Study of *trans*-2-*tert*-Butylcyclopropylcarbene by Laser Flash Photolysis and Chemical Analysis[1]

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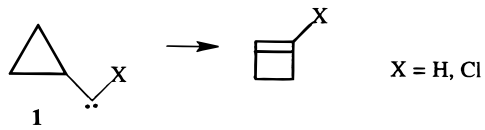
Abstract: Laser flash photolysis (LFP) of *trans*-2-*tert*-butylcyclopropyldiazirine (**4**) produces *trans*-2-*tert*-butylcyclopropylcarbene (**5**). Carbene **5** can be trapped with pyridine to form ylide **6**. The rate of formation of ylide **6** was resolved and found to be linearly dependent on the concentration of pyridine. The lifetime of carbene **5** was determined to be 22 ns (pentane), 18 ns (acetonitrile and $CF_2ClCFCl_2$), 15 ns (cyclohexane), and 27 ns (cyclohexane-d_{12}) at ambient temperature. The lifetime of carbene **5** in solution, at ambient temperature, is controlled substantially by reaction with solvent and only to a minor extent by rearrangement to cyclobutene **7**. Photolysis of **4** (350 nm) in Freon-113 produces 3-*tert*-butylcyclobutene (**7**) along with products derived from attack of the carbene on solvent. Photolysis of **4** in the presence of trapping agents (tetramethylethylene, cyclopentene, propylamine, trifluoroethanol) produces adducts with little or no corresponding decrease in the yield of **7**. The preferred interpretation is that cyclobutene **7** is formed by a rearrangement of the excited state of the diazirine (diazirinyl biradical), and not by a carbenic process at 0 °C and lower temperatures. This mechanism is supported by product analysis of a non-nitrogenous cyclopropylcarbene precursor. At ambient temperature, cyclobutene **7** is formed by both diazirine excited state (diazirinyl biradical) and carbene rearrangement.

I. Introduction

Moritani et al. were the first to apply flash photolysis methods to the study of carbenes in 1968.[3] Closs and Rabinow reported the first absolute rate constant of a carbene reaction in solution, using microsecond time-resolved flash photolysis techniques in 1976.[4] In the 1980's, laser flash photolysis (LFP) methods were used extensively to study bimolecular reactions of carbenes.[5] In the 1990s, however, attention has shifted to the study of unimolecular carbene processes.[1,6]

The rearrangement of cyclopropylcarbene **1** was discovered by Friedman and Shechter at The Ohio State University in the 1960's.[7]



The Moss[8] group ($E_a = 3.0 \pm 0.4$ kcal/mol, log $A = 8.2 \pm 0.2$ s^{-1}) and Bonneau and Liu[9] ($E_a = 7.4$ kcal/mol, log $A = 11.1$ s^{-1}) have studied the dynamics of the rearrangement of chlorocyclopropylcarbene to 1-chlorocyclobutene but obtained rather different Arrhenius parameters.

The calculations of McKee and Shevlin predict that there is a substantial barrier to rotation of cyclopropylcarbene.[10] This is not surprising as the electronic structure of singlet carbene **1** resembles the cyclopropylcarbinyl cation which enjoys stabilization by conjugation with the Walsh orbitals of cyclopropane.[11,12] The barrier to rotation of the cyclopropylcarbinyl cation is calculated to be 17.5 kcal/mol.[13] The barrier to rotation of the α,α-dimethyl derivative is 13.7 kcal/mol.[14] Unsurprisingly, calculations indicate that there are two stable conformers of cyclopropylcarbene, that they interconvert slowly, and that they undergo two different reactions.[10] The syn form prefers fragmentation, whereas the anti form undergoes ring enlargement.

Modarelli et al. probed the lifetime of **1** by LFP, using the pyridine ylide method, in 1993.[15] Conformational issues were

(1) Portions of this work have been communicated previously, see: Platz, M. S.; Huang, H.; Ford, F.; Toscano, J. *Pure Appl. Chem.* **1997**, *69*, 803. Huang, H.; Platz, M. S. *Tetrahedron Lett* **1996**, *37*, 8337.

(2) Current address: Department of Chemistry, Washington University, One Brookings Dr., Campus Box 134 St. Louis, MO 63130.

(3) (a) Moritani, I.; Murahashi, S.; Asitaka, H.; Kimura, K.; Tsobomura, H. *J. Am. Chem. Soc.* **1968**, *90*, 5918. (b) Moritani, I.; Murahashi, S.; Nishino, N.; Tsobomura, H. *Tetrahedron Lett.* **1966**, 373.

(4) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

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(8) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1633.

(9) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989,** *93*, 7298.

(10) (a) Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519. (b) Choa, J.-H.; McKee, M. L.; DeFelppis, J.; Squillacote, M.; Shevlin, P. B. *J. Org. Chem.* **1990**, *55*, 3291.

(11) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

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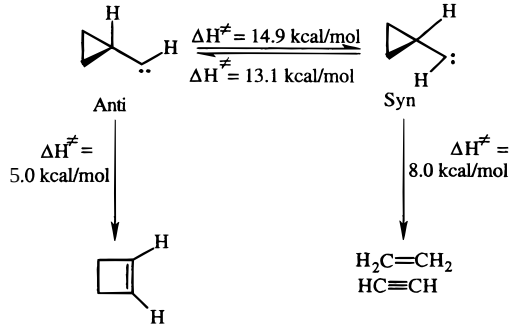


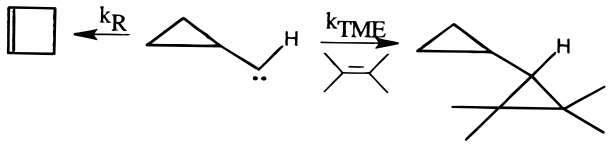
not addressed in that study. The spectrometer used by Modarelli et al.[15] lacked the time resolution needed to directly measure the growth of ylide **2**, produced by LFP of diazirine **3** (Scheme 1). In that study, it was possible to measure the relative yield of ylide as a function of pyridine concentration. Analysis of the data produced a ratio of rate constants (eq 1)

$$\frac{k_{PYR}}{k_R + k_F + k_{SX}[SX]} = k_{PYR}\tau \qquad (1)$$

where τ is the lifetime of the carbene in the absence of pyridine and the rate constants are defined in Scheme 1.[6] After assuming a value of $k_{PYR} = 1 \times 10^9$ M^{-1} s^{-1}, Modarelli et al. deduced that the lifetime of cyclopropylcarbene was 24 ns, in pentane, at ambient temperature.[15]

Modarelli et al. worried that the lifetime of cyclopropylcarbene might be limited, in part, by reaction of the carbene with solvent (k_{SX} [SX], Scheme 1) because the lifetime of **1** is extended from 14 ns in cyclohexane to 21 ns in cyclohexane-d_{12}. Thus, that study of the carbene lifetime did not yield values of $k_F + k_R$ and their associated Arrhenius parameters.

This has prompted the modified strategy of this study. A cyclopropylcarbene will be generated in solution and allowed to partition between reaction with a trap, 2,3-dimethyl-2-butene (tetramethylethylene (TME)) and a unimolecular rearrangement reaction.

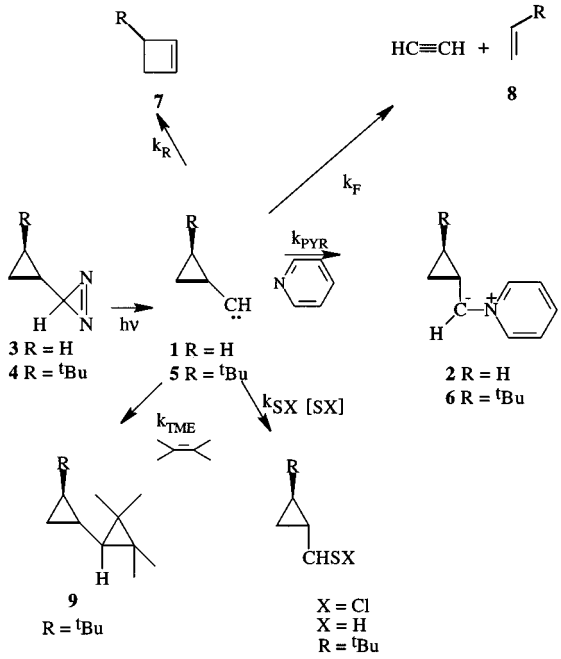


Measurement of the ratio of TME-adduct/cyclobutene as a function of [TME] should, in principle, yield k_{TME}/k_R. Measurement of k_{TME} by LFP would then yield k_R and eventual deduction of the activation parameters by repeating this analysis as a function of temperature. Herein, we are pleased to report the results of this study. The LFP and chemical trapping data will demonstrate that the lifetime of *trans-tert*-butyl-cyclopropylcarbene (**5**) in solution is largely controlled by intermolecular reactions. The data reveal that 3-*tert*-butylcyclobutene (**7**) is not formed by rearrangement of the cyclopropylcarbene in solution at 0 °C or lower temperatures. Cyclobutene **7** is formed, in part, by carbene rearrangement at temperatures above 25 °C but is also formed, we propose, in a rearrangement of the diazirine excited state (diazirinyl biradical). Thus, the goal of measuring the kinetics of the cyclopropylcarbene rearrangement and its associated Arrhenius Parameters has not been realized.

II. Results

II.1. Laser Flash Photolysis (LFP) Studies. Cyclopropyldiazirine is a low boiling substance. *trans*-2-*tert*- Butylcyclopropyldiazirine (**4**) was synthesized to reduce the volatility of the precursor and facilitate the handling and quantitative chemical analysis of the reactions of carbene **5** (Scheme 1).

Scheme 1



First, it is important to demonstrate that the LFP of *trans*-2-*tert*-butylcyclopropyldiazirine (**4**) produces results similar to that obtained by photolysis of cyclopropyl diazirine. LFP (XeF excimer laser 351 nm, 35 nmJ, 17 ns) of diazirine **4** fails to generate a UV−vis active transient. LFP in the presence of pyridine produces the transient spectrum of ylide **6** (see the Supporting Information). It was not possible to resolve the rate of formation of **6** using the excimer laser source due to the 20 ns width of this laser pulse.

The optical yield of ylide **6** (A_y) smoothly increases as a function of the concentration of pyridine in $CF_2ClCFCl_2$ (Freon-113) (Figure 1), in pentane, and in acetonitrile. Double reciprocal plots are predicted[6] and found (Figure 2) to be linear in each solvent. The ratio of intercept/slope of such a plot can be shown to be $k_{PYR}\tau$ where $1/\tau = (k_{SX}[SX] + k_R + k_F)$ (see Scheme 1).[6] Absolute values of k_{PYR} have been obtained by time-resolved LFP methods (*vide infra*) and are used to deduce values of τ. These values are about twice as large as those found by Modarelli et al. with the parent cyclopropylcarbene system.[15]

As seen in Figure 1, the yield of ylide increases steadily up to 0.02 M in pentane (0.04 M in Freon-113, 0.02 M in acetonitrile). Above this concentration, every carbene produced in a laser pulse is captured to form ylide.

However, the yield of ylide produced per laser pulse in the saturation region of [pyridine] ($A_y°$) is reduced in the presence of a competitive carbene trap, such as tetramethylethylene (TME). Under these conditions a plot of $A_y°/A_y$ versus [TME] is linear at constant [pyridine] (Figure 3). The slope of this plot[6] is k_{TME}/k_{PYR} [pyridine] = 6.5 at a concentration of pyridine of 0.041 M. Thus, $k_{TME}/k_{PYR} = 0.27$ in Freon-113 at ambient temperature.

II.2. Nd:YAG LFP. The time resolution of the spectrometer has been recently improved with the addition of a Nd:YAG laser

(15) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 10440.

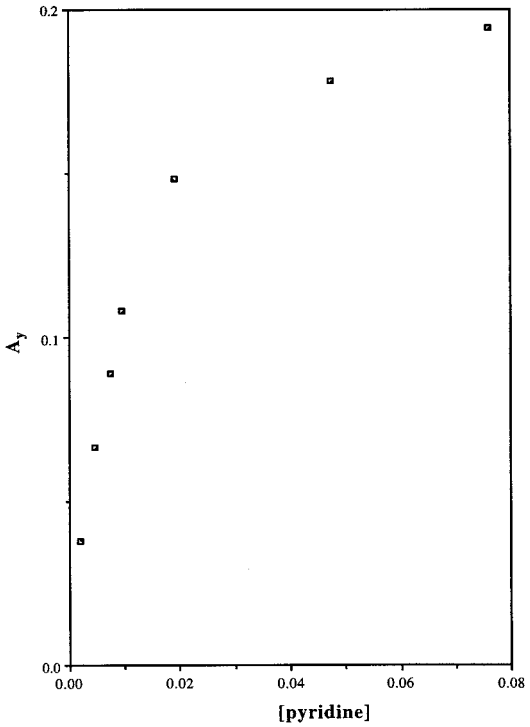


Figure 1. A plot of the optical yield of ylide **6** as a function of [pyridine] produced by LFP of diazirine **4** (351 nm) in Freon-113 at ambient temperature.

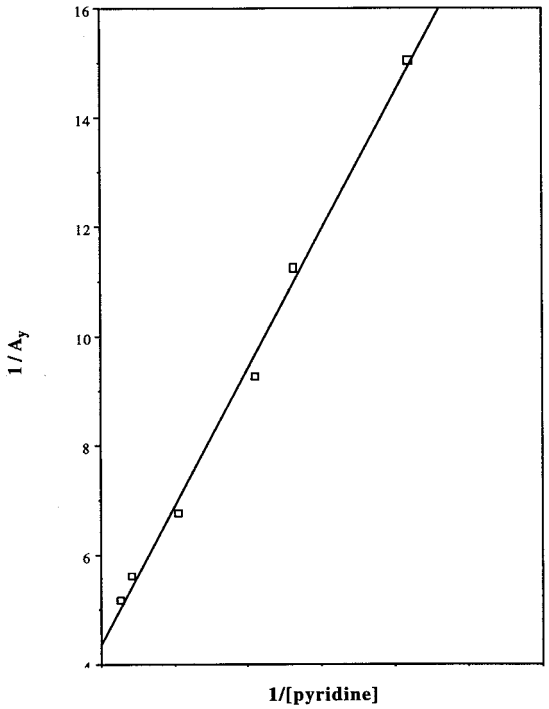


Figure 2. A plot of $1/A_y$ for ylide **6** as a function of 1/[pyridine] resulting from LFP of diazirine **4** (351 nm) in Freon-113.

source which delivers 0.15 ns pulses and improved optics and electronics.[16] With this spectrometer, it is possible to resolve the growth of ylide **6** following LFP of **4** (see the Supporting Information).

The growth of the ylide can be fit to an exponential function and analyzed to yield the observed rate constant of formation of ylide **6**. The observed rate constant (k_{obs}) can be related to

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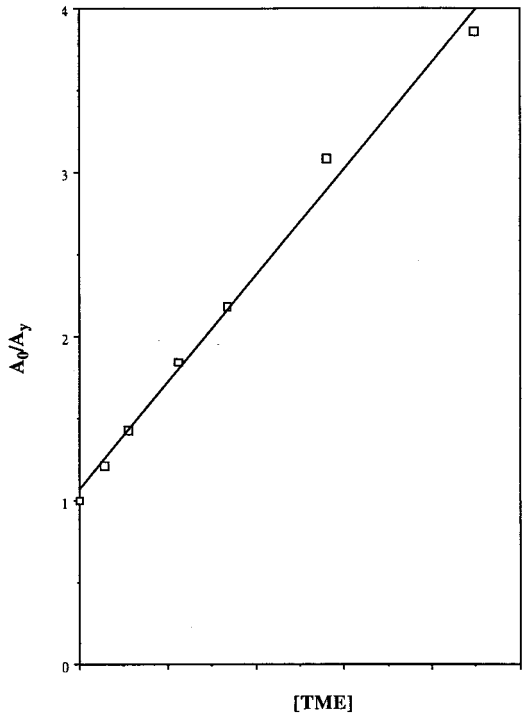


Figure 3. Stern−Volmer quenching of the yield of pyridine ylide **6** by TME in Freon-113.

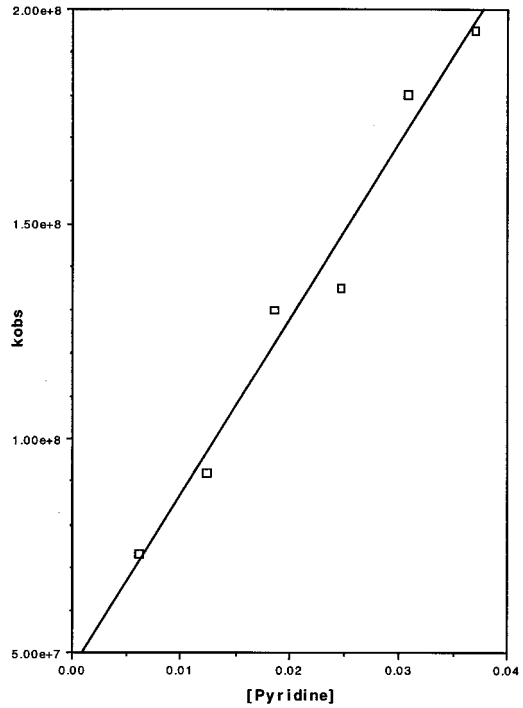


Figure 4. The observed rate constant for the formation of ylide **6** (k_{obs}) upon LFP of diazirine **4** in pentane as a function of [pyridine] at ambient temperature.

the concentration of pyridine by a Scaiano analysis[17] (eq 2)

$$k_{obs} = 1/\tau + k_{PYR}[\text{pyridine}] \qquad (2)$$

where $k_{obs} = 1/\tau = k_R + k_F + k_{SX}[SX]$ and the rate constants are as defined in Scheme 1. The plots of k_{obs} versus [pyridine] are predicted and found to be linear (Figure 4). The absolute rate constants of k_{PYR} and τ determined in various solvents are given in Table 2.

(17) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252.

Table 1. Lifetimes of Cyclopropylcarbene and *trans*-2-*tert*-Butylcyclopropylcarbene Deduced from Double Reciprocal Plots

solvent	k_{pyr} (M^{-1} s^{-1})	$k_{pyr}\tau$	τ(ns)
cyclopropylcarbene (**1**)			
pentane	*a*	24	24[a] (7)[b]
cyclohexane	*a*	14	14[a] (4.5)[b]
cyclohexane-d_{12}	*a*	21	21[a] (6)[b]
trans-2-*tert*-Butylcyclopropylcarbene (**5**)			
Freon-113	2.2×10^9 [c]	86	39
pentane	4.1×10^9 [c]	136	33
acetonitrile	5.8×10^8 [c]	16	28

[a] Data of Modarelli et al.[15] assuming that $k_{pyr} = 1 \times 10^9$ M^{-1} s^{-1} and is independent of solvent. [b] τ values were deduced assuming that k_{pyr} of cyclopropylcarbene is the same as that of *tert*-butyl analogue **5** (see Table 2). [c] *k_{pyr} values are based on results of direct time-resolved LFP data of Table 2.

Table 2. Absolute Values of the Lifetime of Carbene **5**, Measured Directly in Various Solvents, at Ambient Temperature

solvent[a]	k_{pyr} (M^{-1} s^1)	$1/\tau$ (s^{-1})	τ (ns)
pentane	4.1×10^9	4.6×10^7	22
acetonitrile	5.8×10^8	5.6×10^7	18
Freon-113	2.2×10^9	5.5×10^7	18
cyclohexane	3.1×10^9	6.7×10^7	15
cyclohexane-d_{12}	3.4×10^9	3.7×10^7	27

[a] The concentration of diazirine **4** in different solvents was adjusted so that $A_{355\ nm} \approx 1.0$. All solvents were dried and degassed prior to LFP.

The values of k_{PYR} span a factor of 6. As usual, k_{PYR} has the lowest value in the most polar solvent (acetonitrile).[5b,18] Measurement of k_{PYR} in Freon-113 immediately determines that $k_{TME} = 5.9 \times 10^8$ M^{-1} s^{-1}. The absolute values of k_{PYR} also define the values of τ, deduced by double reciprocal analysis (see Table 1).

The τ values of *trans*-2-*tert*-butylcyclopropylcarbene (**5**) directly determined by direct measurement of k_{obs} are in reasonable agreement with those deduced by Modarelli et al.[15] for the parent system but are lower than those deduced by double reciprocal analysis of 2-*tert*-butylcyclopropylcarbene in this work. We believe that the values of τ determined directly (Table 2) are more accurate and precise than those deduced from a double reciprocal plot (Table 1).

We conclude that the 2-*tert*-butyl substituent does not have a large effect on the lifetime of cyclopropylcarbene. The lifetime of *tert*-butylcyclopropylcarbene (**5**) is larger in cyclohexane-d_{12} relative to cyclohexane by roughly a factor of 2. It is clear that the lifetime of **5** in cyclohexane is strongly influenced by the reaction of the carbene with solvent (k_{SX}-[SX] $\geq k_R + k_F$). We suspect this is also true in Freon-113 where the τ value is very similar to that measured in cyclohexane. We conclude that the lifetime values of Table 2 are not cleanly controlled by intramolecular reactions of the cyclopropylcarbene.

II.3. Chemical Analysis of Reaction Mixtures. Photolysis of **4** in Freon-113 ($CF_2ClCFCl_2$) yields 3-*tert*-butylcyclobutene (**7**) and *tert*-butylethylene (**8**). Products were also formed that derived from reaction of carbene **5** with the solvent. The complex mixture of products was analyzed by GC-MS but individual products formed by reaction with solvent were not isolated and characterized. It is likely that carbene **5** abstracts chlorine atoms from Freon-113 to form radical pairs which can combine in various and complex ways.

Upon photolysis of **4** in Freon-113 containing TME, cycloadduct **9** (Scheme 1) is produced. The yield of adduct increases with increasing [TME]. The analytical GC data can be analyzed in a double reciprocal plot using exactly the same formalism applied to the yield of ylide, determined by LFP, as a function of pyridine concentration. A double reciprocal plot of the yield of adduct **9** versus [TME] is linear (Figure 5). Values of $k_{TME}\tau$ at ambient temperature in several solvents are given in Table 3. These data are in good agreement with the LFP data of Table 1, also obtained by a double reciprocal analysis, but again are larger than the absolute values listed in Table 2. A value of k_{TME} at ambient temperature was determined previously in Freon-113 and used to deduce a τ value of the carbene under these conditions.

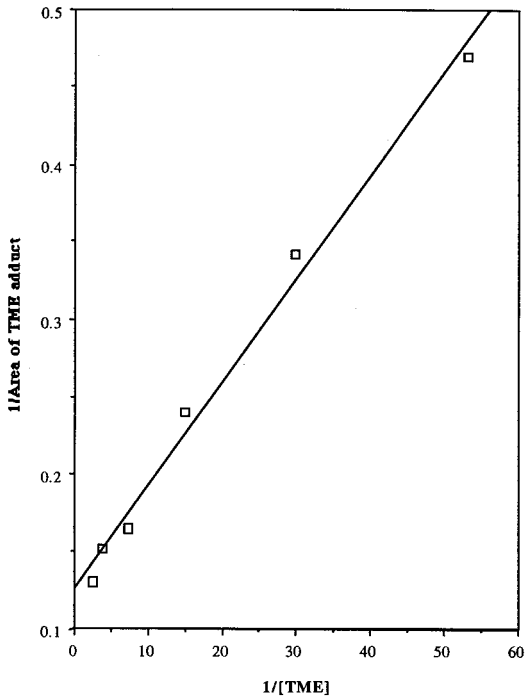


Figure 5. Double reciprocal treatment of the yield of adduct **9** determined by GC, obtained by photolysis of diazirine **4** in Freon-113 in the presence of TME at 25 °C.

Table 3. Summary of $k_{TME}\tau$ Data Obtained with 2-*tert*-Butylcyclopropylcarbene in Several Solvents, by GC Analysis of This Yield of TME Adduct **9**

solvent	$k_{TME}\tau$	τ^a (ns)
Freon-113	18.5	31
cyclohexane	22.1	37
pentane	21.6	37
acetonitrile	3.2[b]	5[b]

[a] Assuming $k_{TME} = 5.9 \times 10^8$ M^{-1} s^{-1} in all solvents. [b] This value is probably too low due to the likelihood of a solvent effect on k_{TME}.

One can argue that adduct **9** is derived by trapping and decomposition of a diazo compound, formed by light-induced isomerization of the diazirine.

Warkentin and co-workers have shown that oxidiazolines efficiently fragment to form diazo compounds.[19] Recently, Lee has shown that photolysis of an oxadiazoline in the presence of 1-pentene produced a pyrazoline which was readily detected by GC.[20]

(18) Jones, M. B.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 1694.

(19) (a) Majchrzak, M. W.; Békhazi, M.; Tse-Sheepy, I.; Warkentin, J. *J. Org. Chem.* **1989,** *54*, 1842. (b) Majchrzak, M. W.; Jefferson, E. A.; Warkentin, J. *J. Am. Chem. Soc.* **1990**, *112*, 1842. (c) Jefferson, E. A.; Warkentin, J. *J. Org. Chem.* **1994**, *59*, 455.

(20) Lee, E.; Platz, M. S. Unpublished research at The Ohio State University.

Table 4. Absolute Yields of Products Formed in the Photolysis (350 nm) of Diazirine **4** in $CF_2ClCFCl_2$ (−25, 0, and 25 °C)

	−25 °C			0 °C			25 °C		
TME (M)	**7** (%)	**9** (%)	**8** (%)	**7** (%)	**9** (%)	**8** (%)	**7** (%)	**9** (%)	**8** (%)
0							50	0	20
0.017	44	13	10	46	10	13	50	7	19
0.034	47	19	10	44	14	12	50	12	18
0.067	45	22	10	46	20	13	49	17	17
0.134	46	26	11	48	24	13	46	22	15
0.269	45	30	11	45	27	12	45	25	15
0.420	46	32	10	47	28	13	44	26	15

Table 5. Absolute Yields of Products Formed in the Pyrolysis of 3-(2-*tert*-Butylcyclopropyl)-3*H*-diazirine (**4**) in $CF_2ClCFCl_2$ (100 °C)

TME (M)	%  **7**	%  **9**	%  **8**
0.0	64	0	14
0.036	64	4.9	13
0.067	65	8.7	12
0.135	64	14	10
0.261	64	20	8.4
0.506	60	26	6.6
0.948	57	32	3.9
1.94	57	37	3.2

However, no pyrazoline intermediates were detected by GC-MS during the course of the photolysis of **4** in the presence of TME.

The agreement between the data obtained by LFP and GC analysis, and the lack of evidence of a pyrazoline intermediate, leads us to conclude that the same species, carbene **5**, has been studied by chemical and physical methods.

The τ value deduced in acetonitrile (Table 3) is certainly much too short as a result of an overestimation of k_{TME} in this solvent. As noted previously, bimolecular rate constants of carbenes are substantially reduced in acetonitrile relative to nonpolar solvents.[5b,18]

The distribution of products formed on photolysis of **4** in Freon-113 as a function of TME concentration and as a function of temperature is given in Table 4. At −25 and 0 °C, the yield of adduct **9** grows with increasing [TME] but without any corresponding decrease in the yield of cyclobutene **7** and *tert*-butylethylene (**8**). However, at 25 °C increasing the concentration of TME leads to a small decrease in the yields of **7** and **8**, but the decrease is far smaller than the increase in yield of adduct **9**.

The absolute yields of cyclobutene **7** at low [TME] concentration increase with the temperature of decomposition of precursor **4**. The yield of **7** is 64% when **4** is pyrolyzed at 100 °C (Table 5). The ability of TME to depress the yield of cyclobutene **7** and *tert*-butylethylene (**8**) increases with pyrolytic decomposition of the diazirine precursor relative to photolytic decomposition.

Similar results were observed upon photolysis of **4** in pentane (Supporting Information) and in acetonitrile (Supporting Information) although it was not possible to measure the yield of *tert*-butylethylene (**8**) in these solvents because this compound eluted with the solvent. Similar results were obtained with a less-hindered alkene, cyclopentene, in pentane (Supporting Information), with *n*-propylamine in pentane (Supporting Information), and with trifluoroethanol in Freon-113 (Supporting Information).

III. Discussion

Photolysis of diazirine **4** in Freon-113 at 0 or −25 °C produces cyclobutene **7** by a rearrangement and *tert*-butylethylene (**8**) by a fragmentation reaction. As the concentration of TME increases from 0.017 to 0.420 M, the yield of carbene−alkene adduct **9** increases from 10−13% to 28−32% without any decrease in yield of cyclobutene **7** or *tert*-butylethylene (**8**). Thus, the intermediate trapped to form adduct **9** does not lead to either **7** or **8** in Freon-113 at 0 or −25 °C. Scheme 1 is incomplete; a second cyclobutene forming pathway must exist.

The need for two product forming pathways in diazirine decompositions was recognized over 30 years ago. Photolysis of ethylmethyldiazirine[21] gives a more complex mixture of products than observed upon pyrolysis of the same precursor. Many more examples of this type were subsequently reported by Shechter[22] and Jones.[23,24]

Several proposals have been advanced which have sought to identify the second product forming pathway.

Tomioka et al. studied the photolysis of benzylchlorodiazirine.[25] Photolysis of this diazirine produces a mixture of β-chlorostyrenes. In the presence of TME, a cycloadduct of benzylchlorocarbene is formed. If a simple mechanism was operative plots of (cycloadduct/β-chlorostyrene) versus [TME] would be linear. Instead, such plots are curved as in the case of carbene **5** (Supporting Information). Thus, there is a route through a non TME trappable intermediate to the formation of β-chlorostyrenes. The second product forming pathway can be attributed to a carbene−olefin complex[25] or to a diazirine excited state.[6] A related pattern of observations with cyclobutanylidene has been recently reported as well.[26]

A carbene complex mechanism requires that carbene **5** forms complexes with TME, cyclopentene, and, by extension, *n*-propylamine and trifluoroethanol and that these complexes partition between adduct formation and rearrangement to cyclobutene. However, theory predicts that carbene−alkene complexes are not bound species,[27] and furthermore, the anomolous effects reported for benzylchlorocarbene disappear when a non-nitrogenous carbene precursor is employed.[28] Thus, we do not believe that carbene complexes explain the results reported in this work.

A special explanation can be postulated for carbene **5** because of the unique conformational isomerism present in cyclopro-

(21) (a) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett* **1966**, 1733. (b) Frey, H. M.; Stevens, I. D. R. *J. Am. Chem. Soc.* **1962**, *84*, 2647. (c) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512.

(22) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082.

(23) (a) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516. (b) Fox, J. M.; Scacheri, J. E. G.; Jones, K. G. L.; Jones, M., Jr.; Shevlin, P. B.; Armstrong, B.; Szytrbicka, R. *Tetrahedron Lett.* **1992**, *33*, 5021.

(24) For a review, see: Platz, M. S. In *Advances in Carbene Chemistry Vol. 2*; Brinker, U., Ed.; JAI Press: Greenwich, CT, in press.

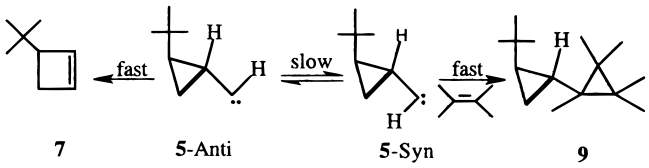
(25) Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454. See also ref 6c for a complete discussion and bibliography.

(26) Pezacki; J. P.; Pole, D. L.; Warkentin, J.; Chen, T.; Ford, F.; Toscano, J. P.; Fell, J.; Platz, M. S. *J. Am. Chem. Soc*. **1997**, *119*, 3191.

(27) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555.

(28) Nigam, M.; Platz, M. S.; Toscano, J. P.; Johnson, R. *J. Am. Chem. Soc*. In press.

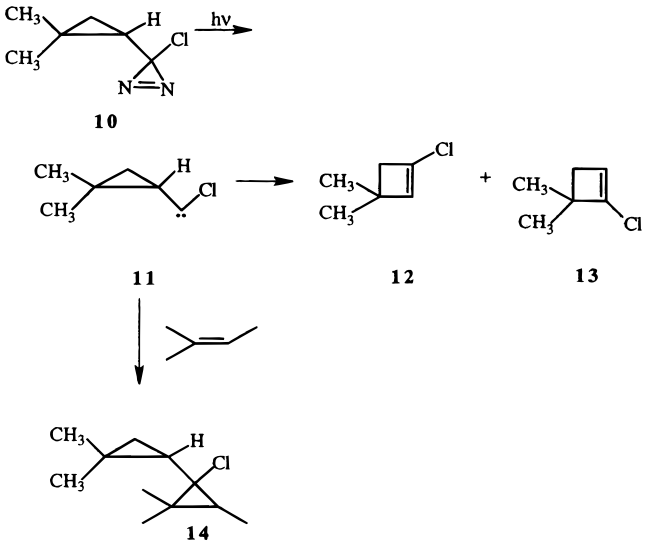
pylcarbenes. One can posit that both conformers of **5** are formed on photolysis of **4** and that **5**-anti is sterically blockaded and consequently is unreactive toward pyridine and TME. If this



mechanism is correct, then adduct **9** is formed preferentially (exclusively at ≤0 °C) from **5**-syn because **5**-anti is "untrappable." Thus, the yield of cyclobutene is not influenced by the presence of TME.

We are reluctant to embrace this point of view because, at 25 °C and higher temperature, there is some decrease in the yield of cyclobutene **7** upon the addition of TME. Thus, the anti-conformer which undergoes rearrangement is not too sterically blockaded to be intercepted at ambient temperature.

We are also strongly influenced by the findings of Moss et al. who studied the photolysis of diazirine **10**, in the presence of trimethylethylene.[29]

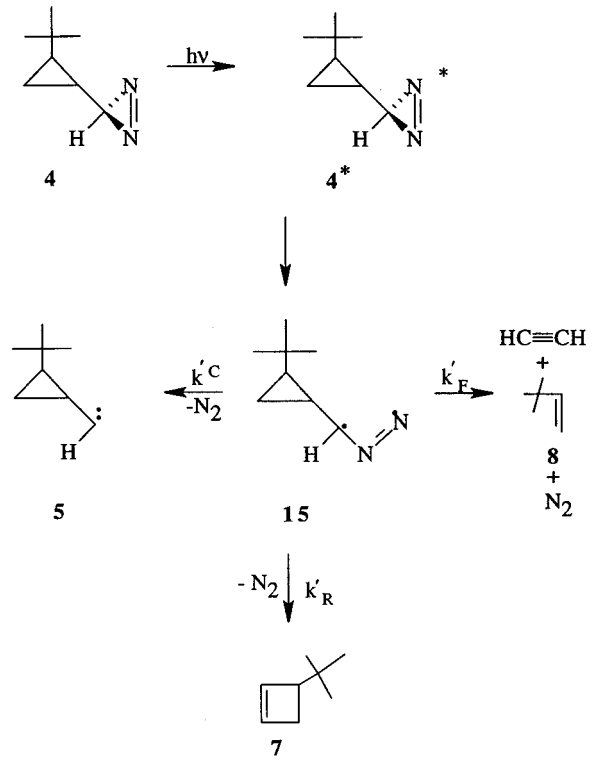


Carbene **11** is certainly more sterically blockaded than **5**, yet photolysis of **10** in the presence of 1.06 M trimethylethylene leads to the formation of four stereoisomeric adducts (including **14**) with this carbene in total yield of 12.8% and reduces the combined yields of **12** and **13** from 81.4 to 67.6%. In this system, the yield of adduct (12.8%) is almost exactly equal to the decrease in yield (13.8%) of the isomeric cyclobutenes. This requires that a TME trappable conformer of **11** rearranges to cyclobutene. Since it seems unlikely that **11**-syn will rearrange to cyclobutene owing to the large energy barrier predicted by theory,[10] **11**-anti (and by inference, **5**-anti) cannot be so crowded as to preclude its trapping with alkene.

The presence of the chlorine substituent at the carbene center increases the ratio of intramolecular rearrangement (k_R) to carbene reaction with solvent (k_{SX}[SX]). This can occur if the chlorine group either increases k_R or reduces k_{SX}[SX]. The latter effect seems more likely based on the ability of chlorine to stabilize singlet carbenes by donation of lone pairs of electrons into the empty p orbital of a carbene.[11,12]

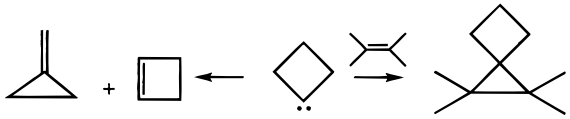
(29) Moss, R. A.; Liu, N.; Krogh-Jespersen, K. *J. Phys. Chem.* **1993**, *97*, 13413.

Scheme 2



Any explanation insisting that **5**-anti is too sterically blockaded to react with TME predicts that using a less sterically encumbered trap will lead to more efficient capture of carbene **4** and greater quenching of the yield of cyclobutene **7**. However, the quenching observed with cyclopentene, *n*-propylamine, and trifluoroethanol mirror that obtained with TME (Supporting Information).

Finally, we note that the same pattern of observations encountered in this study were observed with cyclobutanylidene,[26] where conformational isomerism is not possible. Thus, an

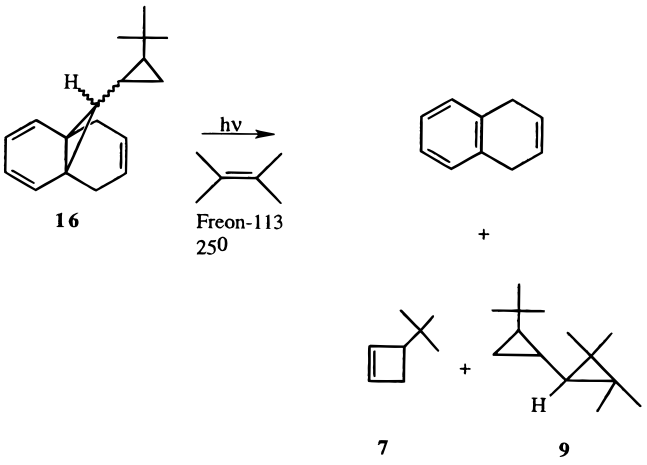


explanation based on conformational isomerism is not necessary to explain our data with carbene **5**. We cannot rule out this mechanism, however, but it requires that the barrier to rearrangement of **5**-anti or the barrier to syn−anti interconversion is smaller than that predicted by theory.[10]

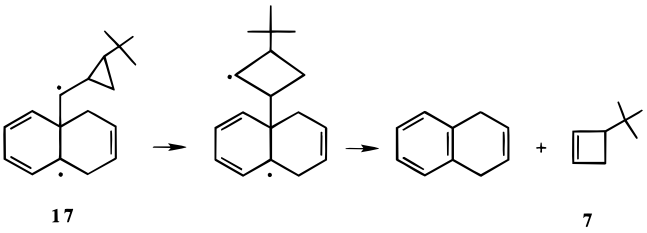
The most economical interpretation is given in Scheme 2. Photolysis of **4** (0, −25 °C) produces an n → π^* excited state which opens to form biradical **15**, a process predicted by theory.[30] Biradical **15** can re-form diazirine **4**, fragment to form carbene **5** (k'_C), undergo a Grob-like fragmentation to form *tert*-butylethylene, acetylene, and nitrogen (k'_F), and undergo carbon−carbon bond migration and cyclobutene formation in concert with nitrogen extrusion (k'_R). Of all the processes available to biradical **15**, the latter reaction is by far the most exothermic. The biradical mechanism can also explain the previously reported data with ethylmethyldiazirine,[21] benzylchlorodiazirine,[25] and cyclobutanylidene.[26]

(30) (a) Bigot, B.; Ponec, R.; Sevin, A.; Devanquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 6573. (b) Müller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* **1985**, *107*, 7275. (c) Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1978**, *116*, 2064.

The mechanism of Scheme 3 predicts that a carbene precursor less prone to rearrangment would increase the ratio of inter- to intramolecular product formation. Accordingly, Jones/Vogel[31] precursor **16** was synthesized.



The ratio of **9**/**7**, at constant concentration of TME is 3−4 times larger with precursor **16**, relative to the ratio of the same products realized with diazirine **4** (Figure 6). Precursor **16** gives more trappable carbene then rearrangement than does diazirine **4**, but it is still not a "perfect" precursor as plots of **9**/**7** versus [TME] are still curved (Figure 6). It is possible that **16** can also open to a biradical (e.g., **17**) and that this species is a "nontrappable" source of **7**.



LFP of **16** does not generate sufficient carbene to produce a pyridine ylide that can be detected. The absolute quantum yield of carbene formation from diazirine **4** is greater than that from precursor **16** even though the diazirine precursor is more prone to rearrangement.

The lifetime of cyclopropylcarbene **5** in alkane solvents and in Freon-113 is approximately 20 ns. Theory predicts that the barrier to interconversion of *syn*- and *anti*-cyclopropylcarbene is rather large. Thus, *syn* and *anti* **5** likely do not interconvert in solution and certainly do not interconvert in the presence of TME.

The growth of ylide **6** can be fit to a single exponential. The kinetics of disappearance of chlorocyclopropylcarbenes are also simple. Given the likelihood of conformational isomerism two explanations are possible; that *syn*- and *anti*-cyclopropylcarbene and -chlorocyclopropylcarbenes (whose decay can be monitored directly at 246 nm)[32] undergo bimolecular reactions with comparable rates or that only the *syn* form is detected and trappable because the *anti* carbene ring expands with great rapidity. Neither explanation is entirely satisfactory. The former interpretation requires coincidences. The latter explanation can be

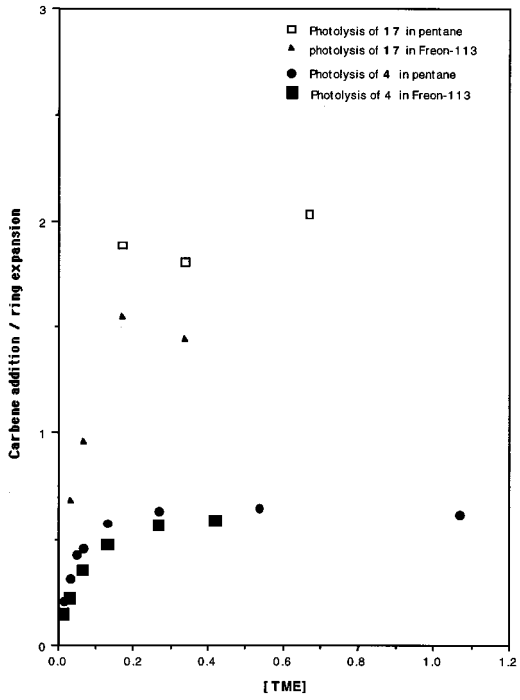


Figure 6. A plot of the ratio of the yield of carbene−TME adduct **9**/cyclobutene **7** using diazirine precursor **4** and non-nitrogenous precursor **15** (□ photolysis of **16** in pentane, △ photolysis of **16** in Freon-113, ○ photolysis of **4** in pentane, ■ photolysis of **4** in Freon-113).

shown to conflict with predicted barriers of carbene rearrangement and/or interconversion.[10] If the activation energy to ring expansion of an *anti*-cyclopropylcarbene is 5 kcal/mol as calculated,[10] and if the preexponential term[8,9] is $10^{8.2-11.1}$ s^{-1}, then the lifetime of an *anti*-cyclopropylcarbene at 25 °C will be between 35 ns and 28 μs, well within the limits of observation and chemical trapping.

IV. Conclusions

Laser flash photolysis (LFP) of *trans*-2-*tert*-butylcyclopropyldiazirine (**4**) produces *trans*-2-*tert*-butylcyclopropylcarbene (**5**). Carbene **5** can be trapped with pyridine to form ylide **6**. The rate of formation of ylide **6** was resolved and found to be linearly dependent on the concentration of pyridine. Upon analysis of the data, the lifetime of carbene **5** was determined to be 22 ns (pentane), 18 ns (acetonitrile and $CF_2ClCFCl_2$), 15 ns (cyclohexane), and 27 ns (cyclohexane-d_{12}). The lifetime of carbene **5** (≤0 °C)in solution is controlled by reaction with solvent. At ambient temperature, carbene **5** is consumed by both reaction with solvent and rearrangement to cyclobutene **7**.

Photolysis of diazirine **4** in Freon-113 ($CF_2ClCFCl_2$) produces 3-*tert*-butylcyclobutene (**7**) and a complex mixture of products derived from reaction of carbene with solvent by chlorine atom abstraction. Photolysis of **4** in the presence of trapping agents (tetramethylethylene, cyclopentene, propylamine, trifluoroethanol) produces adducts with little or no corresponding decrease in the yield of **7**. The most likely interpretation is that cyclobutene **7** is formed by a rearrangement in the excited state of the diazirine (a diazirinyl biradical) and not by a carbenic process at temperatures below 0 °C.

V. Experimental Section

Measurements. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AC-200 NMR spectrometer. Proton spin decoupling spectra

(31) (a) Rautonstrauch, V.; Scholl, H. J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 288. (b) Hartwig, J. F.; Jones, M., Jr.; Moss, R. A.; Tawrynowicz, W. *Tetrahderon Lett.* **1986**, *27*, 5907.

(32) Ho, G.-J.; Krogh-Jesperson, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. S. *J. Am. Chem. Soc.* **1989,** *111*, 6875.

and DEPT spectra were obtained on a Bruker AC 250 NMR spectrometer. Infrared spectra were taken on a Perkin-Elmer 1700 Series FTIR interfaced with a Perkin-Elmer 3700 data station. UV−vis spectra were recorded on a Milton-Roy Spectronic 3000 diode array spectrophotometer. Preparative gas chromatography was performed on a Varian Aerograph-1400 gas chromatograph, using a 5% SP-2100 on a 100/120 Supelco column (6 ft × 1/8 in.). Analytical gas chromatography was performed on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector, using a Supelco fused silica capillary column cross-linked with methyl silicone (i.d. 0.32 mm, length 30 m, film thickness 3 μm). GC/IRD/MSD analyses were performed on a HP-5970B mass spectrometer, 5965A infrared detector connected to a HP-5890 gas chromatograph with a fused silica capillary column cross-linked with 5% phenyl methyl silicone (i.d. 0.25 mm, length 15 m). High-resolution mass spectra were obtained on a VG analytical 70-250S.

Transient spectra were recorded 500 ns after the 351 nm wavelength laser pulse over a window of 500 ns using a EG&G Princeton Allied Research model 1460 optical multichannel analyzer fitted with an EG&G PARC 1304 pulse amplifier, an EG&G PARC 1024 UV detector, and a Jarrell-Ash 1234 grating. The excitation sources available were two excimer lasers, a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 17 ns) and a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 17 ns).

Materials. Freon-113, 2,3-dimethyl-2-butene (tetramethylethylene, TME), and cyclopentene were purified by passing through a neutral alumina column immediately before use. Methanol and acetonitrile were dried by refluxing over calcium hydride followed by distillation. Diethyl ether and tetrahydrofuran were distilled over sodium and benzophenone. Pyridine was distilled over potassium hydroxide. All of the above distillations were performed under nitrogen.

Ethyl *tert*-Butylcyclopropanecarboxylate as a Mixture of Stereoisomers. To a stirred mixture of 3,3-dimethyl-1-butene (8.1 g, 96 mmol) and $CuSO_4$ (1.5 g, 9.4 mmol) was added dropwise a mixture of 3,3-dimethyl-1-butene (6.5 g, 77 mmol) and ethyl diazoacetate (20.2 g, 175 mmol). After the addition was complete, the mixture was refluxed for 30 min. The mixture was then cooled to room temperature and filtered through a sintered glass funnel. The filter cake was washed with ether (100 mL). The combined organic layers were washed successively with 5% HCl solution, 10% $NaHCO_3$, and brine. After the organic layers were dried over anhydrous $MgSO_4$, the ether was removed with a rotary evaporator. Distillation under reduced pressure (70 °C/13 mmHg) gave the ester as two stereoisomers (trans:cis = 3:1) (8.7 g, 30%). ^{1}H NMR ($CDCl_3$) trans isomer: δ ppm 4.05 (q, 2H), 1.48 (m, 1H), 1.24 (t, 3H), 1.20 (m, 1H), 1.00 (m, 1H), 0.85 (s, 9H), 0.75(m, 1H). ^{1}H NMR ($CDCl_3$) cis isomer: δ ppm 4.20 (q, 2H), 1.48 (m, 1H), 1.28 (t, 3H), 1.20 (m, 1H), 1.00 (m, 1H), 0.90 (s, 9H), 0.75 (m, 1H). ^{13}C NMR ($CDCl_3$) mixture of two stereoisomers: δ ppm 174.91, 60.26, 34.08, 29.50, 29.45, 28.07, 16.39, 14.23, 11.59. HRMS: calcd for $C_{10}H_{18}O_2$ (M^+), 170.1307; found, 170.1302.

***trans-tert*-Butylcyclopropanecarboxylic Acid.** To anhydrous ethanol (30 mL) was added potassium (0.23 g, 5.9 mmol) in several portions. After the metal was dissolved, the stereoisomeric mixture of ethyl 2-*tert*-butylcyclopropanecarboxylate (1.0 g, 5.9 mmol) was added to the solution, and the reaction mixture was refluxed under argon for 2 days. Water (10 mL) was added to the reaction mixture, and refluxing was continued for another 3 h. The reaction mixture was cooled in an ice bath and made acidic with concentrated HCl. The crude products were extracted into ether (50 mL × 3). The ether was evaporated *in vacuo*, and an NaOH solution (5%, 100 mL) was added to the residue. After the resulting solution was washed with ether (3 × 50 mL), the aqueous layer was made acidic with 3 M HCl and extracted with petroleum ether (3 × 50 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the trans acid (0.42 g, 50%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.45 (m, 1H), 1.42 (m, 1H), 1.12 (m, 1H), 0.95 (m, 1H), 0.88 (s, 9H). ^{13}C NMR ($CDCl_3$): δ ppm 181.35, 35.09, 29.55, 27.98, 16.29, 12.40. HRMS: calcd for $C_8H_{15}O_2$ (MH^+), 143.1072; found, 143.1066.

***trans-tert*-Butylcyclopropylmethanol**. To a stirred mixture of $LiAlH_4$ (0.33 g, 8.68 mmol) in dry ether (25 mL) was added slowly a solution of *trans-tert*-butylcyclopropylcarboxylic acid (0.41 g, 2.89 mmol) in ether (10 mL). After the addition, the reaction mixture was refluxed gently for 3 h. Methanol was added slowly to quench the excess of $LiAlH_4$. The reaction mixture was then poured into HCl solution (1.0 M, 50 mL) cooled in an ice bath. The ethereal layer was separated, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo to give the alcohol (0.36 g, 97%) as a viscous oil. ^{1}H NMR ($CDCl_3$): δ ppm 3.30 (d, 2H), 2.05 (b, 1H), 0.85 (m, 1H), 0.75 (s, 9H), 0.40 (m, 1H), 0.37 (m, 1H), 0.11 (m, 1H). ^{13}C NMR ($CDCl_3$): δ ppm 67.50, 30.51, 29.12, 28.42, 17.06, 6.05. HRMS: calcd for $C_8H_{15}O$ ($M^+ - H$), 127.1123; found, 127.1126.

***trans-tert*-Butylcyclopropanecarboxaldehyde.** To oxalyl chloride (0.57 g, 4.5 mmol) in methylene chloride (15 mL) solution was added dropwise dimethyl sulfoxide (0.78 g,10 mmol) in methylene chloride (3 mL) while the temperature was maintained below −60 °C. The reaction mixture was stirred for another 15 min before adding *trans-tert*-butylcyclopropylmethanol (0.49 g, 3.8 mmol). Stirring was continued for 45 min, and triethylamine (1.62 g, 16 mmol) was then added to the reaction mixture. The resulting mixture was allowed to warm to room temperature before water (15 mL) was added. The methylene chloride layer was separated, and the aqueous layer was extracted with methylene chloride (3 × 30 mL). The combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated. The residue was taken up in $NaHSO_3$ solution and washed with chloroform to remove any unreacted alcohol. The aqueous solution was then neutralized by 2 M NaOH solution. The aldehyde was extracted by chloroform (3 × 30 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give the aldehyde (0.44 g, 92%). ^{1}H NMR ($CDCl_3$): δ ppm 8.91 (d, 1H), 1.71 (m, 1H), 1.38 (m, 1H), 1.11 (m, 1H), 0.98 (m, 1H), 0.80 (s, 9H). ^{13}C NMR ($CDCl_3$): δ ppm 201.37, 33.84, 29.58, 28.10, 26.75, 10.91. HRMS: calcd for $C_8H_{14}O$ (M^+), 126.1045; found, 126.1048.

***trans*-3-(2-*tert*-Butylcyclopropyl)-3*H*-diazirine (4).** A solution of ammonia (5 mL) in methanol (8 mL) was cooled to −70 °C in a dry ice/acetone bath. To this stirred mixture was added dropwise *tert*-BuOCl (2.2 g, 20 mmol) in methanol (5 mL). The temperature was kept below −60 °C. After the addition, the reaction mixture was stirred at −60 to −50 °C for 30 min. 2-*tert*-Butylcyclopropane-carboxaldehyde (0.44 g, 3.5 mmol) in 10 mL of methanol was then added to the reaction mixture over 10 min. The reaction mixture was stirred at −50 to −40 °C for 2 h, −40 to −30 °C for 3 h, and then allowed to warm to room temperature. The resulting mixture was filtered, and the filter cake was washed with methanol. The filtrate and the methanol washes were combined and evaporated to dryness in vacuo. The white solid powder, which contained the diaziridine and inorganic salt, was dissolved in water (15 mL) and cooled below 5 °C in an ice bath. Pentane (20 mL) was added to the aqueous solution. To the stirred mixture was added $KMnO_4$ (0.56 g, 3.5 mmol) in NaOH solution (1.0 M, 15 mL). The mixture was stirred in the dark for 30 min before $NaHSO_3$ (3.0 g, 2.8 mmol) in water (10 mL) was added to the reaction mixture to react with the excess of $KMnO_4$. The two layers were separated, and the aqueous layer was extracted with pentane (50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was loaded onto a chromatography column with alumina gel and eluted with pentane to give diazirine **4** (100 mg, 20%). ^{1}H NMR ($CDCl_3$): δ 0.95 (d, 1H), 0.78 (s, 9H), 0.60 (m, 1H), 0.50 (m, 1H), 0.38 (m, 1H), 0.25 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 29.03, 28.39, 28.00, 22.68, 13.12, 5.97. MS *m/e* 110 ($M^+ - N_2$).

1-Bromo-2-*tert*-butylcyclopropane. 1-Bromo-2-*tert*-butylcyclopropane was prepared according to the procedure described in the literature with slight modification.[33] Lithium aluminum hydride was used as a reducing reagent instead of tri-*n*-butyltin hydride. 1,1-Dibromo-2-*tert*-butylcyclopropane[33] (5.86 g, 22.9 mmol) in ether (5 mL) was added

(33) Sliwinski; W. F.; Su, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 145.

dropwise to a suspension of $LiAlH_4$ in anhydrous ether (25 mL). Themixture was stirred at room temperature for 24 h. Methanol (2 mL) was added to the mixture to quench the excess of $LiAlH_4$. The reaction mixture was poured into ice cold 5% H_2SO_4 solution. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Fractional distillation through a short Vigreux column gave 1-bromo-2-*tert*-butylcyclopropane (2.5 g, 60%). MS: *m*/*e* 176, 178, M^+, $M^+ + 2$ 176, 178.

11-*tert*-Butylcyclopropyl-11*H*-tricyclo[4.4.1.0^{1,6}]undeca-2,4,8-triene (16). 1-Bromo-2-*tert*-butylcyclopropane (2.2 g, 12.4 mmol) in 5 mL diethyl ether was added to a stirred suspension of chopped lithium (0.18 g, 26 mmol) in anhydrous ether (15 mL) at 0 °C. The mixture was stirred at 0 °C for 45 min. The gray reaction mixture containing alkyllithium was then added to a stirred suspension of CuI (1.2 g, 6.2 mmol) in anhydrous ether (25 mL) over 30 min under argon. The internal temperature was kept below −60 °C during addition by cooling the flask in a dry ice/acetone bath. The mixture was allowed to stir for 45 min at −70 °C, and a solution of 11,11-dibromotricyclo[4.4.1.0^{1,6}]-undeca-2,4,8-triene[31b] (0.45 g,1.4 mmol) in THF (10 mL) was added dropwise over 30 min. The temperature of reaction mixture was kept below −65 °C during the addition. The resulting mixture was allowed to stir for another hour at −70 °C and then allowed to warm to room temperature. Methanol (2 mL) was added, and the reaction mixture was poured into ice water (30 mL). The residue was washed with ether (20 mL), and the combined ether layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product mixture was separated by column chromatography to give **16** (0.17 g, 50%). It was further purified by preparative TLC. MS: *m*/*e* 240, M^+ 240. ^{1}H NMR ($CDCl_3$): δ ppm 6.10, 5.90 (m, 4H, diene-H), 5.45 (m, 2H, alkenyl H), 2.80, 2.70, 2.25, 2.15 (m, 4H, allyl H), 0.65 (s, 9H, *tert*-butyl H), 0.40, 0.15, −0.10 (m, 4H, cyclopropyl H). ^{13}C NMR ($CDCl_3$): δ ppm 128.55, 123.00, 121.37, 32.12, 30.08, 29.47, 28.55, 24.10, 21.01, 20.05, 7.74. HRMS: calcd for $C_{18}H_{24}$ (M^+), 240.1879; found, 240.1879.

Product Studies. Stock solutions of **4** (10 mM) were purified by column chromatography before usage. To the Pyrex tubes were added 250 μL stock solution and the requisite quantity of carbene trapping reagents. All tubes were then degassed using the freeze−pump−thaw method and sealed under vacuum with a torch. The tubes were then submerged in the water bath at desired temperature and subjected to photolysis or pyrolysis. Photolysis was performed in a Rayonet photoreactor fitted with 350 nm UV bulbs. Pyrolysis was accomplished by heating the sealed tubes in a boiling water bath for 30 min. The tubes were then opened, and the resulting solutions were analyzed by analytical GC.

Characterization of Products Derived from Decomposition of Diazirine 4 in the Presence of Various Carbene Quenchers. When diazirine **4** was photolyzed in the presence of TME, the major products are cyclobutene **7**, TME addition product **9**, and *tert*-butylethylene (**8**). Compounds **7** and **9** were separated by preparatory GC and characterized by NMR and GC-MS. Data for **9**: ^{1}H NMR ($CDCl_3$) δ ppm 0.98 (s, 12 H, 4 methyl Hs), 0.7I (s, 9H, *tert*-butyl Hs), 0.48 (m, 1H), 0.35 (m, 1H), 0.22 (m, 1H), 0.09 (m, 1H), −0.42 (d, 1H); ^{1}H decoupling NMR revealed that δ 0.48, 0.35, 0.22, 0.09 are the protons on *tert*-butyl-substituted cyclopropyl ring and δ 0.42 is the proton on tetramethyl-substituted cyclopropyl ring; ^{13}C NMR ($CDCl_3$) δ ppm 38.88, 30.39, 29.66, 28.59, 23.66, 20.87, 17.76, 17.46, 9.81, 7.77; MS *m*/*e* (rel intensity) M^+ 194 (8.0), 137 (16), 109 (100), 95 (46), 81 (40), 57 (50). Data for **7**: ^{1}H NMR ($CDCl_3$) δ ppm 6.05 (m, 1H), 5.98 (m, 1H), 2.63 (m, 1H), 2.36 (d, m, 1H), 2.18 (d, m, 1H), 0.85 (s, 9H); ^{13}C NMR ($CDCl_3$) δ ppm 138.91, 135.65, 55.03, 31.98, 31.17, 26.48; MS *m*/*e* (rel intensity) M^+ 110 (35), 95 (100), 67 (68), 55 (38). Compound **8** was identified by comparison with an authentic sample (purchased from Aldrich Chemical Co.).

When diazirine **4** was photolyzed in the presence of cyclopentene, in addition to cyclobutene **7** and alkene **8**, addition products to cyclopentene were also formed as a pair of stereoisomers. ^{1}H NMR of the adduct revealed that there are no olefinic protons at δ 5.7 ppm. Thus, the carbene does not insert into the allylic C−H bond. Two sharp singlets at δ 0.75 and 0.70 ppm correspond to *tert*-butyl protons. Several multiplets δ ranging from 0.5 to −0.1 ppm correspond to hydrogens on the two cyclopropyl rings. MS stereoisomer **8a**: *m*/*e* (rel intensity) M^+ 178 (1.0), 163 (1.2), 135 (6.0), 108 (32), 93 (100), 79 (67), 67 (61), 41 (63). MS stereoisomer **8b**: *m*/*e* (rel intensity) M^+ 178 (0.5), 163 (1.0), 135 (5.0), 108 (31), 93 (100), 79 (70), 67 (61), 41 (66).

When diazirine **4** was photolyzed in the presence of *n*-propylamine, in addition to cyclobutene **7** and alkene **8**, an adduct of carbene **5** with the amine was also formed. MS: *m*/*e* (rel intensity) M^+ 169 (4.2), 140 (61), 111 (15), 98 (15), 69 (100), 55 (58), 41 (75). Its structure was confirmed by comparison with an authentic sample prepared by reductive amination of the *trans*-*tert*-butylcyclopropanecarboxyaldehyde according to a procedure reported in the literature.[34]

When diazirine **4** was photolyzed in the presence of trifluoroethanol, in addition to cyclobutene **7** and alkene **8**, an adduct of carbene **5** with the alcohol was also formed. The adduct was separated by preparatory GC and characterized by ^{1}H and ^{13}C NMR and GC-MS. ^{1}H NMR ($CDCl_3$): δ ppm 3.72 (q, 2H), 3.38 (d, m, 2H), 0.95 (m, 1H), 0.79 (s, 9H), 0.52 (m, 2H), 0.36 (m, 1H). ^{13}C NMR ($CDCl_3$): δ ppm 68.424, 67.882, 67.340, 29.550, 29.208, 28.923, 28.309, 26.482, 13.582, 6.446. MS: *m*/*e* (rel intensity) M^+ 210 (1.5), 153 (3.6), 139 (6.1), 113 (8.3), 95 (17), 70 (100), 55 (64).

Laser Flash Photolysis.[16] In the laser flash photolysis (LFP) experiments, two types of laser sources were used. In those experiments where optical yields were measured, a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 17 ns) or a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 17 ns) was used. The laser intensity of the two XeF excimer lasers remained stable for a period of several hours and met the experimental requirement of constant laser output. Direct time-resolved LFP experiments were performed with a 150 ps pulse laser generated from a Continuum PY62C-10 Nd:YAG laser (355 nm, 30 mJ, 0.15 ns).

Two kinds of sample cells were used. For the experiments using XeF excimer laser, the cells were made from square quartz tubing purchased from Vitro Dynamics. The length of the cuvettes was 1 cm, and the middle part of the cuvettes where the light passed was close to square-shaped. For the experiments using Nd:YAG laser, a Suprasil quartz flurorescence-free static cell was purchased from Scientific Products. An almost perfectly flat surface of this type of quartz cell results in the minimum scattering of incident laser beam.

Stock solutions of photolabile carbene precursors were prepared immediately before LFP experiment. Absorbances of all diazirine samples used in kinetic studies were close to 1.0 at the wavelength of laser radiation. Laser samples were placed in the appropriate cuvettes fitted with rubber septum or Teflon stopcock, deaerated by bubbling argon for 2−3 min or the freeze−pump−thaw method (3 cycles). Each of the sample cells with varying amounts of pyridine was then irradiated with a laser pulse. The shutter was opened a few milliseconds before the laser pulse to allow the monitoring light beam to pass the sample at a right angle of laser light. The monitoring light was generated from a 150 W Xe arc lamp fitted with an aspherab beam columinator, and it could be pulsed to temporarily increase brightness. After passing through the sample, the monitoring beam was focused on the slit of an Oriel 77200 monochromator, selected for the wavelength of interest, with both front and rear slits set between 0.2 and 0.5 mm depending on the intensity of signal. Signals were obtained with an IP 28 photomultiplier tube detector and were digitized by a Tektronix 7912 A/D transient digitizer. The entire apparatus is controlled by an Macintosh Iix computer which was also used for data storage. The analyses of the data were performed using a program based on the Marquad Algorithm or Igor (designed by Wavemetrics).

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Supporting Information Available: Transient spectrum of ylide **6** and the rate of its formation along with plots of the ratio of yields of (carbene adduct/cyclobutene) and tables of the distribution of products formed on decomposition of **4** under various conditions (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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