Kinetics of the Competitive 1,2-Carbon Migrations of an Unsymmetrically Substituted Cyclopropylchlorocarbene[†]

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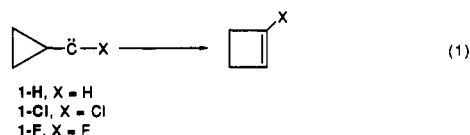
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Photolysis of 3-(2,2-dimethylcyclopropyl)-3-chlorodiazirine (**4**) at 25 °C in pentane affords 81% of the 1,2-C migration products 1-chloro-3,3-dimethylcyclobutene (**5**) and 2-chloro-3,3-dimethylcyclobutene (**6**) in a 4.8:1 distribution, as well as 19% of the fragmentation products, isobutene, and chloroacetylene. Experiments in the presence of the carbene trap trimethylethylene point to product formation from the electronically excited diazirine (**4***), which affords 19–20% of fragmentation products, ∼17% of **5** and **6** (3.8:1), and ∼63% of 2,2-dimethylcyclopropylchlorocarbene (**3**). The carbene ring expands to **5** and **6** (5.2:1). Laser flash photolytic studies afford absolute rate constants for **3** → **5** ($1.3 \times 10^6 \, s^{-1}$) and **3** → **6** ($2.5 \times 10^5 \, s^{-1}$). The 5-fold preference of **3** for CH_2 migration (to **5**) over CMe_2 migration (to **6**) is attributed to differential steric affects. Ab initio calculations afford structures and energies for **3** and the CH_2 and CMe_2 transition state (**8**-CH_2 and **8**-CMe_2). The calculations agree with the experimental findings in that $\Delta G^{\ddagger}$ for CH_2 migration is found to be 1.4 kcal/mol less than $\Delta G^{\ddagger}$ for CMe_2 migration, corresponding to a computed 10-fold kinetic preference for CH_2 migration. The expected additional steric congestion is apparent in the **8**-CMe_2 transition state.

Introduction

The ring expansions of cyclopropylcarbenes (**1**) to cyclobutenes are illustrative of the 1,2-carbon migrations (1,2-C) that are sometimes encountered in the intramolecular chemistry of carbenes;[1] cf. eq 1. The energetics associated with the rearrangement of parent carbene **1**-H have been recently subjected to theoretical analysis,[2] while the kinetics of the 1,2-C shifts in the chloro (**1**-Cl)[3–5] and fluoro (**1**-F)[4] cyclopropylcarbenes have been examined theoretically,[2,3] spectroscopically,[3] and by laser flash photolysis (LFP).[3–5]

1-H, X = H
1-Cl, X = Cl
1-F, X = F

The clearest picture that emerges from the LFP studies of **1**-Cl reveals a 1,2-C migration that occurs with an absolute rate constant of ∼1 × 10⁶ s⁻¹ at 20 °C in isooctane.[3] Activation parameters, obtained from correlations of *k* with 1/*T*, gave best values (averages of four independent kinetic studies) of E_a = 3.0 ± 0.4 kcal/mol, log *A* = 8.2 ± 0.2 s⁻¹, $\Delta G^{\ddagger}$ ∼ 9 kcal/mol, $\Delta H^{\ddagger}$ ∼ 2–3 kcal/mol, and $\Delta S^{\ddagger}$ ∼ –20 to –24 eu.[3b] The very unfavorable entropy of activation observed for the rearrangement of **1**-Cl is consistent with experimental results for carbene **1**-H,[2c] for the 1,2-D migration of CD_3–C–D ($\Delta S^{\ddagger}$ ∼ –17 eu),[6] and for the 1,2-H shift of CH_3–C–Cl ($\Delta S^{\ddagger}$ ∼ –16 eu)[7] and may reflect unusual motions required of the migrating groups during their rearrangements.[2a,3,6] Many energetically favorable collisions will be ineffectively translated into motion along the reaction coordinate and through the transition-state pass, so that the transmission coefficient will be ≪1.0,[3b,6] and an apparent large negative activation entropy will be observed.

However, the *observed* activation parameters for the rearrangement of **1**-Cl are not in good agreement with values *computed* from ab initio electronic structure calculations.[3b] For the *trans*-cyclopropyl/chloro conformer, the latter include $\Delta G^{\ddagger}$ = 9.0 kcal/mol, $\Delta H^{\ddagger}$ = 8.2 kcal/mol, and $\Delta S^{\ddagger}$ = –2.7 eu.[3a] The calculated

and experimental values of $\Delta G^{\ddagger}$ agree well, but $\Delta G^{\ddagger}$(theoretical) is dominated by $\Delta H^{\ddagger}$, whereas $\Delta G^{\ddagger}$(experimental) is dominated by $\Delta S^{\ddagger}$. It has been pointed out that in low activation energy carbene reactions (and more generally), the variational transition state of the reaction, corresponding to the maximum on the $\Delta G^{\ddagger}$ profile, may not coincide with the calculated conventional minimum energy transition state.[8]

The rearrangement of **1**-F is similar to that of **1**-Cl, with *k* ∼ (1.4 ± 0.2) × 10⁵ s⁻¹ (23 °C, isooctane), E_a = 4.2 ± 0.5 kcal/mol, log *A* = 8.3 ± 0.3 s⁻¹, $\Delta G^{\ddagger}$ = 10.1 kcal/mol, $\Delta H^{\ddagger}$ = 3.6 kcal/mol, and $\Delta S^{\ddagger}$ ∼ –22 eu.[4] The fluorocarbene rearranges more slowly than **1**-Cl, presumably because of enhanced stabilization due to better X → C electron donation when X = F, as opposed to X = Cl,[9] resulting in an activation energy that is about 1 kcal/mol higher for **1**-F. However, the rearrangements of both **1**-F and **1**-Cl are dominated by large, negative entropies of activation.

Many years ago, Bird et al.[10] examined the intramolecular competition between the 1,2-C migrations of CH_2 vs. CMe_2 groups of the unsymmetrically substituted cyclopropylmethylcarbene, **2**.[10] From the product analysis, migration of CH_2 prevailed over
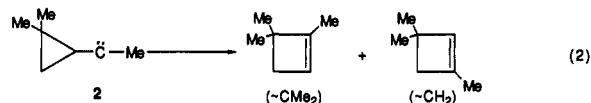
CMe_2 by a factor of 39 at 135–140 °C. Similar, though reduced preferences (factors of 2.6–22) were observed for ∼CH_2 vs -$CHMe$ migrations in monomethyl ring-substituted analogues of **2**.[10] These kinetic selectivities were attributed to the differential steric effects encountered in the alternative 1,2-C shifts: migration and rotation of the CH_2 "vertex" toward the :CMe reaction center is less sterically demanding than the alternative migration of the CMe_2 vertex.[10]

In view of the topicality of cyclopropylhalocarbene rearrangements,[3,5] we decided to apply LFP and ab initio methodologies to the competitive CH_2/CMe_2 rearrangements of 2,2-dimethylcyclopropylchlorocarbene, **3**. In this way, we hoped to "update"
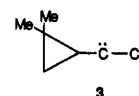
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the experiments of Bird et al.,[10] while simultaneously expanding our understanding of carbene 1,2-C migrations.

Results and Discussion

Synthesis. The precursor of carbene **3**, 3-chloro-3-(2,2-dimethyl)cyclopropyldiazirine, **4**, was prepared by the reactions outlined in Scheme I. The ditosylate of 2,2-dimethyl-1,3-propane diol was converted to 2,2-dimethyl-1-cyclopropane nitrile by treatment with a 3-fold excess of KCN in hot ethylene glycol.[11] Upon successive treatment with HCl/EtOH and NH₃/EtOH, the nitrile afforded the desired amidine (albeit in poor yield). The amidine was characterized by NMR and elemental analysis, and then oxidized to diazirine **4** in ~50% yield by the Graham reaction,[12] using 12% aqueous NaOCl.

SCHEME I
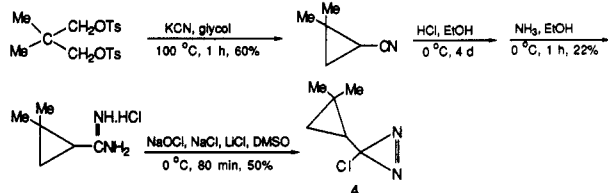
Diazirine **4**, purified by short-column chromatography over silica gel (pentane eluent), had λ_{max} 216, 242, and 346 nm (pentane), as well as an appropriate NMR spectrum (see Experimental Section).

Product Studies. Photolysis of diazirine **4** (A_{346} = 1.5, λ > 320 nm) in CDCl₃ at 21 °C for 30 min gave the 1,2-C migration products, cyclobutenes **5** and **6**, together with the fragmentation products, isobutene and chloroacetylene; cf., eq 3. Similar product distributions attended photolyses in CDCl₃ or pentane, as shown in eq 3. These distributions derive from NMR analysis (CDCl₃) or calibrated capillary GC analysis on a CP-Sil 5CB column at 27 °C (pentane solvent). In both cases, the crude products were very clean; less than 2% of other components were detected by NMR or GC.

CDCl₃:	59.2%	19.7%	(21.1%)
Pentane:	67.4%	14.0%	(18.6%)
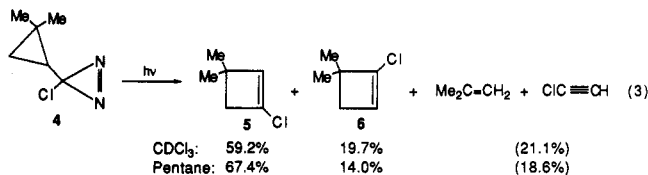
Identification of **5** and **6** proceeded from their strong GC-MS parent ions (65%) at m/e 101 and 103 ($M - CH_3$), and base peaks at m/e 81 (100%, $M - Cl$). Their ¹H NMR spectra substantiated their structures and permitted differentiation of the isomers. In particular, **5**, showed δ (CDCl₃) 1.21 (s, 6H, 2Me), 2.48 (s, 2H, CH₂), and 5.91 (s, 1H, =CH); whereas **6** exhibited 1.18 (s, 6H, 2Me), 2.21 (s, 2H, CH₂), and 5.75 (s, 1H, =CH).[13] Note that the CH₂ adjacent to the chloro substituent in **5** (δ 2.48) is *deshielded* relative to the CH₂ that is "para" to the chloro substituent in **6** (δ 2.21). In the parent 1-chlorocyclobutene, these CH₂ resonances appear at δ 2.75 and 2.39, respectively,[14] so that, in **5** and **6**, they are each shifted to higher field due to shielding by the adjacent *gem*-dimethyls.

The fragmentation products were identified spectroscopically. The NMR resonances of isobutene at δ_CDCl₃ 1.72 and 4.65 were identical with those of an authentic sample, whereas the spectroscopic parameters of the known[15] chloroacetylene included M^+ (100%) at m/e 60, 62 (3:1), and δ_CDCl₃ at 1.86.

The relatively large yield of fragmentation products, obtained upon photolysis of **4** (~20%), was suggestive of excited-state diazirine chemistry (see below), so that we also examined thermolytic decomposition of **4**. Sealed tube pyrolysis of **4** (A_{346} = 1.5) in pentane at 60 °C (24 h) or 80 °C (7.5 h) gave **5**:**6**

fragmentation product distributions of 81.4:17.3:1.2 or 80.4:17.6:2.0, respectively, in which the fragmentation was very markedly reduced. This result supports the idea that most of the fragmentation accompanying the photolysis of **4** stems from excited state diazirine. Further evidence in favor of this conclusion appears below.

From the product ratio of **5/6**, it is clear that the competitive 1,2-C ring expansions proceed with preferential CH₂ migration (to **5**). The observed –CH₂/–CMe₂ ratios are 3.0 or 4.8 by photolysis in CDCl₃ or pentane, or 4.6–4.7 by pyrolysis in pentane. Although the preference for CH₂ migration from **4** agrees with earlier observations on carbene **2**, eq 2,[10] the magnitude of the CH₂/CMe₂ selectivity is reduced from 39 (at 135–140 °C) for **2** to only ~5 (in pentane) for **4** (and carbene **3**). This will be discussed further below.

Excited-State Diazirine. Platz presented compelling evidence that the photolyses of dimethyldiazirine,[16a] as well as several alkylchlorodiazirines,[16b] generate electronically excited diazirines that can undergo 1,2-H rearrangements, concerted with nitrogen loss, and in competition with simple nitrogen loss to the appropriate carbenes. Thus, the intramolecular "carbene" products actually have two sources, with the chemistry of the excited diazirine mimicking that of the carbene.

We have also reported significant excited-state diazirine incursion in 1,2-H and 1,2-C rearrangements that had been previously ascribed solely to neopentylchlorocarbene[17] and cyclobutylchlorocarbene.[18] Accordingly, we examined the photochemical decomposition of diazirine **4** for products from **4***.

Pentane solutions (A_{346} = 1.0) of **4** were photolyzed at 25 °C, together with varying quantities of trimethylethylene, using a 200-W focused Osram XE UV lamp (λ > 320 nm), until the diazirine had been destroyed. In addition to the products shown in eq. (3), 4 stereoisomeric carbene/alkene adducts, **7a–d** were
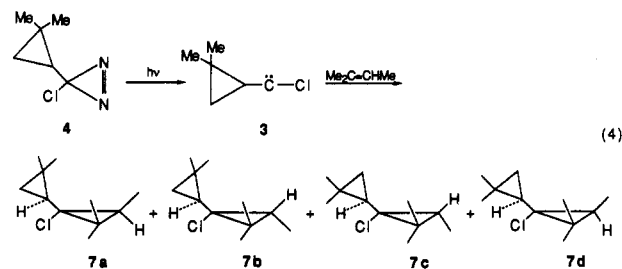
formed; cf. eq 4. Capillary GC (column as above, 27–240 °C) revealed a distribution of 8.1:10.4:1.8:1 for these adducts, which were characterized by GC-MS (M^+ at m/e 186 and 188, ratio 3:1 for each adduct) and ¹H NMR spectroscopy (as a mixture). The cyclopropanes were not separated because only the total yield of **7a–d** is needed for purposes of following the competition between the rearrangement of **4***(3) and the addition of carbene **3** to trimethylethylene.[19] In Tables I and II, we display the normalized product distributions obtained from the photolyses of diazirine **4** in trimethylethylene–pentane solutions, with analyses by calibrated capillary GC.

If *all* of the products were derived from carbene **3** (as in Scheme II), then the product ratio **7a–d**/(**5 + 6** + fragmentation) would be proportional to k_{add} [Me₂C=CHMe]/(k_{re} + k_{frag}) and should increase linearly with increasing concentration of the alkene.[1a] However, a plot of the observed product ratios, "addn/others" (Table II) vs [Me₂C=CHMe] is clearly nonlinear (Figure 1), just as analogous correlations are curved in the cases of benzylchlorocarbene,[20] methylchlorocarbene,[21] neopentylchlorocarbene,[17] and cyclobutylchlorocarbene.[18]

In the earlier examples, it was found that the *inverse* plots of "rearr/addn" vs 1/[alkene] were linear. A similar result is found here; correlations of rearr/addn [(**5 + 6**)/**7a–d**] or others/addn [(**5 + 6** + frag)/**7a–d**] vs 1/[Me₂C=CHMe] (Table II) are indeed linear, with excellent correlation coefficients (r > 0.99).

TABLE I: Product Yields from the Photolyses of Diazirine 4 in Me$_2$C=CHMe–pentane^a

[Me$_2$C=CHMe], M	5(–CH$_2$)	6(–CMe$_2$)	5/6	frag^b	addn^c
0.000	67.4	14.0	4.81	18.6	0.00
0.265	62.2	14.0	4.44	20.1	3.65
0.400	60.4	13.9	4.34	20.2	5.46
0.526	59.5	13.8	4.31	19.5	7.22
1.06	54.7	12.9	4.24	19.7	12.8
2.12	47.8	11.5	4.16	20.2	20.5
3.18	42.5	10.4	4.09	19.6	27.5
4.25	39.1	9.69	4.04	18.4	32.9
5.31	36.8	9.26	3.97	18.9	35.0
6.38	35.9	9.21	3.90	18.6	36.2
7.44	33.8	8.84	3.82	19.0	38.4
8.49	33.3	8.65	3.85	18.8	39.3
9.03	32.4	8.52	3.80	19.0	40.1

^{a} Conditions: pentane solution, 25 °C, A_{346} = 1.0. ^{b} Yield of isobutene and chloroacetylene. ^{c} Yield of adducts 7a–d.

TABLE II: Product Ratios from the Photolyses of Diazirine 4^a

[Me$_2$C=CHMe], M	addn/others^b	1/[Me$_2$C=CHMe]	others/addn^c	rearr/addn^d
0.000	0.00			
0.265	0.0379	3.77	26.4	20.9
0.400	0.0578	2.50	17.3	13.6
0.526	0.0781	1.90	12.8	10.2
1.06	0.147	0.943	6.82	5.28
2.12	0.258	0.472	3.88	2.89
3.18	0.379	0.314	2.64	1.92
4.25	0.490	0.236	2.04	1.48
5.31	0.538	0.188	1.86	1.32
6.38	0.568	0.157	1.76	1.25
7.44	0.621	0.134	1.61	1.11
8.49	0.645	0.118	1.55	1.07
9.03	0.671	0.111	1.49	1.02

^{a} Data calculated from the product yields in Table I. ^{b} Yields of 7a–d/[(5 + 6) + isobutene and chloroacetylene]. ^{c} Inverse of the ratio in b. ^{d} (5 + 6)/7a–d.

SCHEME II
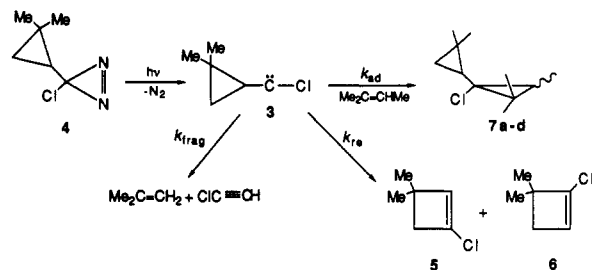
To satisfy the observed kinetic form, it is necessary to postulate a second product-forming intermediate,[22] which, in accord with Platz,[16] we take as the excited diazirine, 4*; cf. Scheme III. Here carbene 3 still appears as a precursor of the intermolecular addition products 7a–d, as well as of the 1,2-C rearrangement products, 5 and 6. In addition, however, the excited diazirine 4* is depicted as forming carbene 3 by nitrogen loss, as well as cyclobutenes 5 and 6 by rearrangement concerted with nitrogen loss,[16] and is the *sole* precursor of the fragmentation products.

Reference to Table I shows that the yield of fragmentation products is effectively constant at ~18–20%, and *independent* of alkene concentration from 0 to 9 M. Fragmentation thus seems not to come from the carbene because, although almost all of the carbene must be trapped by addition at 9 M alkene, we observe no diminution of fragmentation.

This conclusion is reinforced by our observation that the 18–20% of fragmentation resulting from photolysis is reduced to only 1–2% upon pyrolysis of 4 (see above). At 25 °C, therefore, little if any fragmentation can be attributed to carbene 3. Ab
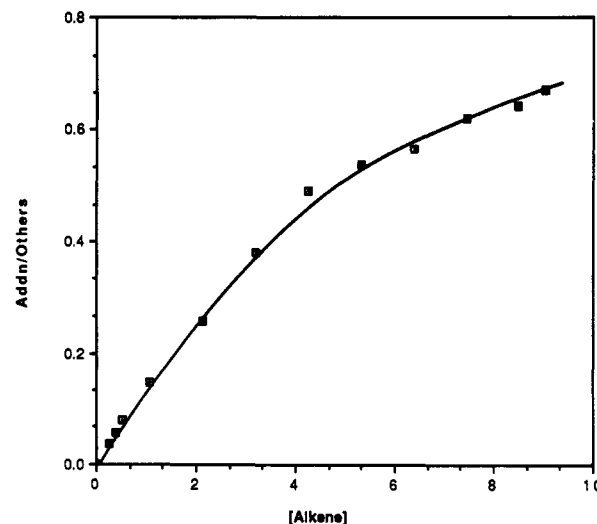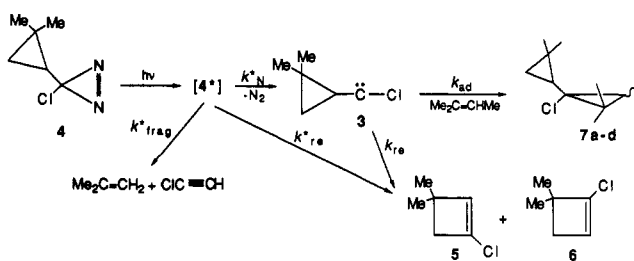
Figure 1. Addition to fragmentation plus rearrangement product ratio, [7a–d]/[frag + 5 + 6] vs [alkene] for the photolysis of 4 in trimethylethylene.

SCHEME III

initio calculations on parent carbene 1-H (trans conformation) agree that fragmentation is not competitive with rearrangement to cyclobutene.[2b]

From Scheme III we obtain eq 5 for the relation between the product ratio (5 + 6)/7a–d (rearr/addn) and 1/[Me$_2$C=CHMe].

$$(5 + 6)/7a\text{–}d = k^*_{re}/k^*_N + [k_{re}(k^*_N + k^*_{re})]/k^*_N k_{ad}[MeC\text{=}CHMe] \quad (5)$$

The predicted linearity of the product distribution with 1/[alkene] is observed (Table II and Figure 2, line 2), and the y intercept (0.30) of the correlation affords the partition ratio of excited diazirine between 1,2-rearrangement to 5 and 6 and simple nitrogen loss to carbene 3;[1a] cf. eq 5. Thus, if we ignore the fragmentation of 4*, and normalize to 100%, 4* gives 23% of rearrangement to 5 and 6, in competition with 77% loss of nitrogen to carbene 3.

If we include fragmentation, and take the y intercept (0.59) of the correlation between [5 + 6 + fragmentation] and 1/[alkene] (Figure 2, line 1), then the product contribution of 4* increases to 37%. Interestingly, there appears to be little contribution to product formation from the excited diazirine formed from the *parent* cyclopropylchlorodiazirine.[3,16b] Presumably, the *gem*-dimethyl group of 4 augments both concerted nitrogen loss with fragmentation or rearrangement from 4*, relative to analogous processes for excited cyclopropylchlorodiazirine.

From Table I at the highest alkene concentration, we take 3.80 as the ratio of 5/6 (–CH$_2$/–CMe$_2$) due only to the rearrangement of 4*. On the other hand, at [Me$_2$C=CHMe] = 0, the observed 5/6 (4.81) represents a 23:77 blend of excited diazirine and carbene rearrangements (see above). Obviously, the 5/6 partition of the 2 intermediates, 4* and 3, need not be identical. As illustrated in Table III, a 5/6 ratio of ~5.2 for the 1,2-C rearrangement of carbene 3 satisfies the constraints.
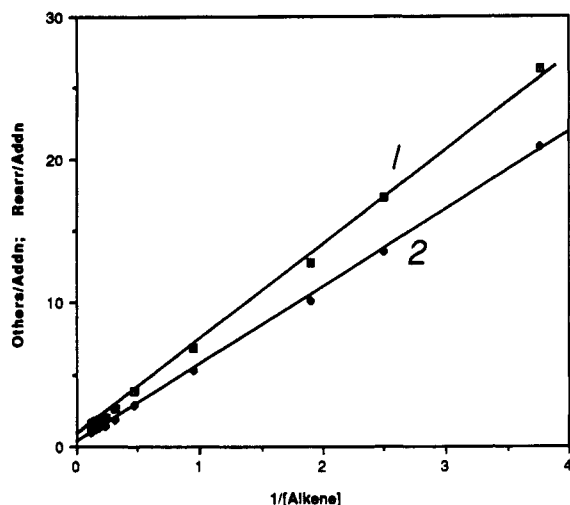
Figure 2. Line 1: fragmentation plus rearrangement to addition product ratio [frag + **5** + **6**]/[**7a–d**] vs 1/[alkene] for the photolysis of **4** in trimethylethylene. Line 2: rearrangement to addition product ratio [**5** + **6**]/[**7a–d**] vs 1/[alkene] for the same reaction.

TABLE III: Rearrangement of Excited Diazirine 4* and Carbene 3[a]

rearrangement	from 4*[b]	from 3[c]	total[d]
–CH₂ to **5**	18.2	64.6	82.8
–CMe₂ to **6**	4.8	12.4	17.2

[a] Based on 100 molecules of diazirine **4***. *[b]* From a **5/6** distribution from **4*** of 3.8:1 at [Me₂C═CHMe] = 9 M, contribution to products of 23%. *[c]* By difference, total – **4***. *[d]* From **5/6** = 4.81:1 at [Me₂C═CHMe] = 0, normalized to 100%.

The dimethylcyclopropylchloro system resembles the neopentylchloro and cyclobutylchloro cases in that diazirine photolysis leads to substantial product formation from the excited diazirine as well as from the carbene. The product contribution of **4*** is ~37%, with ~20% fragmenting to isobutene and chloroacetylene, while 17% ring expands to **5** and **6** in a distribution of 3.8:1. The remaining 63% of **4*** goes on to carbene **3**, which largely eschews fragmentation, affording 1,2-C products **5** and **6** with selectivity of 5.2:1.

In comparison to the dimethylcyclopropyl*methyl*carbene (**2**) of Bird et al., where the CH₂/CMe₂ migration selectivity is 39 at 135–140 °C,[10] our dimethylcyclopropyl*chloro*carbene (**3**) is much less selective, with –CH₂/–CMe₂ only about 5.2 at 25 °C (i.e., **5/6** = 64.6:12.4, Table III). If we accept a largely steric origin for the preference for CH₂ migration,[10] then the greater selectivity in the rearrangement of **2** can be attributed to the larger size and greater steric demand of the carbenic methyl substituent of **2**, relative to the carbenic chloro substituent of **3**.[23]

Absolute Rearrangement Rates. Laser flash photolysis[24] of diazirine **4** did not afford a useful transient absorption from **3**. However, in the presence of pyridine, reaction between **3** and pyridine gave a strong ylide absorption, λ_{max} = 370 nm. We could therefore use Platz's methodology[25] to obtain the overall rate of rearrangement of **3** to cyclobutenes **5** and **6**. This method is independent of excited diazirine because it follows reactions of the carbene; it is known that excited diazirines do not live long enough to react with pyridine.[6,16a]

Accordingly, **3**, was generated by LFP (351 nm, 14 ns, 70–90 mJ, XeF excimer laser)[24] of solutions of **4**, A_{346} ~ 1.0, in pentane that was 3.84–153 mM in pyridine. The apparent rate constants for growth of the pyridinium ylide absorption, monitored at 275 nm, were plotted against [pyridine], affording the linear correlation (r > 0.99) shown in Figure 3. From the slope of the correlation, k = (4.7 ± 0.2) × 10⁷ M⁻¹ s⁻¹ for the formation of the ylide, and k_0 = (1.5 ± 0.1) × 10⁶ s⁻¹ for the rearrangement of carbene **3**.
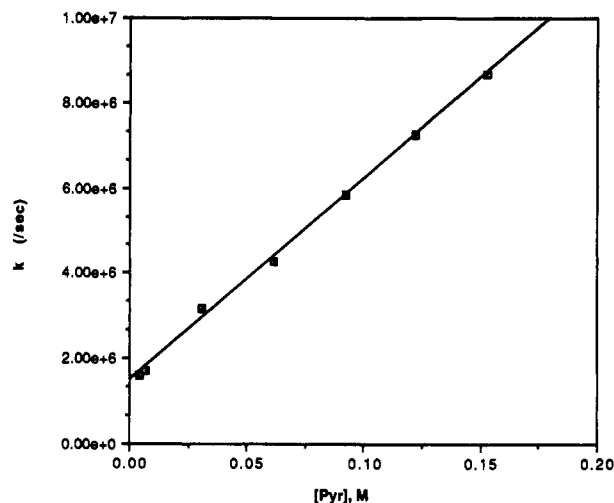

Figure 3. Observed rate constants (s⁻¹) for the formation of the pyridinium ylide from carbene **3** and pyridine vs [pyridine], M.

The k_0 value is the y intercept of the correlation, where [pyridine] = 0, and reflects the sum of all processes that destroy the carbene in the absence of an external trap. In our case, the product mixture from photolysis of **4** is quite clean; no azine or carbene dimer is found, and only fragmentation (from **4***) and rearrangement products (from **3** and **4***) are formed. Because the ylide method only visualizes reactions of the carbene, we can equate k_0 with k_{re} for the conversion of **5** and **6** (Scheme III).

From k_{re}(total) = 1.5 × 10⁶ s⁻¹, and our conclusion that **3** affords **5** and **6** in a ratio of 5.2 (Table III), we derive rate constants for the competitive rearrangements **3** → **5** (–CH₂) and **3** → **6** (–CMe₂) as 1.3 × 10⁶ and 2.5 × 10⁵ s⁻¹, respectively. The rate constant for the 1,2-CH₂ migration of parent carbene **1-Cl** is ~1.0 × 10⁶ s⁻¹,[3,5] or ~0.5 × 10⁶ s⁻¹ per CH₂ group. From this perspective the CH₂ migration of **3** is about twice as fast as that of **1-Cl**.

Theoretical Studies. A series of ab initio electronic structure calculations have been carried out to elucidate the origin of the measured difference in rate constants. The molecular structure of the reactant, **3**, and the transition states for CH₂ (**8-CH₂**) and CMe₂ (**8-CMe₂**) migration were located at the Hartree–Fock

8-CH₂   8-CMe₂
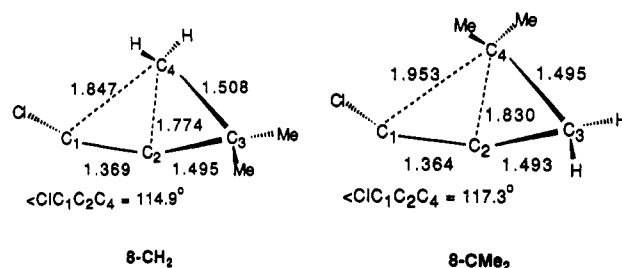
level with a split valence plus polarization function basis set (HF/6-31G*//6-31G*) and fully characterized by normal mode analysis.[26,27] Only transition states for concerted ring expansion originating in the lowest energy conformer of **3** (exo; cyclopropyl trans to Cl) on singlet potential energy surfaces were investigated.[2,3,28] Improved total energies for **3** and **8** were obtained from single-point calculations on the optimized geometries including electron correlation energy contributions via Møller–Plesset perturbation theory to fourth order (MP4 (SDQ)/6-31G*//6-31G*). Enthalpies of activation ($\Delta H^{\ddagger}$) were based on these MP4(SDQ) internal energies, corrected for differential zero-point vibrational and thermal excitation (T = 298 K) contributions. Activation free energies ($\Delta G^{\ddagger}$) were subsequently evaluated using absolute entropies for **3** and **8** obtained from the application of standard statistical mechanical formulas.[26]

The computed internal energy barriers to rearrangement are ΔE = 11.9 kcal/mol and ΔE = 13.1 kcal/mol for **3** → **8-CH$_2$** and **3** → **8-CMe$_2$**, respectively, thus preferentially favoring CH$_2$ group migration by about 1.2 kcal/mol.[29] Consideration of differential zero-point energy and finite temperature corrections further favors CH$_2$ migration, with $\Delta H^{\ast}$ = 11.0 kcal/mol for **3** → **8-CH$_2$** and $\Delta H^{\ast}$ = 12.4 kcal/mol for **3** → **8-CMe$_2$**. As with **1-Cl**,[3a] the computed entropies of activation are negative but small (~-3 eu) for both transition states, leading to $\Delta G^{\ast}$ = 11.9 and 13.3 kcal/mol for **3** → **8-CH$_2$** and **8-CMe$_2$**, respectively. The computed differential free energy of activation, $\Delta\Delta G^{\ast}$ = 1.4 kcal/mol, corresponds to a rate constant ratio of ~10.5 in favor of CH$_2$ group migration, in good agreement with the experimentally determined ratio (~5).

Quantum mechanical tunneling effects may play a small role in producing the different group migration rates. Evaluation of the tunneling *correction* factor (k_t) based on the assumption of an infinitely high parabolic barrier ($k_t = u_{\neq}/\sin(u_{\neq})$, $u_{\neq} = 0.5h|\nu_{\neq}|/kT$, $\nu_{\neq}$ = transition-state imaginary frequency)[30] leads to k_t = 1.55 for **8-CH$_2$** ($\nu_{\neq} = 645i$ cm^{-1}) and 1.33 for **8-CMe$_2$** ($\nu_{\neq} = 531i$ cm^{-1}), respectively. Tunneling is thus predicted by this expression to favor CH$_2$ migration by an additional factor of 1.55/1.33 ~ 1.2. However, given the gross approximation regarding the shape of the activation energy barrier and the large computed values of $\nu_{\neq}$,[30] this result should be considered only as qualitative. It is well established that the shapes of the potential energy surfaces governing these 1,2-C shifts are quite complex.[2,3]

What is the major factor selecting in favor of CH$_2$ migration? The overall difference in barrier heights for **3** → **8-CH$_2$** vs **8-CMe$_2$** is established by the basic electronic structure calculation and modified only by the vibrational and finite temperature corrections (see above). A traditional formulation of the 1,2 shift would assign substantial negative charge to the migrating group, but electronic population analyses using the Mulliken[31a] or NBO[31b] partitioning schemes do not present a picture consistent with this idea. In addition, the two analysis schemes are not consistent with each other. They agree in assigning additional negative charge (~-0.2e) to the carbenic (C$_1$) and additional positive charge (~0.2-0.3e) to the nonmigrating (C$_2$) carbon atoms in **8** relative to **3**. However, the changes in atomic net charges on the central carbon atom of the migrating group (C$_4$) are not only quite small in absolute magnitude (0.05-0.10e), but the direction of the charge changes on C$_4$ (and C$_3$) from **3** to **8** varies among the transition states and the partitioning methods with no clearcut trend emerging. Additional charge separation does develop in **8** as witnessed by an increase in dipole moment (μ ~ 4.9 D) relative to **3** (μ ~ 3.3 D). A significant rate dependence on solvent polarity should thus be anticipated,[32] but a substantial differential migration rate arising from solvation effects in unlikely since the computed dipole moments for **8-CH$_2$** and **8-CMe$_2$** differ by only 0.05 D.[33]

Previous experimental studies have concluded that an increased tendency for migration exists for the stronger and less substituted carbon–carbon bond in cyclopropylcarbenes.[10] Judging from the optimized bond lengths in **3** (R(C–CH$_2$) = 1.548$_7$ Å; R(C–CMe$_2$) = 1.548$_4$ Å) we would predict that only a minimal difference exists between the two relevant C–C bond strengths. Rather, the size of the substituents on C$_4$ appear to be of crucial importance, with closer inspection of the optimized geometries for **8** revealing apparent differences in steric interactions.

Overall, the geometrical structures of **8-CH$_2$** and **8-CMe$_2$** are similar and they also resemble strongly the transition states for CH$_2$ migration in **1-Cl** or **1-H**.[2] In **8**, the migrating carbon (C$_4$) is situated well above the nearly fully formed C$_1$–C$_2$ double bond, roughly equidistant to C$_1$ and C$_2$, and seemingly interacting in a π-complex type manner. However, the C$_4$–C$_1$ (C$_4$–C$_2$) distances are 0.11 Å (0.06 Å) *longer* in **8-CMe$_2$** than in **8-CH$_2$**. The distance between the central carbon in one of the Me groups and the Cl

atom in **8-CMe$_2$** is 3.6 Å, indicating van der Waals contact (R_{vdw}(Me) = 2.0 Å, R_{vdw}(Cl) = 1.8 Å).[23] Furthermore, the distances from C$_1$ to the carbons in the methyl groups of **8-CMe$_2$** (2.6 and 3.0 Å) suggest the presence of moderate to strong steric interactions (R_{vdw}(C) = 1.6 Å). The corresponding interactions in **8-CH$_2$** between the methylene hydrogens and C$_1$ are less severe (R(H–C$_1$) ~ 2.2-2.5 Å; R_{vdw}(H) = 1.2 Å) and there are no van der Waals contacts with the Cl atom. We consequently believe that the energy difference between **8-CH$_2$** and **8-CMe$_2$** is largely steric in origin.

Conclusions

Photolysis of diazirine **4** in pentane gives excited state diazirine **4*** which fragments (19-20%) to isobutene and chloroacetylene, loses nitrogen concerted with ring expansion (17%) to chlorocyclobutenes **5** and **6** (3.8:1), and affords carbene **3** (63%) by simple nitrogen loss. The carbene ring expands to **5** and **6** with k_5 = 1.3 × 10^6 s^{-1} and k_6 = 2.5 × 10^5 s^{-1}. Ab initio calculations afford transition state structures **8-CH$_2$** and **8-CMe$_2$** for the **3** → **5** and **3** → **6** rearrangements. In agreement with experiment, $\Delta G^{\ast}$ for the **3** → **5** rearrangement is calculated to be 1.4 kcal/mol less than that for the **3** → **6** rearrangement. The preference of carbene **3** for CH$_2$ migration (to **5**) over CMe$_2$ migration (to **6**) is due to differential steric effects.

Experimental Section

General Techniques. NMR spectra were determined with a Varian XL-200 spectrometer at 200 MHz. Chemical shifts are reported in ppm relative to Me$_4$Si. UV spectra were determined with a Hewlett-Packard Model 8451A spectrometer. LFP studies were carried out with our previously described installation.[24] Preparative GC used Varian Models 90 or 1700 instruments; capillary GC employed a Varian Model 3700 flame-ionization unit. Mass spectra were measured with a Finnigan MAT 8230 instrument. Microanalyses were performed by Robertson Laboratory, Madison, NJ.

3-(2,2-Dimethylcyclopropyl)-3-chlorodiazirine (4). 2,2-Dimethylcyclopropane nitrile was prepared via Nelson's method.[11] A mixture of 2,2-dimethyl-1,3-propanediol ditosylate[11] (90 g, 0.22 mol) and 43 g (0.66 mol) of KCN in 1 L of ethylene glycol was heated to 100 °C for 1 h and then distilled at 140-175 °C under aspirator pressure. The top layer of the distillate was retained while the lower phase was extracted with 3 × 50 mL of pentane. The pentane extract and retained distillate were combined and the pentane was removed by rotary evaporation. The residue was distilled at 154-155 °C (lit.[11] bp 154.5-155.5 °C) to give 12.5 g (0.13 mol, 60%) of 2,2-dimethylcyclopropane nitrile.

The nitrile (12.5 g, 0.13 mol) was dissolved in 24 g (0.52 mol) of ethanol in an Erlenmeyer flask. HCl gas (5.2 g, 0.14 mol) was passed into the solution. The flask was sealed and the reaction mixture was allowed to stand for 4 days at ambient temperature. Then, 100 mL of saturated ammonia in ethanol was added at 0 °C, and the reaction mixture was stirred for 1 h. Precipitated NH$_4$Cl was filtered and the volume of the filtrate was reduced to 20 mL by rotary evaporation. Finally, 120 mL of ether was added. White, solid 2,2-dimethylcyclopropylamidine hydrochloride (4.2 g, 0.028 mol, 22%) formed, was isolated by filtration, and dried *in vacuo*, mp 179-181 °C. NMR (DMSO-d_6): δ 0.89 (dd, J = 5.6, 7.9 Hz, 1 H), 1.34 (t, J = 5.6 Hz, 1H), 1.67 (dd, J = 5.6, 7.9 Hz, 1H) [3 cyclopropyl H's], 1.03 and 1.16 (2s, 3H each, Me's), 8.77 (s, 4H, 2NH$_2$).

Anal. Calcd. for C$_6$H$_{13}$N$_2$Cl: C, 48.5; H, 8.82; N, 18.9; Cl, 23.9. Found: C, 48.0; H, 8.84; N, 18.8; Cl, 24.3.

The amidine was oxidized to **4** by the Graham method.[12] In a 1000-mL, three-neck, round-bottom flask, equipped with a thermometer, dropping funnel, and magnetic stirring bar, was placed 2 g (13 mmol) of the amidine, 80 mL of DMSO, and 4

g of LiCl. While the mixture was stirred at 0 °C, 100 mL of 12% NaOCl solution (saturated with NaCl) was added dropwise over 20 min. The reaction mixture was stirred for an additional hour and then washed with 1 L of ice water and 50 mL of pentane in a large separatory funnel. The pentane layer was separated, washed twice with 300-mL portions of water, dried over $CaCl_2$, and purified by chromatography on a short silica gel column (pentane eluent). We thus obtained ca. 0.9 g (6 mmol, 46%) of 3-(2,2-dimethylcyclopropyl)-3-chlordiazirine, **4**. NMR (δ, $CDCl_3$) –0.22 (t, J = 5.2 Hz, 1H), 0.44 (dd, J = 5.2, 8.8 Hz, 1H), 1.61 (dd, J = 5.2, 8.8 Hz) [3 cyclopropyl H's], 1.11 and 1.46 (2s, 3H each, Me's). The UV spectrum of **4** is described above.

Product Studies. Photolytic and thermolytic conditions for the decomposition of **4** and details of product isolation and identification are described above. Product yields and distributions appear in Tables I and II. The NMR spectrum of the **7a–d** mixture (δ, $CDCl_3$) showed 0.4–0.84 (m, 3H) and 1.24–1.44 (m, 1H) [cyclopropyl H's], 0.96–1.2 (m 18 H, 6 Me's).

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