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Tunneling in the C–H Insertion of a Singlet Carbene: *tert*-Butylchlorocarbene

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Insertion into C–H bonds is a fundamental reaction of carbenes.[1] Considerable experimental evidence indicates that triplet carbenes insert via an H-abstraction/recombination sequence.[1,2] Singlet carbenes, on the other hand, are believed to undergo concerted insertion.[1,2] Ab initio calculations suggest that singlet C–H insertions may have negligible energy barriers, depending on the carbene substituents.[3] Although the kinetics of triplet carbene H-abstraction reactions have been extensively studied spectroscopically, primarily by Platz and co-workers,[2,4] there is not as much direct information on the concerted insertions of singlets.[5,6] Low-temperature experiments on H-abstractions of triplet carbenes, examined by EPR and laser time-resolved spectroscopy, strongly support the involvement of quantum mechanical tunneling.[2,4,7] Recent evidence also suggests that tunneling may contribute to 1,2-H shifts in singlet carbenes at low temperatures,[8] and even in solution.[9] We now report direct spectroscopic evidence for tunneling in an *intramolecular* 1,3-C–H insertion reaction of a singlet carbene, *tert*-butylchlorocarbene (**1**).

Irradiation of *tert*-butylchlorodiazirine (**2**)[10,11] in a N_2 matrix at 11 K (1:800, 334 nm, 0.5 h) caused the disappearance of its IR and UV/vis spectra and led to the appearance of a new species with major IR absorptions at 1480 (m), 1348 (w), 985 (w), 844 (s), 782 (m), and 727 (w) cm^{-1}. Concurrently, a broad absorption in the UV/vis at 520–650 nm (λ_{max} 570 nm) was observed to grow in. A small amount of cyclopropane **3**, identified by comparison to matrix-isolated authentic material,[12,13] also appeared in the IR of the irradiated matrix. Subsequent irradiation of the matrix at 570 nm led to the rapid, simultaneous disappearance of the IR and UV/vis spectra of the initial photoproduct and a corresponding increase in the IR of **3**.

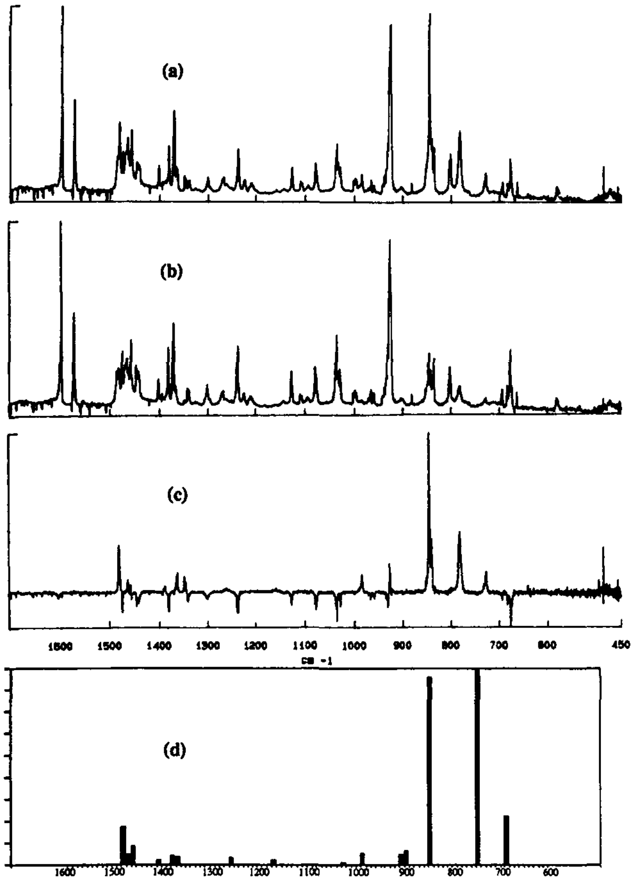

Figure 1. (a) IR spectrum (in absorbance) of 11 K N_2 matrix containing *tert*-butylchlorodiazirine (**2**) after 2-h irradiation at 334 nm. (b) IR of same matrix after an additional 6 hours at 11 K. (c) Difference of spectra b and a above. Positive peaks correspond to carbene **1**, and negative peaks represent cyclopropane **3**. (d) Calculated IR spectrum of **1** at the 6-31G* level (frequencies scaled by 0.89).

Trapping experiments support the assignment of carbene **1** as the observed initial photoproduct of **2**. Irradiation of an HCl-containing N_2 matrix (0.5% HCl, 11 K) of **2** produced small amounts of **1**, negligible **3**, and mainly the product of HCl reaction (**4**) in the IR.[14] Warming the matrix to 35 K caused the disappearance of the bands of **1** and a slight increase in those of **4**, although the trapping experiment was hampered by the intramolecular reactions (vide infra) of the carbene.

Interestingly, carbene **1** was thermally labile toward unimolecular reaction at even the lowest temperatures of the matrix experiments. On standing at 11 K, the IR and UV/vis absorptions of **1** slowly disappeared, and the IR bands of **3** simultaneously increased (Figure 1). The carbene decay kinetics were followed by measuring the decrease in intensity of the strongest IR band of **1** at 844 cm^{-1} versus time. As is often observed in low-temperature matrix reactions,[2,4] first-order plots of ln [carbene] vs time were curved, although plots vs $t^{1/2}$ were reasonably linear. Such deviations from first-order kinetics are generally attributed to a broad distribution of matrix-site-dependent reaction barriers.[2,4] These nonlinearities make it difficult to extract absolute rate constants. Approximately, the disappearance rate constant for **1** ranged from 4×10^{-4} s^{-1} initially to a value of 3×10^{-5} s^{-1} measured 250 min after photochemical generation, where roughly one-half of the initial carbene intensity remained. Surprisingly, the insertion rate was insensitive to temperature. Warming the matrix from 11 to 30 K caused no abrupt increase in the disappearance of **1**. Moreover, the concentration versus time

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(6) There is a growing appreciation that C–H insertion into hydrocarbon solvents can compete with intramolecular reactions of singlet alkylcarbenes. (a) Modarelli, D. A.; Platz, M. S.; Sheridan, R. S.; Ammann, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 10440 and references therein. (b) Kirmse, W.; Meinert, T.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8918.

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(11) The matrix isolation and irradiation details were essentially identical with those described previously in the following: Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.

(12) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1960**, *82*, 5723.

(13) No more than trace amounts of 2-chloro-3-methylbutene were observed in the IR spectra. Minor amounts of the corresponding diazo compound at 2044 cm^{-1} were observed in matrix irradiations of **1** and **5**.

(14) An authentic sample of **4** was synthesized by HCl trapping of carbene **1** in solution.

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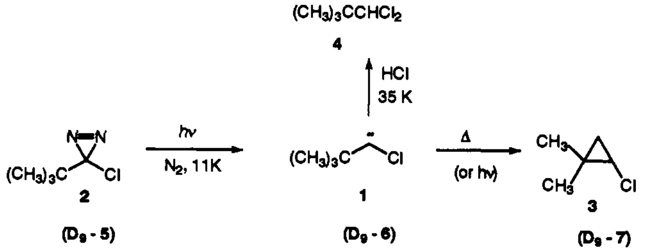
Scheme 1



profile of **1** was the same at 30 K as at 11 K. The above observations are summarized in Scheme 1.

Similar experiments, albeit with somewhat different results, were carried out with *tert*-butylchlorodiazirine-d_9 (**5**).[15] Irradiation of **5** matrix isolated in N_2 at 11 K (334 nm) produced the corresponding deuterated carbene **6**, which exhibited major IR absorptions at 828 (vs), 823 (s) 821 (s), 770 (s), 768 (s), and 729 (s) cm^{-1}.[16] The deuterated carbene showed a much more intense broad band in the 460–680-nm (λ_{max} 570 nm) region in the UV/vis, lending a distinct violet color to the matrix. Small amounts of another photoproduct, presumed to be cyclopropane **7** by analogy to the protio carbene **1**, were also observed in the IR. The carbene could again be selectively converted to **7** by irradiation at 570 nm. In contrast to **1**, however, the deuterated carbene **6** was stable toward C–D insertion under the matrix conditions. No changes were observed in the IR or UV/vis spectra of **1** after 40 h at 14 K followed by 48 h at 30 K, and the carbene survived even the highest temperatures attainable before matrix destruction (up to 40 K for 10 min).

To learn more about this system we carried out ab initio calculations on **1** and **6** at the HF/6-31G* level.[17] Although no energy minima with C_s symmetry were found, a slightly unsymmetric conformational minimum was located, with the C–Cl bond of **1** situated nearly anti to one of the C–CH_3 bonds.[17] The vibrational frequencies and intensities calculated at the 6-31G* level (scaled by a factor of 0.86) fit the experimental IR spectrum of **1** rather well (Figure 1). The calculated and observed spectra of **6** similarly agree.[16] Finally, CIS/6-31G* calculations of the excited states of **1** predict an S_0–S_1 transition at 566 nm, again offering an excellent match with experiment. The similarity between the calculated and experimental spectra also supports the contention that **1** is a ground-state singlet.[18]

Quantum mechanical tunneling[19] has been suggested in the interpretation of the kinetics of a number of low-barrier reactions of triplet reactive intermediates.[2,4] Two key observations that are often attributed to tunneling are non-Arrhenius or minimal temperature dependence of the reactions at low temperatures, and unusual isotopic sensitivity of the kinetics. We believe that the 1,3-CH insertion reaction of carbene **1** also involves tunneling. Moss and coworkers[20,21] have reported that **1** has a lifetime in solution, limited by intramolecular C–H insertion, of ca. 10^{-6} s at 294 K. Although the activation parameters for reaction of **1** have not been accurately determined, a "two-point" Arrhenius treatment of the room temperature rate and our average value at 11 K would give $E_a = 0.5$ kcal/mol and $A = 2 \times 10^6$ s^{-1}. Such parameters, however, would predict an increase in rate of ca. 7 orders of magnitude on an increase in temperature from 10 to 30 K. The observed temperature insensitivity at low temperatures thus implies a very curved "non-Arrhenius" behavior, incompatible with a classical barriered pathway.[22] Perdeuteration of the carbene also completely shuts down the low-temperature insertion reaction. An ordinary C–H insertion would similarly be expected to show a large primary kinetic isotope effect at these temperatures, but this observation is a necessary consequence of a tunneling mechanism.[2,4,19]

In summary, the 1,3-CH insertion reaction of *tert*-butylchlorocarbene (**1**) cannot be stopped even at 11 K, and experimental results suggest that this reaction involves quantum mechanical tunneling. The formation of a C–C bond during this process suggests that heavy atom tunneling[19] might also be involved and distinguishes this reaction from both 1,2-H shifts[8,9] and its triplet counterpart.[2,4] We are currently investigating substituent effects on these tunneling reactions and are probing the generality of this mechanism.[23]

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Supplementary Material Available: Ab initio geometries for **1** and calculated and experimental IR spectra for **6** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(15) Synthesized[10] from pivalonitrile-d_9: Frost, J. C.; Leadbetter, A. J.; Richardson, R. M.; Ward, R. C.; Goodby, J. W.; Gray, G. W.; Pawley, G. S. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 179.

(16) The experimental and ab initio calculated IR spectra of deuterated carbene **6** can be found in the supplementary material.

(17) Ab initio calculations were carried out with Gaussian 90, Revision J: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990. The geometry of **1** was fully optimized at the HF level of theory with the 6-31G* basis set, with no symmetry constraints. Vibrational frequency calculations gave zero imaginary frequencies. The optimized geometric parameters may be found in the supplementary material.

(18) Cl is known to stabilize the singlet relative to the triplet state of carbenes. (a) Shin, S. K.; Goddard, W. A., III; Beauchamp, J. L. *J. Phys. Chem.* **1990**, *94*, 6963 and references therein. (b) Seburg, R. A.; McMahon, R. J. *J. Org. Chem.* **1993**, *58*, 979.

(19) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980.

(20) (a) Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* **1990**, *112*, 5642. (b) Moss, R. A.; Liu, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1597.

(21) Moss and co-workers[20] also observed CH_3-shifted product, which *increased* in comparison to C–H insertion as the temperature was lowered. Trapping results suggested that the olefin arose directly from excited diazirine. The absence of 2-chloro-3-methyl-2-butene in our experiments suggests that a different mechanism for carbene formation may be operative at low temperatures.

(22) For additional examples of curved Arrhenius plots in carbene intramolecular reactions at low temperatures, and discussions of alternative explanations, see: McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683 and references therein.

(23) Although all of the IR bands attributed to **1** disappear together on irradiation at 570 nm, they decrease in intensity at different apparent rates thermally at 11 K. We tentatively believe that several conformations of the carbene are present, with slightly different IR intensities and decay rates.