A Computational and Experimental Investigation of "Free" *tert*-Butylmethylene, a Carbene Stabilized by σ Bond Participation

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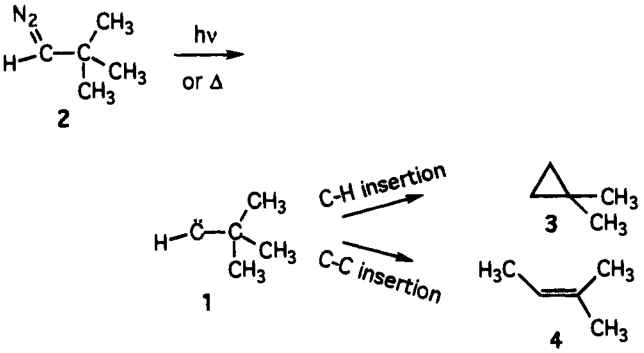
Abstract: The reactivity of *tert*-butylmethylene, **1**, has been explored computationally and experimentally by C atom deoxygenation of 2,2-dimethyl-propanal, **5**. Ab initio calculations ([QCISD(T)/6-31+G(2d,p)]// MP2/6-31G(d)) indicate that intramolecular C−H insertion to generate 1,1-dimethylcyclopropane, **3**, is more favorable than intramolecular C−C insertion to produce 2-methyl-2-butene, **4** ($\Delta H^{\ddagger}_{C-C} - \Delta H^{\ddagger}_{C-H} = 3.7$ kcal/mol (1 atm, 298 K) and $\Delta S^{\ddagger}_{C-C} - \Delta S^{\ddagger}_{C-H} = 0.5$ eu). In agreement with these theoretical predictions, deoxygenation of **5** by C atoms at 77, 158, and 195 K yields only the C−H insertion product **3**. The MP2 geometry of **1** reveals that this carbene is stabilized by participation of the neighboring C−C and C−H bonds ($C_1-C_2-C_3$ angle = 79.2°). The enthalpy barrier to the loss of N_2 from 2,2-dimethyl-1-diazopropane, **2**, to generate **1** at the MP2/6-31G(d)+ZPC level was 32.7 kcal/mol in a reaction exothermic by 30.5 kcal/mol. This decomposition of **2** did not show any tendency to bypass the free carbene in going to **3** and/or **4**.

Introduction

Like that of many carbenes, the reactivity of *tert*-butylmethylene, **1**, appears to be dependent upon its method of generation. For example, photolysis of 2,2-dimethyl-1-diazopropane, **2**, yields approximately equal amounts of the intramolecular C−H insertion product 1,1-dimethyl-cyclopropane, **3**, and the C−C insertion product 2-methyl-2-butene, **4**.[1] However, thermolysis of **2** at 403 K gives **3** and **4** in a 9:1 ratio.[1,2] Since the accepted explanation for this discrepancy is that a free carbene intermediate is not involved in one of these reactions,[3] we have investigated the energetics of the formation of both **3** and **4** from free carbene **1** computationally and have compared these results to products resulting from **1** generated by C atom deoxygenation of 2,2-dimethylpropanal, **5**.



Computational Methods

All geometries were optimized at the HF/6-31G(d) and MP2/6-31G(d) levels.[4] Vibrational frequencies were determined at both levels to determine the nature of the potential energy surface and to make zero-point corrections (frequencies weighted by a 0.90 factor for HF/6-31G(d) and a 0.95 factor for MP2/6-31G(d). Single-point calculations were made at the QCISD(T)/6-31G(d) and MP2/6-31+G(2d,p) levels on MP2/6-31G(d) geometries and combined[5] to estimated relative energies at the [QCISD(T)/6-31+G(2d,p)] levels, which, when zero-point corrections have been added, will constitute our "standard" level. Table 1 shows energies of reactants, products, and transition states along with entropies and zero point corrections.

Heat capacities and entropy corrections were made using unscaled frequencies and standard statistical procedures[6] to determine enthalpies and free energies at 298 K. Table 2 shows relative energies of relevant species along with thermodynamic values at 298 K.

Experimental Section

Reaction of Arc Generated Carbon Vapor with 5. The reactor design has been reported by Skell, Wescott, Goldstein, and Engel.[7] In a typical reaction, **5** was condensed on the reactor walls at temperatures ranging from 77 to 195 K. Carbon was vaporized by striking an intermittent arc between two graphite rods attached to water-cooled brass electrodes and condensed on the walls of the reactor containing **5** at the appropriate temperature. This procedure was repeated 15 times with a total of 13.8 mmol of **5** and resulted in the loss of 63.1 mmol

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Table 1. Absolute Energies (hartrees) and Zero-Point Energies (kcal/mol), Heat Capacity Corrections (kcal/mol), and Entropies (cal/(mol·K)) of Relevant Species[a]

	//6-31G(d)				//MP2/6-31G(d)					
	PG	HF/A	ZPE[b]	MP2/A	MP2/A	QCISD (T)/A	MP2/B	ZPE[b]	C_p[c]	S
1 (C_1)	C_1	−195.027 28	89.24 (0)	−195.656 45	−195.661 33	−195.747 67	−195.799 64	86.12 (0)	4.06	75.95
1′ (C_s)	C_s	−195.026 61	88.87 (1)	−195.654 64	−195.655 58	−195.746 72	−195.793 06	85.41 (1)	3.92	75.38
TS1/3	C_1	−195.008 04	89.11 (1)	−195.666 18	−195.661 15	−195.746 46	−195.799 98	85.68 (1)	3.69	73.76
TS1/4	C_1	−195.004 96	89.70 (1)	−195.657 04	−195.657 89	−195.740 87	−195.797 09	86.10 (1)	3.74	74.23
3	C_{2v}	−195.132 72	92.41 (0)	−195.788 01	−195.788 70	−195.867 82	−195.916 97	88.70 (0)	3.62	72.06
4	C_s	−195.145 77	91.50 (0)	−195.793 84	−195.794 96	−195.878 56	−195.926 91	87.56 (0)	4.35	79.87
1″ ($^3A''$)	C_s	−195.067 16	89.30 (0)	−195.674 30	−195.675 00	−195.759 90	−195.806 38	85.98 (0)	4.23	79.19
2	C_s	−303.984 48	98.04 (0)	−304.967 54	−304.972 24					
TS2/1+N_2	C_1	−303.952 69	96.02 (1)	−304.916 52	−304.917 25					
N_2	$D_{\infty h}$	−108.943 95	3.94 (0)	−109.248 19	−109.255 28					

[a] Basis set "A" is 6-31G (d). Basis set "B" is 6-31+G(2d,p). *b* Zero-point energy (kcal/mol). Number of imaginary frequencies in parentheses. [c] Heat capacity corrections to 298 K.

Table 2. Relative Energies (kcal/mol) of Species on the C_5H_{10} or $N_2C_5H_{10}$ Potential Energy Surfaces[a]

	//HF/6-31G(d)			/MP2/6-31G(d)					thermo. value	
	HF	MP2	MP2 + ZPC[b]	MP2/A	QCISD (T)/A	MP2/B	[QCI/B][c]	[QCI/B] + ZPC[d]	ΔH(298 K)	ΔS(298 K)
1 (C_1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1′ (C_s)	0.4	1.1	0.8	3.6	0.6	4.1	1.1	0.4	0.3	−0.6
TS1/3	12.1	−6.1	−6.2	0.1	0.8	−0.2	0.5	0.1	−0.3	−2.2
TS1/4	14.0	−0.4	0.0	2.2	4.3	1.6	3.7	3.7	3.4	−1.7
3	−66.2	−82.5	−79.7	−79.9	−75.4	−73.6	−69.1	−66.7	−67.1	−3.9
4	−74.4	−86.2	−84.2	−83.8	−82.1	−79.9	−78.2	−76.8	−76.5	3.9
1 ($^3A''$)	−25.0	−11.2	−11.2	−8.6	−7.7	−4.2	−3.3	−3.4	−3.2	3.2
2	0.0	0.0	0.0	0.0				0.0[e]		
TS2/1+N_2	19.9	32.0	30.2	34.5				32.7[e]		
1 + N_2	8.3	39.5	35.1	34.9				30.5[e]		

[a] Basis set "A" is 6-31G(d). Basis set "B" is 6-31+G(2d,p). [b] Zero-point correction calculated at the HF/6-31G(d) level and weighted by a 0.9 factor is included. [c] Additivity approximation is used. ΔE [QCI/B] = ΔE (QCISD(T)/A) + ΔE(MP2/B) − ΔE (MP2/A). [d] Zero-point correction calculated at the MP2/6-31G(d) level and weighted by a 0.95 factor is included. [e] Relative energy calculated at the MP2/6-31G(d) //MP2/6-31G(d) level with zero-point correction made at the HF/6-31G(d) level and weighted by a 0.9 factor.

of carbon from the graphite rods. Although this procedure results in lower yields than the standard cocondensation of carbon with substrate,[7] it is necessary to ensure that the carbene is generated at the correct temperature and that gas-phase pyrolysis does not occur. At the conclusion of the reaction, volatile products were pumped from the reactor into a trap at 77K. The contents of the trap were analyzed by GC and ^1H NMR to reveal **3** but no **4**. The use of authentic samples of **3** and **4** enabled us to estimate that **4** could have been detected if it were present in an amount equal to 0.3% of **3**. Typically, **3** was formed in 0.1% yield based on carbon lost from the graphite rods. Since much of the C is physically removed from the graphite rods as large chunks during the arcing process, this is a lower limit on the yield of **3**.

Results and Discussion

Since intramolecular rearrangements of carbenes proceed via the singlet state[8] and much of the experimental work on carbene **1** involves initial generation of the singlet,[9] our computational investigations have concentrated on the reaction coordinate for singlet **1**. However, we have calculated the energy of triplet **1** and find that it is lower than that of the singlet by 3.4 kcal/mol at the [QCISD(T)/6-31+G(2d,p)]//MP2/6-31G(d)+ZPC level. At this level, the CH_2 singlet−triplet splitting is calculated to be 10.8 kcal/mol, an overestimation of about 2 kcal/mol with respect to experiment.[10] If we assume that the S−T splitting in **1** is overestimated by this same amount, the best guess for the S−T in **1** is 1−2 kcal/mol in favor of the triplet. These results indicate that the singlet and triplet will be in thermal equilibrium and intramolecular reactions will occur via the singlet.

An initial computational investigation of the energetics of the rearrangement of **1** demonstrated a marked sensitivity to electron correlation. Geometry optimization at the HF/6-31G(d) level gave barriers to C−H and C−C insertion of 12.1 and 14.0 kcal/mol, respectively. Reoptimization of the geometries at the MP2/6-31G(d) level, without ZPC, lowered these barriers dramatically to only 0.1 kcal/mol for C−H insertion and 2.1 kcal/mol for C−C insertion. Since carbene **1** has neither been trapped in an intermolecular reaction nor detected spectroscopically, these latter low activation barriers appear to best describe its chemistry.[11]

Geometry optimization of **1** was initially attempted with C_s symmetry ($H-C_1-C_2-C_3$ dihedral = 180°, Figure 1a) at the HF/6-31G(d) and the MP2/6-31G(d) levels. However, these searches led to structures which were found to be transition states as they had one negative eigenvector in their force constant matrices. A slight distortion of the C_s structures followed by geometry optimization at the HF/6-31G(d) and the MP2/6-31G(d) levels gave energy minima of C_1 symmetry which were lower in energy than the C_s states by 0.4 and 3.6 kcal/mol, respectively. An examination of the MP2 optimized carbene (Figure 1b) along with that of the transition state for C−H insertion (**TS1/3**, Figure 1c) provides a rationale for the extremely low barrier calculated for the C−H insertion. Inclusion of electron correlation at the MP2 level brings about a dramatic change in geometry in which the $C_1-C_2-C_3$ angle is

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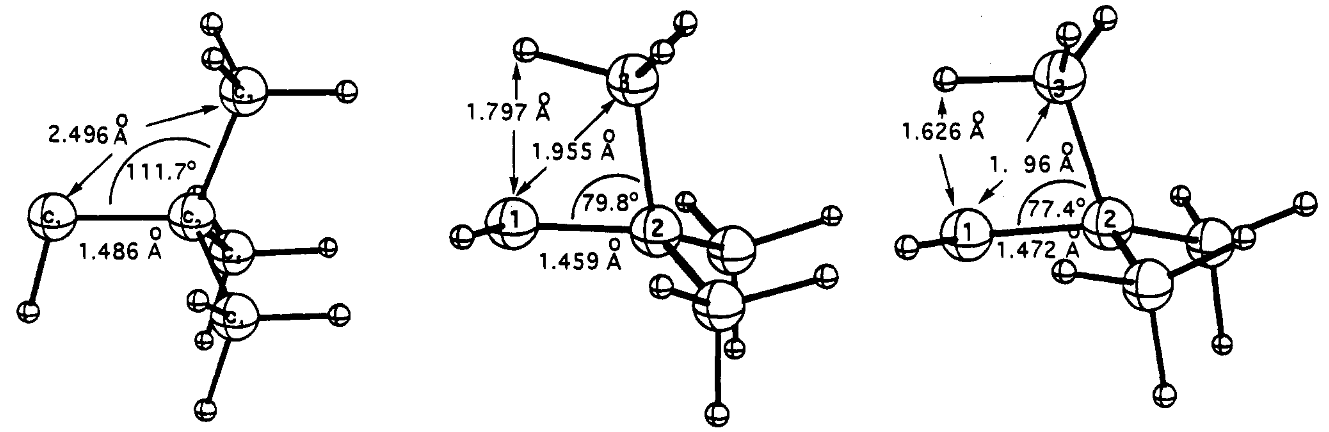
(8) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84.

(9) Production of **1** by photolysis of **2** at 298 K with triplet photosensitizers gives **3** and **4** in ratios essentially identical to those of the thermolyses at 403−453 K.[1]

(10) Leopold, D. G.; Murray K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

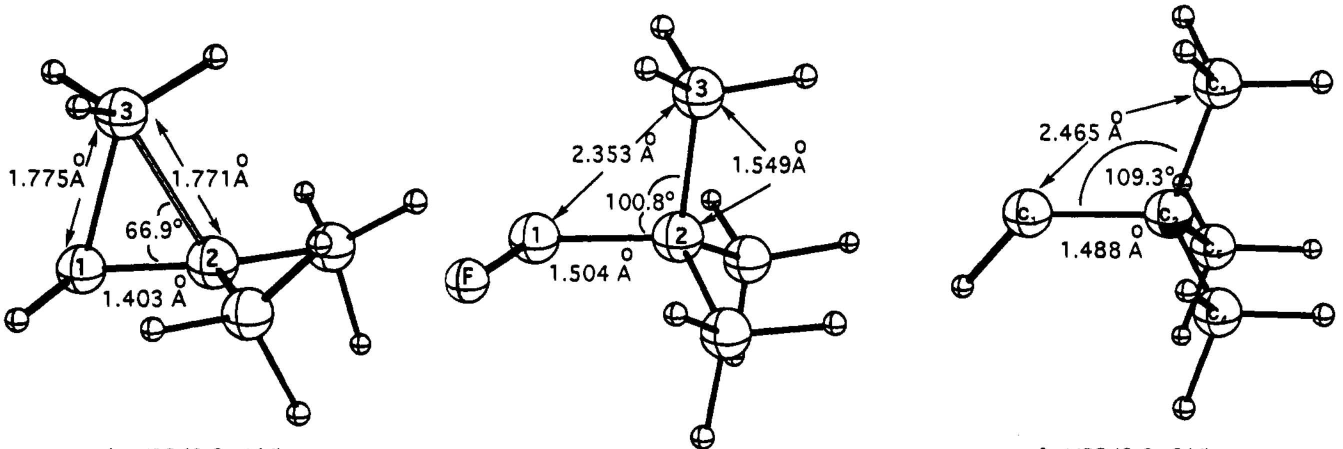
(11) The more stable *tert*-butylchlorocarbene, which has a singlet ground state, has been observed and trapped.[3a,11a−c] (a) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 4123. (b) Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* **1990**, *112*, 5642. (c) Jackson, J. E.; Soundarajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, 110, 5595.



a. MP2/6-31G(d) geometry of 1 (C_s symmetry).

b. MP2/6-31G(d) geometry of 1 (C_1 symmetry).

c. MP2/6-31G(d) geometry of C-H insertion transition state (TS1/3).



d. MP2/6-31G(d) geometry of C-C insertion transition state (**TS1/4**).

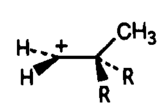
e. MP2/6-31G(d) geometry of **8** (C_1 symmetry).

f. MP2/6-31G(d) geometry of triplet 1 (C_s symmetry).

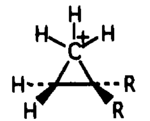
Figure 1. MP2/6-31G(d) geometries.

reduced from 100.0° to 79.8° (Figure 1b). The fact that this calculated geometry is strikingly similar to that of the transition state for C–H insertion renders this reaction quite facile. Although there is a bit more geometric reorganization in going from **1** to the transition state for C–C insertion (**TS1/4**, Figure 1d), similar arguments apply and rationalize the low barrier calculated for this rearrangement.

Since the minimum energy of **1** in Figure 1b is reached by removing the symmetry constraints on the structure in Figure 1a, which is of quite different geometry, it is likely that Figure 1b represents an energy minimum for **1**. The calculated MP2 geometry of **1**, with its considerable "bridged" character, is striking and may be rationalized when one considers that the factors that stabilize carbonium ions, with their empty p orbitals, also act to lower the energy of the corresponding isoelectronic carbenes.[12] Carbene **1** is isoelectronic to a primary carbonium ion and it is well-known that such species, to the extent that they are energy minima at all, are stabilized by participation of neighboring σ bonds. A well-studied example is the *n*-propyl cation, **6**, in which the lowest energy species is the corner protonated cyclopropane, **6a**.[13] Although the geometry of **7**, the carbonium ion exactly analogous to **1**, has not been explored computationally, a similar bridged species is expected. As the stability of carbonium ions increases in going from 1° → 2° → 3°, the need for neighboring σ bond involvement decreases and these species are less bridged.[14] In order to demonstrate that this effect is also operative as carbene stability increases, we have calculated the geometry of *tert*-butylfluoromethylene (**8**, Figure 1e) at the MP2/6-31G(d) level. The fact that the C_1–C_2–C_3 angle increases from 79.8° to 100.8° in going from **1** to the more stable **8** (which is calculated to have C_1 symmetry) indicates that the unusual geometry of **1** is due to stabilization of this relatively high energy carbene by σ bond involvement. Another indication that **1** is stabilized by bridging is the fact that its MP2 energy decreases by 3.1 kcal/mol in going from the HF to the MP2 geometry. In contrast, these same geometry changes bring about decreases in MP2 energies of **3** and **4** of only 0.6 and 0.4 kcal/mol.



6; R=H
7; R=Me



6a; R=H
7a; R=Me

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[12] This effect is well-documented in cyclopropylmethylene: Shevlin, P. B.; Mckee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519 and references therein.

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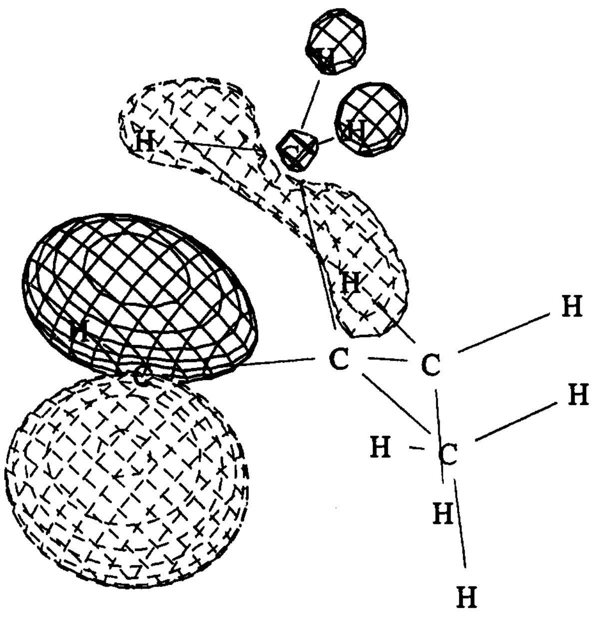

Figure 2. LUMO of carbene 1.

Thus we feel that **1** adopts its unusual bridged geometry due to an interaction between the empty p orbital and a symmetric C−C + C−H σ combination. This interaction is best visualized by examing the LUMO of **1** which is shown in Figure 2. Normally one would expect this orbital to be purely the carbene p orbital. Instead, the Figure reveals considerable mixing of this orbital with the C−C and C−H bonds of the bridging methyl. Of course, this bridging interaction will be most favorable when the p orbital is empty and one would not expect to observe significant bridging in triplet **1** with its singly occupied p orbital. An examination of the geometry of the triplet, which is calculated to have C_s symmetry (Figure 1f), shows a C−C−C angle of 109.3° bearing out this assumption.

This interesting stabilization of a carbene center by a neighboring σ bond is also reflected in calculations of the geometry of methylcarbene at the CCSD/TZ2P(f,d) level of theory by Ma and Schaefer.[15] In this case, the interaction is with a neighboring C−H bond and the :C−C−H bond angle is calculated to be 95.4°. The fact that this angle is little changed from that calculated at the MP2/6-31G(d) level (93.6°)[16] indicates that our geometry of **1** is reliably estimated at the MP2/6-31G(d) level. In analogy with the present results, Evenseck and Houk[16] find that the :C−C−H angle in methylcarbene decreases by 8° in going from the RHF to the MP2 level.

Although the fact that **1** has such a low barrier to C−H insertion leaves open the question of whether it is actually an energy minimum, we may nevertheless use the calculated differences in activation enthalpies and entropies for C−H and C−C insertion to predict ratios of products as a function of temperature. At the MP2/6-31G(d)//MP2/6-31G(d)+ZPC level, $\Delta H^{\ddagger}_{\mathrm{C-C}} - \Delta H^{\ddagger}_{\mathrm{C-H}} = 2.5$ kcal/mol and $\Delta S^{\ddagger}_{\mathrm{C-C}} - \Delta S^{\ddagger}_{\mathrm{C-H}} = 0.5$ eu; when the calculations are repeated at the [QCISD(T)/6-31+G(2d,p)]//MP2/6-31G(d)+ZPC level, $\Delta H^{\ddagger}_{\mathrm{C-C}} - \Delta H^{\ddagger}_{\mathrm{C-H}} = 3.7$ kcal/mol (1 atm, 298 K). These latter calculations predict that "free" carbene **1** will produce little of the C−C insertion product **4** at moderate temperatures.

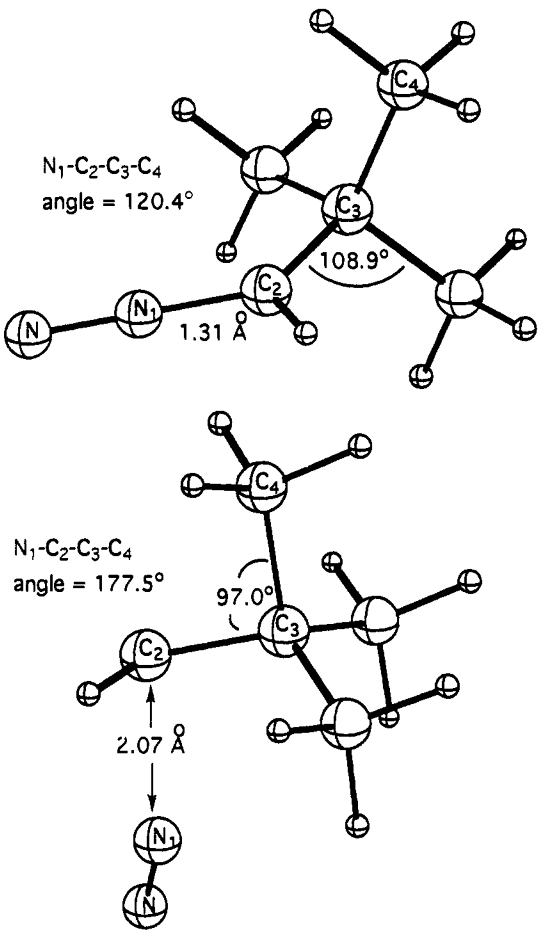

Figure 3. MP2/6-31G(d) optimized geometry of **2** (a) and of transition state for loss of N_2 from **2** (**TS2/1**) (b).

In order to test this prediction experimentally, we have generated **1** at low temperatures by the carbon atom deoxygenation of **5**, a well-established route to carbenes[2e,18] utilizing nitrogen-free precursors and thought to proceed via "free" carbenes.[18] When arc-generated carbon is condensed onto a layer of aldehyde **5** at 77, 158, and 195 K, only the C−H insertion product **3** is detected by gas chromatography or ^1H NMR spectroscopy. Since the above QCISD(T) calculated activation parameters predict only 0.01% of **4** at 195 K and even less at lower temperatures, these experiments bear out the above computational predictions. Due to complications resulting from gas-phase pyrolysis, it is unfortunately impractical to carry out the C atom deoxygenation of **5** at higher temperatures at which detectable amounts of **4** are expected.[19]

5 **1**

However, loss of N_2 from either **2** or the corresponding diazirine at elevated temperatures does generate both **3** and **4**.[1,2] For example, thermolysis of the diazirine precursor to **1** at 433 K gives a 7:1 ratio of **3**:**4**[1] while our above calculated activation parameters predict a ratio of 68:1. Although these numbers represent a difference of only 1.9 kcal/mol in the calculated and experimental $\Delta\Delta G^{\ddagger}$, the difference between them may result

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[18] Fox, J. M.; Gillen, J. E.; Jones, K. G. H.; Jones, M., Jr.; Shevlin, P. B.; Armstrong, B.; Sztyrbicka, R. *Tetrahedron Lett.* **1992**, *33*, 5021.

[19] A previous investigation of the deoxygenation of **5** by carbon gave **3** and **4** in a 15.6:1 ratio.[2d] We feel that this small amount of **4** is due to gas-phase reaction brought about by too rapid introduction of substrate. We have avoided this problem by condensing **5** completely prior to condensing the carbon.

from a transition state for thermal loss of N_2 in which the free carbene is bypassed, a process which has been postulated in other systems.[3c,18] In order to examine this possibility, we have investigated the thermal loss of N_2 from **2** computationally. The enthalpy barrier to the loss of N_2 from **2** at the MP2/6-31G(d) level was 32.7 kcal/mol in a reaction exothermic by 30.5 kcal/mol.[20] A comparison of the MP2/6-31G(d) geometries of **2** and the transition state for loss of N_2 in Figure 3 shows a decrease in the $C_2-C_3-C_4$ angle from 108° to 97° in going to the transition state. Thus, N_2 loss is assisted by the neighboring C−C σ bond. Since the geometry of the transition state for nitrogen loss resembles that of the carbene, there seems to be little tendency to bypass the carbene and proceed to **3** or **4** directly. In order to further examine the possibility that a transition state connecting **2** to **4** bypasses the free carbene, we have carried out an additional calculation starting with the MP2 geometry of the transition state leading from **1** to **4** (**TS1/4**) with the nitrogen 1.8 Å from C_2, the $N_1-C_2-C_3$ angle = 90°, and the $N_1-C_2-C_3-C_4$ dihedral = 180°. When this geometry was allowed to optimize in an HF transition state search, the N_2 moved 3.7 Å away and the remaining atoms adopted the HF geometry of **TS1/4**. Since this transition state appears to derive no benefit from a neighboring nitrogen, we conclude that loss of N_2 from **2** leads to free carbene **1** rather than to **4** directly. Although we have not carried out analogous calculations starting from the diazirine, it is expected that the reaction will proceed through **TS2/1** in Figure 3b and that similar arguments will apply. These computational investigations suggest that thermolysis of diazo compound **2** will proceed via the free carbene and should produce little **4**. However, up to 10% of **4** is observed in the thermolysis of **2** at temperatures where we would predict less than 2%. It is possible that **1** is nonstatistically energized[21] when produced from **2** with the channel leading to C−C insertion selectively populated. The fact that the atomic motions leading to **TS2/1** are also those which will take this transition state directly to **4**, lends credence to this idea. Alternately, the discrepancy between experiment and calculation may reflect either small inadequacies in the theoretical treatment or experimental difficulties in achieving completely uncatalyzed decompositions of **2**.

Conclusions

These investigations demonstrate that carbene **1** exists in a bridged geometry in which the carbene p orbital is stabilized by interaction with C−C and C−H bonds of an adjacent methyl group. This interaction apparently serves to stabilize the carbene in much the same way that a carbocation is stabilized by bridging. Both the computational and experimental results indicate that the dominant reaction of free carbene **1** will be intramolecular C−H insertion to produce **3**. Reactions in which substantial amounts of the C−C insertion product **4** are generated must have significant contributions from pathways which bypass a free carbene.

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[20] The calculated (MP2/6-31G(d)//3-21G+ZPC) barrier to formation of cyclopropylmethylene from the diazo compound was ca. 25.5 kcal/mol. Chou, J.-H.; McKee, M. L.; De Felippis, J.; Squillacote, M.; Shevlin, P. B. *J. Org. Chem.* **1990**, *55*, 3291.

[21] This possibility has been raised by a referee. For a discussion of these effects in other systems see: Carpenter, B. K. *Acc. Chem. Res.* **1992**, *25*, 520.