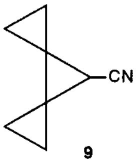
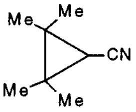
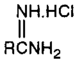


**9**

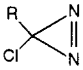


**10**



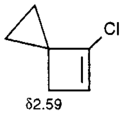
$\overset{NH.HCl}{\overset{\|}{RCNH_2}}$

**11**

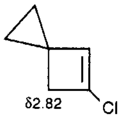


**12**

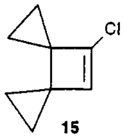
Photolyses of the diazirines in pentane solutions ($\lambda > 320$ nm, 21 °C) gave the anticipated rearrangement products of carbenes **5**–**7**: from carbene **5**, we obtained isomeric spiro[2.3]hex-4-enes **13** and **14** in a 2:1 ratio; carbene **6** afforded **15**, and carbene **7** gave cyclobutene **16**. The reactions leading to **13** and **14**, or **15**, were very clean; capillary GC (CP–Sil-5CB, 40 °C) revealed <2% of other components. No azine formation was observed. Carbene or excited-state fragmentation did not occur in these cases. However, the generation and rearrangement of carbene **7** was accompanied by ~16% of fragmentation to tetramethylethylene (TME) and chloroacetylene, both identified by GC–MS ($M^+$) and $^1H$ NMR. As in the case of carbene **2**,[6] the fragmentation observed here probably originates with the excited diazirine precursor of **7**.



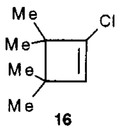
**13**



**14**



**15**



**16**

Rearrangement products **13**–**16** were characterized by appropriate $^1H$ NMR spectra, GC–MS, and high-resolution GC–MS (**16**).[15] In particular, NMR allowed the differentiation of **13** and **14**; isomer **13** (the product of cyclopropyl migration in **5**) revealed an allylic $CH_2$ singlet at $\delta$ 2.59, whereas the corresponding resonance of **14** (product of $CH_2$ migration in **5**) fell at $\delta$ 2.82, additionally deshielded by the adjacent Cl atom. An analogous situation obtained with **3** and **4**,[6] and parallel assignments for **13** and **14** appear in ref 8.

The 2:1 product ratio for the rearrangement of carbene **5** to cyclobutenes **13** and **14** indicates that cyclopropyl migration (**5** → **13**) occurs twice as fast as $CH_2$ migration (**5** → **14**). For carbene **2**, however, $CH_2$ migration (**2** → **3**) is ~5 times faster then $CMe_2$ migration (**2** → **4**). Thus, mutation of the *gem*-dimethyl groups of **2** into the cyclopropyl unit of **5** induces a 10-fold enhancement of the disubstituted carbon's migratory aptitude, relative to $CMe_2$.

When **5** was generated by the action of *n*-BuLi on ethereal **17**,[8] **13** and **14** formed in 91% yield with a 55:36 (1.53) distribution.[9,16] Although the **13**/**14** distributions are similar

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(3) Ho, G.-J.; Krogh-Jespersen, K.; Moss, R. A.; Shen. S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875. (b) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638. (c) Moss, R. A.; Ho, G.-J.; Liu, W. *J. Am. Chem. Soc.* **1992**, *114*, 959.

(4) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (b) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7298.

(5) Wang, R.; Deng, C. *Tetrahedron* **1988**, *44*, 7335. (b) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 470.

(6) Moss, R. A.; Liu, W.; Krogh-Jespersen, K. *J. Phys. Chem.* **1993**, *97*, 13413.

(7) For an excellent review of oligospirocyclopropane systems, see: (a) de Meijere, A.; Kozhushkov, S. I. *Chem. Rev.* **2000**, *100*, 93. See also: (b) Seebach, M. V.; Kozhushkov, S. I.; Boese, R.; Benet-Buchholz, J.; Yufit, D. S.; Howard, J. A. K.; de Meijere, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2495.

(8) Kuznetsova, T. S.; Kozhushkov, S. I.; Gromov, A. V.; Vatlina, L. P.; Kozlovskii, V. I.; Zefirov, N. S. *J. Org. Chem. USSR* (Engl. Trans.) **1992**, *28*, 256; *Zh. Org. Khim.* **1992**, *28*, 317.

(9) de Meijere, A.; Kozhushkov, S. I. Unpublished results cited in ref 7a, p 126 and note 121.

(10) Maier, G.; Reisenauer, H. P.; Rademacher, K. *Chem. Eur. J.* **1998**, *4*, 1957.

(11) Köster, R.; Arora, S.; Binger, P. *Synthesis* **1971**, 322. Caubere, P.; Coudert, G. *Bull. Soc. Chim. France* **1971**, 2234.

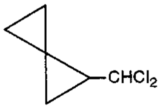
(12) de Meijere, A.; Kozhushkov, S. I.; Spaeth, T.; Zefirov, N. S. *J. Org. Chem.* **1993**, *58*, 502.

(13) Garigipati, R. S. *Tetrahedron Lett.* **1990**, *31*, 1969. Moss, R. A.; Ma, W.; Merrer, D. C.; Xue, S. *Tetrahedron Lett.* **1995**, *36*, 8761.

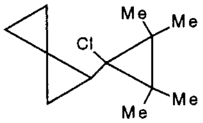
(14) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(15) Products **13**–**15** were previously known; see refs 8 and 9.

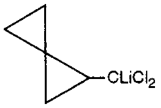
for organometallically or photochemically generated **5**, the actual intermediates are probably different. Thus, the organometallic species cannot be intercepted by alkenes,[9] whereas the diazirine-generated **5** adds to both isobutene and TME affording, in the latter case, adduct **18**.[17] Presumably, the reaction of BuLi and **17** yields lithium carbenoid **19**, which rearranges more rapidly than it can be intercepted by an alkene.



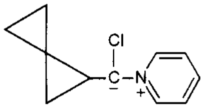
**17**



**18**



**19**



**20**

When **5** was generated from the diazirine in TME/pentane mixtures ([TME] = 0.0−2.8 M), the product ratio of addition to rearrangement, [**18**/(**13** + **14**)], was *linear* in [TME]. This behavior suggests that the rearrangement products stem only from carbene **5**, without intervention of an excited diazirine as a direct precursor of **13** or **14**.[18] Interestingly, neither carbenes **6** nor **7**, as photochemically generated from diazirines, could be captured by isobutene; presumably they are too encumbered by substituents to be successfully intercepted by alkenes in competition with rearrangement.

Absolute rate constants for the rearrangements of carbenes **5**−**7** were determined by LFP,[19] using the pyridine-ylide methodology.[20] LFP at 351 nm and 21 °C of the diazirine precursor of **5** ($A_{346}$ = 1.0, pentane) in the presence of pyridine produced an absorption at 384 nm due to ylide **20**. A correlation of the apparent rate constants for ylide formation vs pyridine concentration was linear, with a slope of $4.65 \times 10^{8}$ $M^{-1}$ $s^{-1}$, equivalent to the rate constant for ylide formation, and a *Y*-intercept of $3.08 \times 10^{6}$ $s^{-1}$. The latter value can be equated with $k_{re}$ for the rearrangements of **5** to **13** and **14**. Given the 2:1 product distribution of **13** and **14**, the aggregate rate constant can be decomposed into $k_{re}$(**5** → **13**) = $2.1 \times 10^{6}$ $s^{-1}$ and $k_{re}$(**5** → **14**) = $1.0 \times 10^{6}$ $s^{-1}$.[21]

Analogous LFP studies of carbenes **6** and **7** afforded ylides absorbing at 384 nm and pyridine ylide kinetics of comparable quality, from which we obtained $k_{re}$(**6** → **15**) = $8.25 \times 10^{6}$ $s^{-1}$ and $k_{re}$(**7** → **16**) = $1.79 \times 10^{6}$ $s^{-1}$. The rate constants are collected in Table 1, including previous results for carbenes **1** and **2**; cf. Schemes 1 and 2.[3,6] To simplify direct comparisons between the symmetrically substituted (**1**, **6**, **7**) and unsymmetrically substituted (**2**, **5**) carbenes, $k_{re}$ of the former are divided by 2 to give "per migrant carbon" rate constants.

**Table 1.** Rate Constants for Carbene Rearrangements[a]

| carbene | product(s) | migrant group | $10^{-6}k_{re}$ $(s^{-1})^{b}$ | $k_{rel}$ | $k_{rel}^{calc}$ |
|---|---|---|---|---|---|
| **1** | ***c*** | $CH_2$ | $0.45^{d}$ | 1.0 | 1.0 |
| **2** | **3** | $CH_2$ | $1.3^{e}$ | 2.9 | 2.2 |
| **2** | **4** | $CMe_2$ | $0.25^{e}$ | 0.56 | 0.79 |
| **5** | **14** | $CH_2$ | 1.0 | 2.2 | 24 |
| **5** | **13** | $Cy^{f}$ | 2.1 | 4.7 | 62 |
| **6** | **15** | $Cy^{f}$ | 4.1 | 9.1 | 500 |
| **7** | **16** | $CMe_2$ | 0.90 | 2.0 | 1.5 |

[a] By LFP at 20−25 °C; errors ± 10−15%. Observed and computed rearrangement rate constants relative to that of **1** are denoted $k_{rel}$ and $k_{rel}^{calc}$, respectively. [b] Per migrant group; see text. [c] See Scheme 1. [d] Ref 3a,b. [e] Ref 6. [f] Cy = cyclopropyl.

Arrhenius studies were carried out for the rearrangements of carbenes **5**−**7** in pentane from −40 to 30 °C. With **6** and **7**, good correlations of ln $k_{re}$ vs 1/*T* were obtained (eight points, *r* = 0.987 or 0.990). For **6** → **15**, $E_a$ = 4.0 kcal/mol, log *A* = 9.74 $s^{-1}$, and $\Delta S^{\ddagger} = -15.9$ eu; for **7** → **16**, $E_a$ = 4.4 kcal/mol, log *A* = 9.58 $s^{-1}$, and $\Delta S^{\ddagger} = -16.6$ eu. These Arrhenius parameters are similar to each other and also to those obtained for the parent cyclopropylchlorocarbene **1**[3b] (see above); again, we observe large, negative values of $\Delta S^{\ddagger}$ attributable to the motionally demanding nature of these rearrangements.[3,5] Arrhenius studies of carbene **5** led to considerable scatter in the correlation of ln $k_{re}$ vs 1/*T* and an effectively flat "line." In our experience with LFP carbene kinetics, this occurs when $E_a < 4$ kcal/mol.

Table 1 reveals several trends in the experimental data: (a) Mutation of *gem*-dimethyl substituents to a cyclopropyl ring enhances the migratory aptitude; in similarly substituted carbenes, the 1,2-cyclopropyl shift is 8.4 times (**5** vs **2**) or 4.6 times (**6** vs **7**) faster than the 1,2-$CMe_2$ shift. (b) Although a 1,2-$CH_2$ shift is preferred (5.2:1) to a 1,2-$CMe_2$ shift in carbene **2**, a 1,2-cyclopropyl shift is preferred (2.1:1) to the 1,2-$CH_2$ shift in carbene **5**. The relative rate constants in Table 1 generally support the migratory aptitude ordering cyclopropyl > $CH_2$ > $CMe_2$. (c) Substitution at the nonmigrant carbon of the cyclopropylchlorocarbene enhances migration of the adjacent (migrant) carbon atom; relative to the 1,2-$CH_2$ shift of carbene **1**, the $CMe_2$ shift of **7** ($CMe_2$ adjacent) is 3.6 times faster (2.0/0.56) than the $CMe_2$ shift of **2** ($CH_2$ adjacent). Similarly, the Cy shift of **6** (Cy adjacent) is ca. twice as fast (9.1/4.7) as the Cy shift of **5** ($CH_2$ adjacent).

Computational studies were performed to help understand these trends. Electronic structure calculations (B3LYP/6-31G*)[22−24] were carried out on the carbene minima **1**, **2**, **5**, **6**, and **7**; all prefer the *exo*-conformation with Cl *trans* to

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(16) Reversed distributions appear in refs 7a and 8; the former (cited here) is correct: de Meijere, A. Private communication, 4 December, 2000.

(17) Adduct **18** was characterized by GC−MS and $^{1}H$ NMR.

(18) See ref 2a, pp 66−67. (b) Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, A.; Abbot, S. C.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055 and references therein.

(19) For a description of our LFP apparatus, see: Moss, R. A.; Johnson, L. A.; Merrer, D. C.; Lee, G. E., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 5940.

(20) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

(21) The absolute rate constant for addition of **5** to TME was determined as $1.8 \times 10^{6}$ $M^{-1}$ $s^{-1}$ by LFP using the pyridine-ylide method.[3b,20] This reaction is 6.7 times slower than the analogous addition of **1** to TME ($k = 1.2 \times 10^{7}$ $M^{-1}$ $s^{-1}$),[3a] very likely as a result of increased steric problems originating at the additional cyclopropyl unit of **5**.

cyclopropyl. Transition states were located for the rearrangements **1** → chlorocyclobutene; **2** → **3** or **4**; **5** → **13** or **14**; **6** → **15**; and **7** → **16**. All stationary points were characterized by normal-mode analysis. The thermodynamic parameters were evaluated ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$; $T = 298$ K, 1 atm) and relative rates of migration were calculated. The calculated relative rates appear in Table 1, and the calculated activation parameters are shown in Table 2.

**Table 2.** Calculated (B3LYP/6-31G*) Activation Parameters for Carbene Rearrangements[a]

| carbene | product(s) | migrant group | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta G^{\ddagger}$ |
|---|---|---|---|---|---|
| **1** | **b** | $CH_2$ | 10.82 | −2.8 | 11.65 |
| **2** | **3** | $CH_2$ | 10.38 | −2.7 | 11.18 |
| **2** | **4** | $CMe_2$ | 11.06 | −2.4 | 11.79 |
| **5** | **14** | $CH_2$ | 8.91 | −2.8 | 9.74 |
| **5** | **13** | Cy[c] | 8.21 | −3.2 | 9.17 |
| **6** | **15** | Cy[c] | 6.93 | −3.2 | 7.91 |
| **7** | **16** | $CMe_2$ | 10.15 | −4.2 | 11.40 |

[a] $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ in kcal/mol, $\Delta S^{\ddagger}$ in eu. [b] See Scheme 1. [c] Cy = cyclopropyl.

Inspection of the activation parameters in Table 2 reveals that the calculations predict only modest (negative) activation entropies but substantial enthalpic barriers for these 1,2-C rearrangements. The computed and experimental free energy barriers appear to differ only by a few kcal/mol ($\Delta G^{\ddagger}_{comp} > \Delta G^{\ddagger}_{exp}$), but the apportionment between enthalpy and entropy contributions to the barrier is reversed, as we have previously noted.[3b]

The computed relative rates display precisely the same trends as the observed relative rates, although the computed rate changes for rearrangements of the spiropentyl- and triangulylchlorocarbenes, **5** and **6**, are much larger than observed. On the other hand, the observed relative rates of $CH_2$ and $CMe_2$ migrations in carbenes **1**, **2**, and **7** are remarkably well reproduced by the calculations; cf. Tables 1 and 2. According to the calculations, the variations in rearrangement rates result from variations in activation enthalpies.

Turning to trends (a)−(c) in the data, we note first that our previous calculations for the rearrangements of **2** identified differential steric effects in the transition states as the principal reason for the greater migratory aptitude of $CH_2$ vs $CMe_2$.[6,25] The **2** → **4** rearrangement is the only case where a decrease in rate (observed and computed) is indicated relative to $CH_2$ migration in **1**. Table 2 shows that $CMe_2$ migration in fully methylated **7** is entropically less favorable than $CMe_2$ migration in half-methylated **2**, providing an additional indication that steric hindrance plays a role in depressing the migration rate of the bulky $CMe_2$ unit. 1,2-Cy migration is similarly expected to be less sterically demanding than 1,2-$CMe_2$ migration, so that 1,2-cyclopropyl shifts (**5** vs **2**, **6** vs **7**) should be faster than 1,2-$CMe_2$ shifts solely for this reason [trend (a)].

With the notable exception of the **2** → **4** rearrangement, we note a general decrease in activation enthalpy with increasing degree of cyclopropyl or *gem*-dimethyl group substitution. We attribute this trend to the ability of a neighboring *gem*-dimethyl or cyclopropyl group to better stabilize the partial positive charge that develops on the migration origin in the TS. This rationalizes the increases in the relative rates of $CH_2$ migration (**2** vs **1**), $CMe_2$ migration (**7** vs **2**), and Cy migration (**6** vs **5**) [trend (c)]. Cyclopropyl is a stronger donor than *gem*-dimethyl so that Cy provides a larger stabilizing effect than *gem*-dimethyl on adjacent $CH_2$ migration; viz. **5** → **14** vs **2** → **3**.

The relative rates of Cy vs $CH_2$ migration in **5** are predicted correctly by the calculations (exp, 4.7/2.2 ≈ 2.1; calc, 62/24 ≈ 2.6), but the computed rates are overestimated by approximately a factor of 10 relative to that of Scheme 1. The strain energies associated with three-membered rings are notoriously difficult to compute accurately, and it is tempting to propose that the calculations overestimate the release of strain energy in the rearrangements of carbenes **5** and **6**. The increased migratory aptitude of Cy vs $CH_2$ cannot be steric in origin. The computed geometries suggest an explanation for this result and thus provide a clue to trend (b). The computed $C_2{-}C_4$ bond length in **5** is considerably shorter than that in **2**, whereas the $C_2{-}C_3$ bond length in **2** is somewhat shorter than that in **5** (cf. Figure 1). The Walsh-type orbital associated with the $C_2{-}C_4$ bond in **5** may therefore overlap better with the vacant carbene p-orbital on $C_1$ than does the $C_2{-}C_3$ bond orbital. This affords a stabilizing interaction which results in a greater migratory aptitude of Cy over $CH_2$. Considerations of orbital overlap between the origin and terminus of the bond that migrates may also play a minor role in the preferred migration of $CH_2$ vs $CMe_2$, cf. the bond lengths calculated for **2**.

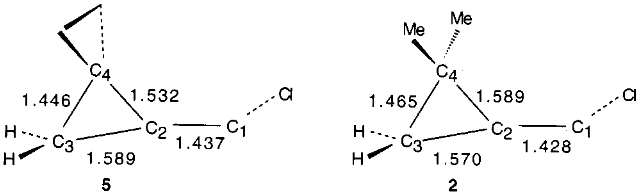

**Figure 1.** Computed bond lengths (Å) for carbenes **5** and **2**.

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(22) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(23) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. Pople, J. A.; Hariharan, P. C. *Theor. Chim. Acta*, **1973**, *28*, 213. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(24) Frisch, M. J. et al. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(25) Steric effects are also central in the analogous rearrangements of 2,2-dimethylcyclopropylmethylcarbene: Bird, C. L.; Frey, H. M.; Stevens, I. D. R. *Chem. Commun.* **1967**, 707. Stevens, I. D. R.; Frey, H. M.; Bird, C. L. *Angew. Chem., Int. Ed.* **1968**, *7*, 646.