

# Equilibrium between Homocub-1(9)-ene and Homocub-9-ylidene<sup>1</sup>

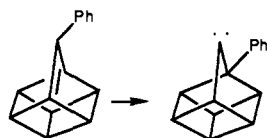
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**Abstract:** A combination of chemical trapping and laser flash photolysis experiments is used to demonstrate that homocub-9-ylidene and homocub-1(9)-ene are in equilibrium. The equilibrium constant can be shown to be close to unity at +20 °C ( $0.23 \leq K \leq 4$ ).

## Introduction

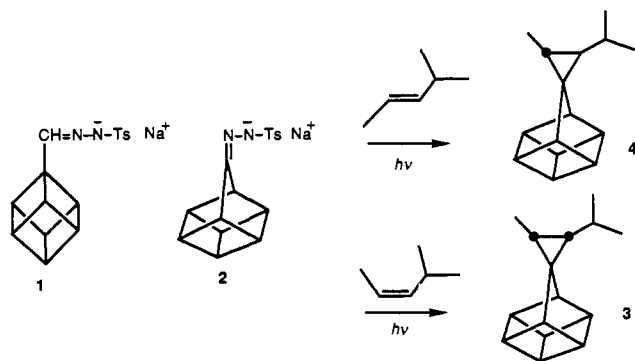
Insertions into adjacent carbon-hydrogen and carbon-carbon bonds are reactions characteristic of singlet alkyl- and dialkyl-carbenes.<sup>3</sup> In simple systems the great exothermicity of these reactions makes them irreversible under normal conditions. One successful strategy for initiating the reverse reaction is irradiation with short-wavelength, high-energy ultraviolet light. This produces a carbene that can be trapped by conventional intramolecular reactions.<sup>4</sup> Another approach is the construction of highly strained alkenes for which the reversion to the divalent state is energetically possible.<sup>5</sup> An example of this approach is the work of Eaton and Hoffmann in which 9-phenyl-1(9)-homocubene appeared to revert to the related carbene, 1-phenyl-9-homocubylidene.<sup>6</sup>



In this paper we describe our work on the related parent system. We show that the bridgehead alkene and carbene are interconverting, and we are able to estimate the value of the equilibrium constant. In the course of our description a diazo compound masquerading as a carbene will appear, as will a new, hydrocarbon source of divalent carbon.

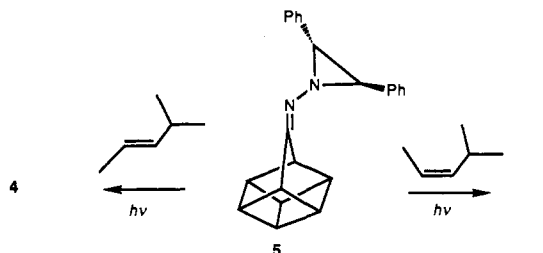
## Results and Discussion

We originally hoped to use thermal decompositions of tosylhydrazone salts **1** and **2** to produce carbenes. Although we found that photolysis of heterogeneous mixtures of **2** in *cis*- or *trans*-4-methyl-2-pentene led in each case to a single, different product, **3** or **4**, decompositions of both **1** and **2** inevitably led to substantial amounts of sulfur-containing compounds.<sup>7</sup>



Luckily, we were alerted<sup>8</sup> to the work of Eschenmoser on the thermal decompositions of aziridylimines.<sup>9</sup> We reckoned that photochemical activation might be effective as well and were pleased to find that photolysis of **5** in *cis*- or *trans*-4-methyl-2-

pentene led to the same cyclopropanes as had the tosylhydrazone salt, **2**.



Proof of stereochemistry rests on spectroscopic experiments which allowed us to determine the coupling constant between the two cyclopropyl hydrogens in **3** and **4** (**3**,  $J = 8.4$  Hz; **4**,  $J = 5.3$  Hz). By way of comparison, the *cis* and *trans* coupling constants in cyclopropane itself are 9.0 and 5.6 Hz, respectively.<sup>10</sup> There is no detectable amount of the "wrong" stereoisomer. This observation agrees with the results of Eaton and Hoffmann<sup>6</sup> and with the earlier report of Moss and Dolling that 7-norbornylidene added stereospecifically to the 4-methyl-2-pentenes.<sup>11</sup> At this point a reasonable person might be pardoned for assuming nothing more than a simple, garden-variety addition of the carbene **6** to an alkene. However, this is not the case, and the apparent simplicity of this reaction hides a deeper, more complex process.

For years, carbene chemists have sporadically worried about precursor chemistry. Could the diazo compounds (and related species) they traditionally used as sources of carbenes be re-

(1) It gives us the greatest pleasure to dedicate this paper to Prof. Dr. W. Kirmse on the occasion of his 60th birthday. This work was supported both at Ohio State (CHE-881950) and Princeton (CHE-8800448) by the National Science Foundation. The authors are indebted to Prof. J. C. Sciano for his advice regarding the kinetics presented in Appendix 2. Preliminary work has been previously published. (a) Chen, N.; Jones, M., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305. (b) Chen, N.; Jones, M., Jr. *Tetrahedron Lett.* **1989**, *30*, 6969. (c) White, W. R.; Platz, M. S.; Chen, N.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 7794.

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(7) Erker, G. E.; Kammula, S. L. Unpublished work.

(8) Our thanks go to Professor A. Dreiding for alerting us to the possibilities of this precursor for carbenes. Fefor, Norway, September 1987.

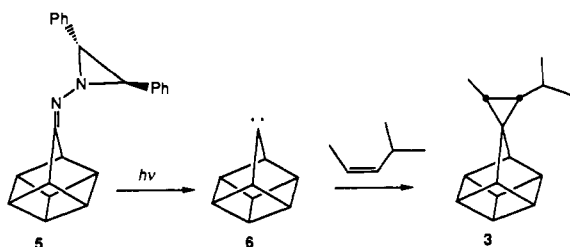
(9) Felix, D.; Wintner, C.; Eschenmoser, A. *Org. Synth.* **1976**, *55*, 52. Müller, R. K.; Joos, R.; Felix, D.; Schreiber, J.; Wintner, C.; Eschenmoser, A. *Org. Synth.* **1976**, *55*, 114. Felix, D.; Müller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 1276.

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(11) Moss, R. A.; Dolling, U.-H. *Tetrahedron Lett.* **1972**, 5117.

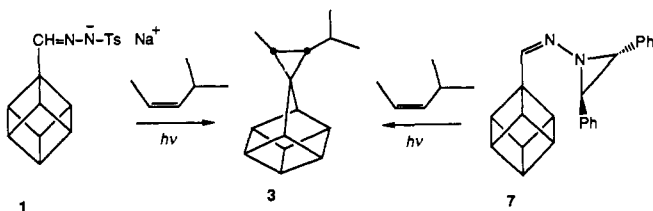
<sup>†</sup> Princeton.

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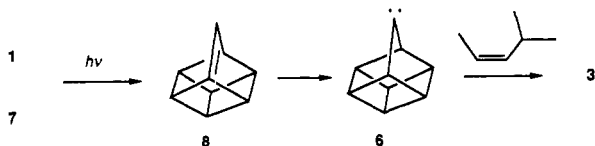


sponsible for some (or all) of the observed "carbene" chemistry?<sup>12</sup> Intramolecular chemistry might be particularly bedeviled by such reactions, in which diazo compounds played the roles traditionally assigned to carbenes. Chang and Shechter collated earlier work and provided new examples which showed that thermal and photochemical decompositions of simple diazo compounds and diazirines led to distinctly different ratios of the products of intramolecular rearrangement. Thermal reactions were far more selective than photochemical decompositions.<sup>13</sup> Similar results have been reported for intermolecular reactions.<sup>14</sup> Certainly **2** and **5** are prime candidates for intramolecular, Wolff-like reactions as the homocubyl skeleton is notorious for its ease of rearrangement.<sup>15</sup>

It became clear that something out of the ordinary was happening when we found that photolysis of **1** or **7** in *cis*-4-methyl-2-pentene led to the same product, **3**, as formed from **2** or **5**. Similar results have been observed by Eaton and Hoffmann in the phenyl-substituted series.<sup>6</sup>



Homocubylidene **6** must be involved in decompositions of both the cubyl precursors (**1** and **7**) and the homocubyl species (**2** and **5**). This was originally held to imply direct ring expansion to the bridgehead alkene **8** and subsequent rearrangement to the carbene **6**. The ring expansion is an unexceptional reaction<sup>16</sup> and the formation of the carbene from the strained alkene has precedent.<sup>5</sup> In the phenyl series, Eaton and White have shown that this ring expansion takes place through migration of a cage carbon-carbon bond, not by phenyl shift.<sup>16a</sup>



The picture for the homocubyl compounds **2** and **5** is less clear. In principle, the reaction might be as simple as it appears on the surface: a straightforward decomposition to a carbene followed by an even more straightforward addition to an alkene. However, the results in the cubyl case (as well as good advice<sup>12</sup>) made us consider carefully the possibility that the route to cyclopropanes was more circuitous. Reaction could be through initial ring

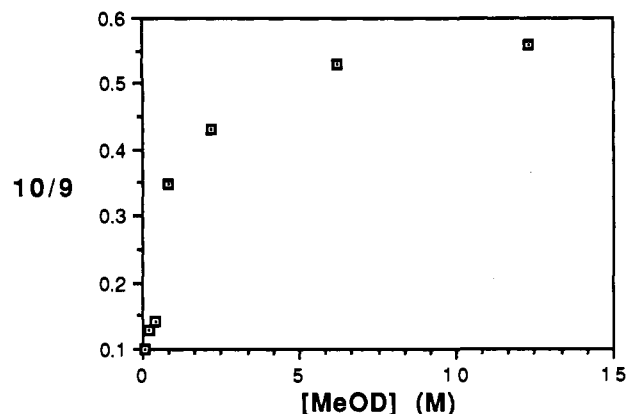
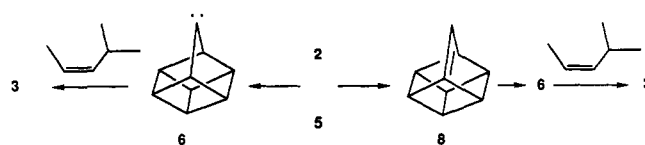
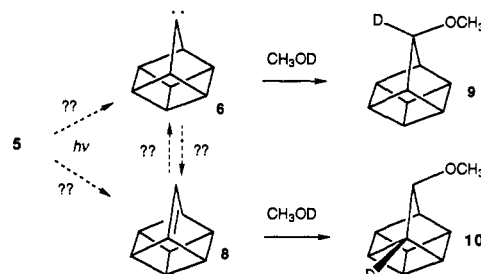


Figure 1. The relative amounts of **10** and **9** produced by photolysis of **5** in the presence of  $\text{CH}_3\text{OD}$ .

expansion to bridgehead alkene **8** which only *subsequently* forms carbene **6**, as in the cubyl case.



Irradiation of **5** in  $\text{CH}_3\text{OD}$ /benzene leads to the methanol-trapped products of *both* **6** and **8**, but this result does not identify which of the two intermediates is formed first. Carbene product **9** is easily identified from  $^1\text{H}$  and  $^2\text{H}$  NMR spectra, and **10** was synthesized through a sequence starting from the ethylene ketal of 1-bromohomocuban-9-one. Quantitative analysis of the products was most easily done with the  $^2\text{H}$  NMR signals (**9**,  $\delta = 3.94$ ; **10**,  $\delta = 3.28$ ).



At this point it is possible that either pure **6** or **8** is produced initially, only to form the other, or even that a mixture of **6** and **8** is formed. If only a single reactive intermediate is formed, then either the carbene forms the alkene or the alkene reverts to the carbene. A distinction between these last two scenarios was made by examining the dependence of the **10/9** ratio on the concentration of  $\text{CH}_3\text{OD}$ . If carbene **6** is the first formed intermediate, **9** should increase as  $[\text{CH}_3\text{OD}]$  increases, and conversely, if alkene **8** is the initial intermediate, it should be the percentage of **10** that grows as  $[\text{CH}_3\text{OD}]$  increases. In the event, it is the latter situation that obtains (Figure 1). Ring expansion to **8** must be the dominant reaction when **5** is photolyzed. Notice that Figure 1 shows a nonlinear relationship between  $[\text{CH}_3\text{OD}]$  and **10/9**. Other precursors will show the expected linear relationship (vide infra), and we will later attempt to explain the curved plot of Figure 1. These results are also consistent with the initial formation of a mixture of both **6** and **8**, as long as this mixture is enriched in **8**, relative to the equilibrium value.

Now we know that the bridgehead alkene forms the carbene, but does the conventional reaction, the rearrangement of the carbene to the alkene, take place? If it does, **6** and **8** become the first example of an interconverting carbene-bridgehead alkene pair. Nothing in the data so far requires that the two species, **6** and **8**, be in equilibrium, only that one be formed from the other.

To probe this question an unimpeachable source of the carbene is needed. Obviously, no conventional nitrogenous source will do,

(12) We thank Professor P. E. Eaton for pressing this point upon us.

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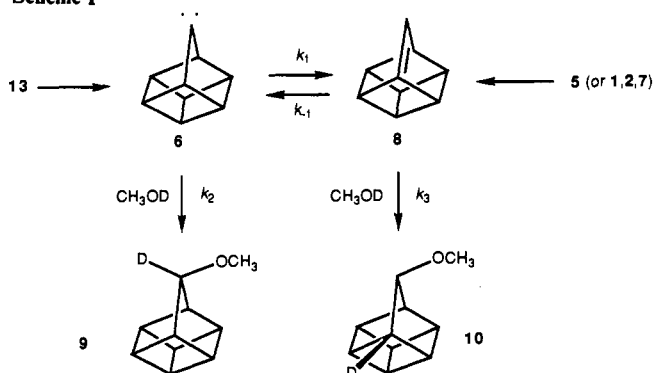
(14) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516.

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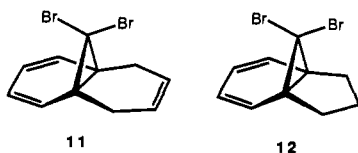
(16) (a) Eaton, P. E.; White, A. J. *J. Org. Chem.* **1990**, *55*, 1321. (b) Sellers, S. F.; Klebach, Th. C.; Hollowood, F.; Jones, M., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 5492 and references therein.

(17) Chen, N. Unpublished work. N.C. thanks Prof. J. E. Jackson for helpful discussions concerning the properties of **15**.

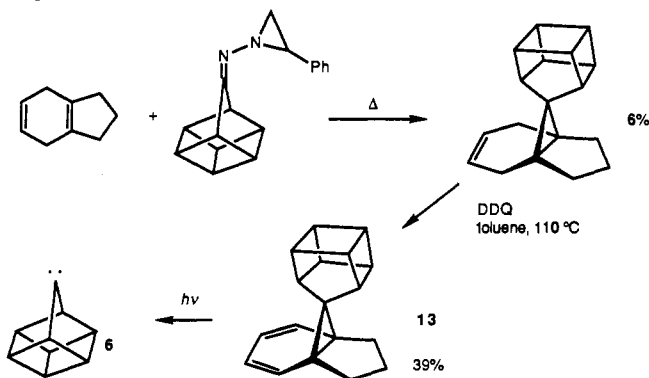
Scheme I



as such precursors are all too likely to lead to ring expansion to 8. Some years ago we adapted work of Vogel and his co-workers<sup>18</sup> ultimately to produce 11 and 12 as efficient photochemical precursors of dihalocarbenes.<sup>19</sup> We used a similar synthesis to



produce 13, a potential source of carbene 6. Unlike hydrolysis of haloforms which leads to intermediates highly selective for the tetrasubstituted double bond of dihydroindan, decomposition of a monophenyl derivative of 5 in this hydrocarbon led mostly (>80%) to addition to the less substituted, but also less encumbered, double bond on the periphery of the molecule. Only a 6% yield of the useful adduct was realized. Nevertheless, this route sufficed to produce enough 13 for the appropriate mechanistic experiments.



Irradiation of 13 in  $\text{CH}_3\text{OD}$ /benzene gives both 9 and 10. If 13 gives only 6, we immediately know that the carbene and the bridgehead alkene are interconverting as shown in Scheme I. If carbene 6 really is the first-formed intermediate we would anticipate that, unlike the earlier experiment with 5, it should be the carbene adduct 9 that increases as the concentration of  $\text{CH}_3\text{OD}$  increases. And so it is, as Figure 2 shows.<sup>1</sup> However, we shall soon show that the assumption that 6 is cleanly produced from 13 is unnecessary. Recently, Eaton and Appell have used a carbon-labeling experiment to show that these two species are interconverting.<sup>20</sup> A legitimate concern in all these reactions in methanol is the question of protonation to give the degenerate 9-homocubyl cation.<sup>15</sup> Might the observed formation of both 9 and 10 be merely the result of one stage in this process? We think not, for two reasons. First, <sup>2</sup>H NMR spectroscopy would easily

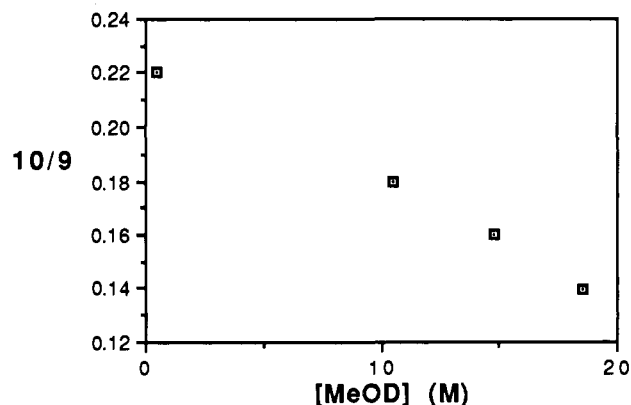
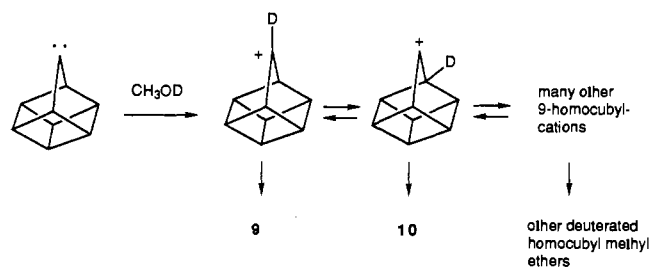


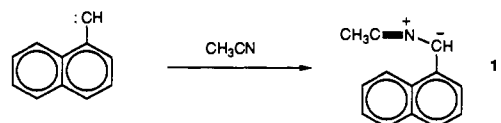
Figure 2. The relative amounts of 10 and 9 produced by photolysis of 13 in the presence of  $\text{CH}_3\text{OD}$ .

be able to detect the products of further rearrangement, and none are seen. Second, we find different ratios of 10/9 from the three precursors, 5, 13, and the diazine 15. Were a common intermediate carbocation involved, this should not be the case. Even if protonation of a diazo compound were the source of the cation, 5 and 15 should give the same ratio.



It now remains to determine the equilibrium constant relating the two reactive intermediates. The kinetic scheme is as shown in Scheme I. Our plan was to use laser flash photolysis (LFP) to determine some of the absolute rate constants of Scheme I and to combine this information with conventionally determined relative rate ratios to arrive at an estimate for  $K = k_1/k_{-1}$ .

In the past decade the dynamics of carbene processes have been intensively monitored by LFP techniques.<sup>21</sup> Early work concentrated on arylcarbenes so as to take advantage of the aromatic chromophore for ultraviolet/visible (UV-vis) detection of the reactive intermediate.<sup>22</sup> However, it was quickly realized that reactions of arylcarbenes that produce ylides gave species whose spectral properties were far better suited to the LFP detection than were those of the carbene itself.<sup>23</sup> For example, the dynamics of 1-naphthylcarbene were much more easily obtained by monitoring the formation of nitrile ylide 14 than by the disappearance of the carbene itself.<sup>23,24</sup>



Reactions of carbenes with acetonitrile are generally slow processes. Indeed, carbenes such as diphenylcarbene or chloro-

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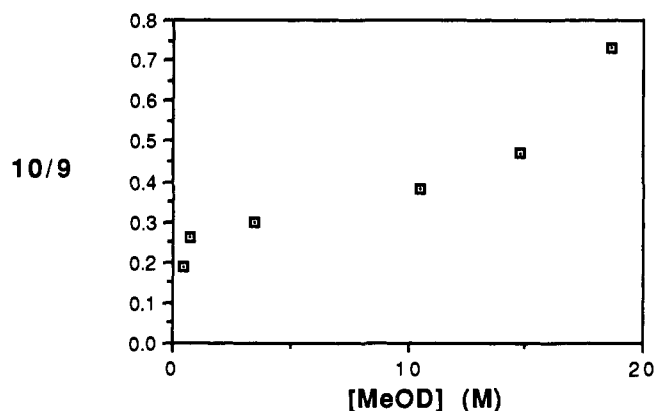
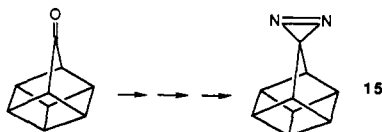


Figure 3. The relative amounts of 10 and 9 produced by photolysis of 15 in the presence of  $\text{CH}_3\text{OD}$ .

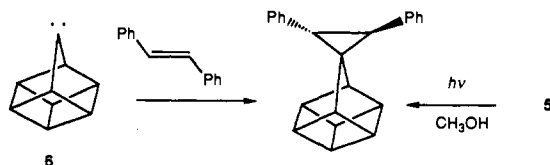
phenylcarbene are not sufficiently reactive at 298 K to form ylides.<sup>25</sup> These reluctant carbenes can be visualized through reaction with pyridine to form ylides whose UV-vis absorption maxima are longer lived, more intense, and red-shifted relative to those of nitrile ylides. This combination of high reactivity, favorable spectroscopic properties, and long ylide lifetime has allowed the study of the dynamics of several hitherto invisible carbenes (benzylchlorocarbene, *tert*-butylchlorocarbene, chlorocyclopropylcarbene, and adamantylidene are examples) by LFP.<sup>23,26</sup>

Neither 2 nor 5 lent itself to laser flash photolysis work, and so we synthesized diazirine 15 from homocuban-9-one by conventional techniques. (Caution! Compound 15 is explosive and must be treated with the utmost care.<sup>17</sup>)



We first had to be certain that 15 recapitulated the properties of the other nitrogenous homocubyl precursors. This turned out to be the case, as photolysis of 15 in  $\text{CH}_3\text{OD}$ /benzene gave results generally resembling those from 5, although the linear relationship of Figure 3, obtained from 15, was absent when 5 was photolyzed (Figure 3; see also Figure 1).

We must now address briefly the question of why linear plots are obtained from both 13 and 15 but not from 5 (see Figures 1, 2, and 3). It appears that "intramolecular" stilbene, formed within the same solvent shell as 6, has a substantial kinetic advantage in the interception of the carbene over the intermolecular trapping agent methanol, at least at relatively low concentrations of methanol (0.5–2.0 M). Homocubylidene adds to stilbene to give the normal cyclopropane adduct. This compound can also be found on photolysis of 5 in methanol and is especially prominent when the concentration of methanol is low. Formation of the product of addition of 6 to stilbene complicates photolyses of 5 but not, of course, those of 13 or 15.



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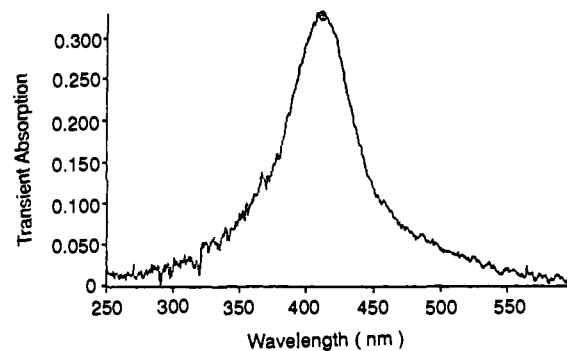


Figure 4. The transient spectrum of ylide 16a produced by LFP of diazirine 15 in  $\text{CH}_2\text{Cl}_2$  in the presence of pyridine.

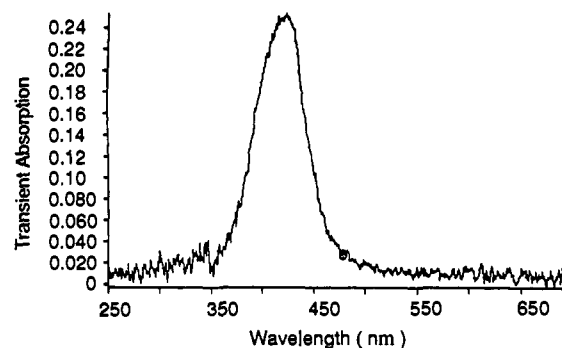


Figure 5. The transient spectrum of ylide 16b produced by LFP of diazirine 15 in  $\text{CH}_2\text{Cl}_2$  in the presence of *p*-cyanopyridine.

Figures 1, 2, and 3 demonstrate that photolyses of precursors 5, 13, and 15 in neat  $\text{CH}_3\text{OD}$  produce different initial mixtures of carbene 6 and bridgehead alkene 8. If 6 and 8 are immediately trapped by solvent, the ratio of adducts 10/9 gives a snapshot of the initial mixture of intermediates formed after photolysis of a given precursor. However, upon dilution of  $\text{CH}_3\text{OD}$ , the initial mixture of reactive intermediates has time to relax to equilibrium. Comparison of Figures 1, 2, and 3 reveals that below a  $\text{CH}_3\text{OD}$  concentration of 1 M, 10/9 converges to the value of ca. 0.2. Thus, an equilibrium mixture of 6 and 8 can be reached starting from three different initial mixtures.

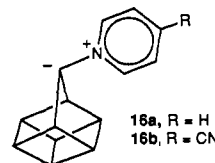
The ratio 10/9 can be related to the equilibrium constant  $K$  as in eqs 1 and 2.

$$0.2 = 10/9 = (8/6)(k_3/k_2) = (k_3/k_2)K \quad (1)$$

or

$$K = 0.2(k_2/k_3) \quad (2)$$

Laser flash photolysis of 15 in the presence of acetone or acetonitrile yields no spectra attributable to ylides, but irradiation in the presence of pyridine or *p*-cyanopyridine produces the transient spectra of Figures 4 and 5. These transients are not observed in the absence of pyridines and we attribute them to ylides 16a and 16b.



This assignment is strengthened by the similarity of the spectrum to the spectra of ylides derived from other carbenes (Table I) and is further supported by the observation that LFP of 15 in the presence of carbene scavengers such as  $\text{CH}_3\text{OD}$  or alkenes lowers the yield of 16a (vide infra). Decomposition of 15 in a mixture of tetramethylethylene and  $\text{CH}_3\text{OD}$  leads to cyclopropane 17 and the products of reaction of 6 and 8 with methanol, 9 and 10. From these data we can extract the relative rates of reaction of 6 with tetramethylethylene and methanol. Reaction with

**Table I.** Absorption Maxima of Ylides Derived from the Reaction of Dialkyl- and Alkylchlorocarbenes with Pyridine

	400 <sup>a</sup>		370 <sup>d</sup>
	376 <sup>b</sup>		379 <sup>e</sup>
	375 <sup>c</sup>		

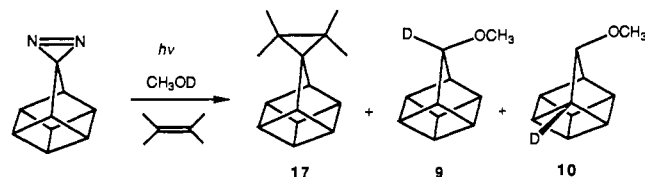
<sup>a</sup>Morgan, S. C.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* Submitted. Morgan, S. C. M.S. Thesis, The Ohio State University, 1989, p 25. <sup>b</sup>Reference 25a. <sup>c</sup>Moss, R. A.; Ho, G.-J. *Tetrahedron Lett.* 1990, 31, 1225. <sup>d</sup>Ho, G.-J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* 1989, 111, 6875. <sup>e</sup>Reference 26c.

**Table II.** Absolute Rate Constants for the Reactions of Singlet Carbenes with Alcohols

carbene	$k$ , M <sup>-1</sup> s <sup>-1</sup>	alcohol
diphenylcarbene <sup>a</sup>	$5 \times 10^9 - 3 \times 10^{10}$	CH <sub>3</sub> OH
xanthylidene <sup>b</sup>	$5.1 \times 10^9$	C <sub>2</sub> H <sub>5</sub> OH
	$1.8 \times 10^9$	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH
	$1.6 \times 10^9$	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OD
3,6-dimethoxyfluorenylidene <sup>c</sup>	$5.6 \times 10^9$	CH <sub>3</sub> OH
	$4.8 \times 10^9$	CH <sub>3</sub> OD
10,10-bis(trimethylsilyl)anthrylidene <sup>d</sup>	$1.5 \times 10^8$	CH <sub>3</sub> OH
<i>p</i> -chlorophenylchlorocarbene <sup>e</sup>	$4.3 \times 10^9$	CH <sub>3</sub> OH
fluorenylidene <sup>f</sup>	$6.3 \times 10^8$	CH <sub>3</sub> OH
	$4.6 \times 10^8$	CH <sub>3</sub> OD
methoxyphenylcarbene <sup>g</sup>	$> 1 \times 10^{10}$	CH <sub>3</sub> OH
dimethoxycarbene <sup>h</sup>	$2.5 \times 10^6$	CH <sub>3</sub> OH
methylmethoxycarbene <sup>i</sup>	$7 \times 10^9$	CH <sub>3</sub> OH

<sup>a</sup>Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Phys. Chem.* 1983, 87, 2283. Sitzmann, E. V.; Langan, J. G.; Eisenthal, K. B. *Chem. Phys. Lett.* 1984, 112, 111. <sup>b</sup>Reference 26a. <sup>c</sup>Reference 27b. <sup>d</sup>Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* 1983, 1257. <sup>e</sup>Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* 1982, 104, 5549. <sup>f</sup>Composite reactivity of spin equilibrated singlet and triplet fluorenylidene, see ref 29, pp 84-86 and references therein. <sup>g</sup>Reference 28b. <sup>h</sup>Reference 28c. <sup>i</sup>Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wtostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G. *J. Am. Chem. Soc.* 1988, 110, 7563.

methanol is favored by a factor of 1.9, and thus 6 seems to be quite an ordinary carbene.

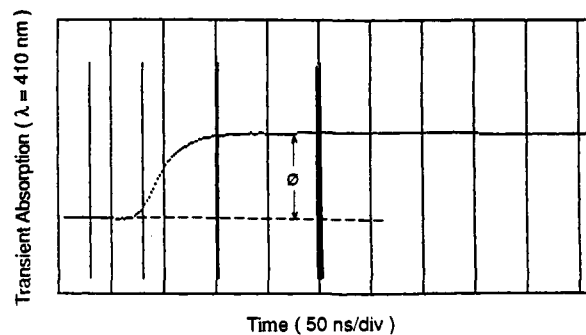
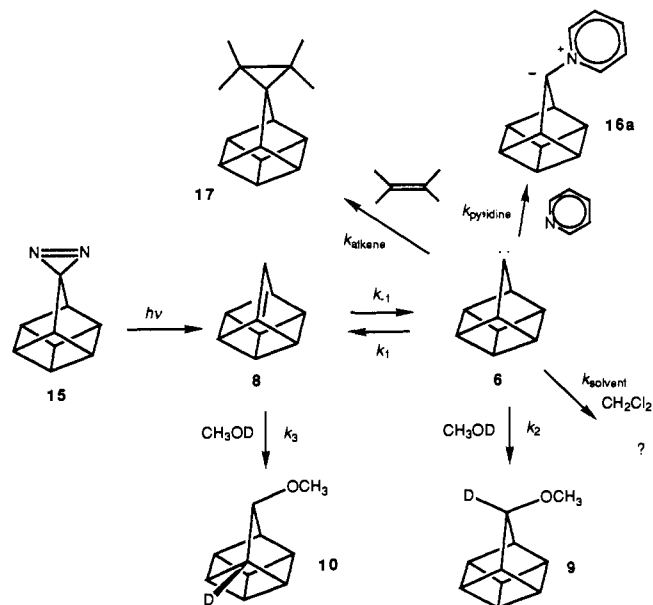


Representative rate constants for the reactions of singlet carbenes with methanol are collected in Table II. Dimethoxycarbene and fluoromethoxycarbene are exceedingly stable species (for carbenes) and react relatively slowly with methanol. However, all other known carbenes, including those substituted with a single  $\alpha$  oxygen, react with methanol with rate constants within a factor of 3 of diffusion control ( $k_{\text{dif}} = 1-2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ). As carbene 6 shows no obvious stabilization, and as kinetic isotope effects in singlet carbene insertion reactions are typically quite small,<sup>27</sup> it is reasonable to assume that  $k_2$  is close to  $k_{\text{dif}}$ . Given this assumption, the ratio of  $k_2/k_3$  must be equal to or greater than 1. This means that the equilibrium constant  $K$  must be  $\geq 0.20-0.23$  (eq 3). If the carbene is roughly 5-fold more reactive toward

$$k_2/k_3 \geq 1, K \geq 0.20-0.23 \quad (3)$$

methanol than is the bridgehead alkene, an equilibrium constant of ca. 1 results. If the two species react equally fast with methanol,

(27) Griller, D.; Liu, M. T. H.; Montgomery, C. R.; Scaiano, J. C. *J. Org. Chem.* 1983, 48, 1359. Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* 1985, 41, 1525. Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Wtostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* 1987, 109, 4341. Moss, R. A.; Wtostowski, M.; Shen, S.; Krogh-Jespersen, K.; Matro, A. *J. Am. Chem. Soc.* 1988, 110, 4443.

**Figure 6.** The absolute rate of formation of ylide 16a following LFP of diazirine 15 in the presence of dilute pyridine in CH<sub>2</sub>Cl<sub>2</sub>.**Scheme II**

that is, if the bridgehead alkene reacts at essentially the diffusion controlled rate, carbene 6 could be preferred thermodynamically to alkene 8, but this preference is at most slight.

Figures 1, 2, and 3 demonstrate that equilibrium between 6 and 8 is achieved when  $[\text{CH}_3\text{OD}] < 1 \text{ M}$ . As the concentrations of methanol and pyridine employed in LFP experiments range between 0.001 and 0.1 M, the rates of isomerization of intermediates 6 and 8 far exceed their rates of capture  $k_1$  vs  $k_2$  [ $\text{CH}_3\text{OD}$ ];  $k_{-1}$  vs  $k_3$  [ $\text{CH}_3\text{OD}$ ]]. It can be confidently predicted that under LFP conditions the two intermediates will be in rapid equilibrium at ambient temperature.

Next, we will slightly elaborate Scheme I to produce Scheme II which includes rate constants for reaction of carbene 6 with solvent as well as pyridine and alkenes. LFP of a methylene chloride solution of 15 in the presence of 0.5-2.0 M pyridine produces a particularly intense ylide absorption that is formed extremely rapidly (Figure 6). The rate of formation of ylide 16a can be fit to an exponential function. The lifetime of the ylide growth varies between 15 and 20 ns, which is likely the time resolution of the apparatus. This corresponds to an observed rate constant  $k_{\text{obs}} \geq 5 \times 10^7 \text{ s}^{-1}$ .

The yield of ylide produced in a single laser pulse is denoted by  $\phi$  and is defined in Figure 6. A plot of  $\phi$  vs [pyridine] is given in Figure 7. Of course  $\phi = 0$  when [pyridine] = 0, but  $\phi$  grows rapidly as [pyridine] increases. The yield of ylide levels off when [pyridine] reaches 0.04 M. Thus, when [pyridine] exceeds 0.05 M all of the carbenes and alkenes present after the laser flash are ultimately converted to ylide 16a. At [pyridine] = 0.002 M, the value of  $\phi$  is one-half the value of  $\phi$  at saturation. At this concentration of pyridine (0.002 M), eq 4 is valid, where  $k_0$  is

$$k_{\text{pyr}}[\text{pyridine}] = k_0 \quad (4)$$

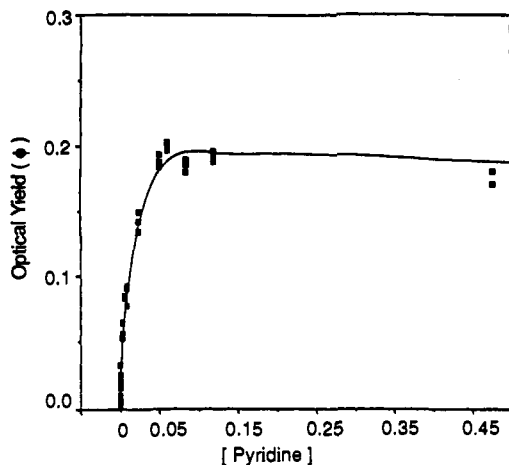


Figure 7. Optical yield ( $\phi$ ) of ylide **16a** produced by LFP of diazirine **15** in  $\text{CH}_2\text{Cl}_2$  at 20 °C as a function of pyridine concentration.

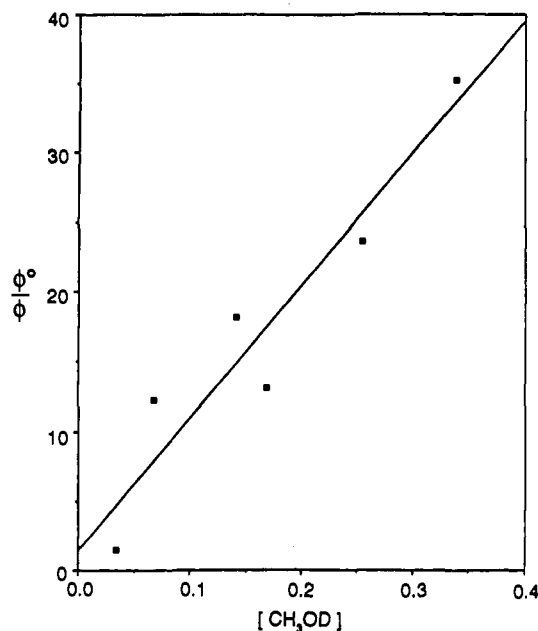


Figure 8. Stern-Volmer analysis of quenching of **16a** with  $\text{CH}_3\text{OD}$  in  $\text{CH}_2\text{Cl}_2$  at 20 °C with  $[\text{PYR}] = 0.0412 \text{ M}$ .

the total of all first-order and pseudo-first-order processes which consume either **6** or **8** in methylene chloride in the absence of pyridine. These processes include reactions with solvent, impurities, and precursor. Considering the time scales of our measurements, the concentrations of quenchers employed, and the nature of the solvent, it seems reasonable to associate  $k_0$  with the pseudo-first-order rate constant for reaction of carbene **6** with solvent. It can be shown (Appendix 1) that the ratio  $\phi^0/\phi$ , where  $\phi^0$  is the yield of ylide in the absence of  $\text{CH}_3\text{OD}$ , is given by eq 5.

$$\phi^0/\phi = 1 + \{(k_2 + k_3K)/(k_{\text{pyr}}[\text{pyridine}] + k_0)\}[\text{CH}_3\text{OD}] \quad (5)$$

When  $[\text{pyridine}] > 0.04 \text{ M}$ , eq 5 reduces to eq 6.

$$\phi^0/\phi = 1 + \{(k_2 + k_3K)/k_{\text{pyr}}[\text{pyridine}]\}[\text{CH}_3\text{OD}] \quad (6)$$

Therefore, a plot of  $\phi^0/\phi$  vs  $[\text{CH}_3\text{OH}]$  should be linear, with a slope of  $(k_2 + k_3K)/k_{\text{pyr}}[\text{pyridine}]$ .

The kinetics of reactions of carbenes with methanol have been plagued by oligomerization of the alcohol.<sup>28</sup> For example, chlorophenylcarbene reacts much more rapidly with oligomeric methanol than with the monomer. The opposite behavior is ob-

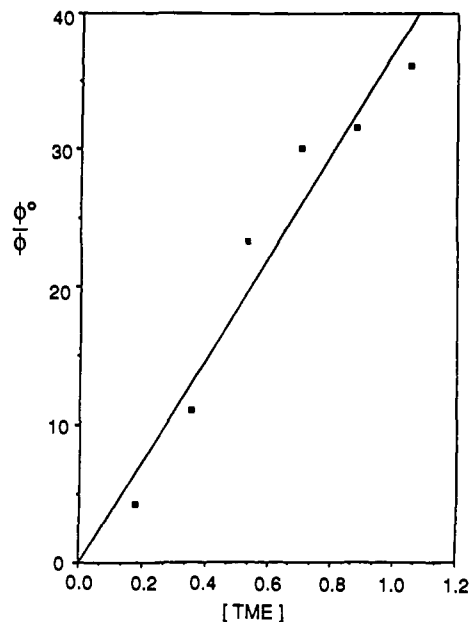


Figure 9. Stern-Volmer analysis of quenching of **16a** with tetramethylethylene in  $\text{CH}_2\text{Cl}_2$  at 20 °C with  $[\text{PYR}] = 0.0515 \text{ M}$ .

Table III. The Relative Reactivity of Homocub-9-ylidene toward Various Quenchers Determined with the Pyridinium Ylide Probe **16a**

quencher	rel reactivity (25 °C)	rel reactivity of CPC <sup>b</sup> (25 °C)	rel reactivity (-60 °C)
$\text{CH}_3\text{OD}$	3.3	3.8 [ $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ]	6.5
TME <sup>a</sup>	1.9	0.2–0.4 [ $0.7\text{--}1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ]	0.6
pyridine	1.0	1.0 [ $3.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ]	1.0

<sup>a</sup> Tetramethylethylene. <sup>b</sup> Chlorophenylcarbene.

served with chlorophenylcarbene and *tert*-butyl alcohol. The concentrations of pyridine (0.4 M) and methanol (0.1–0.4 M) used in this work ensure that we are working in a regime in which methanol is uniformly oligomeric. Thus a linear plot is produced and the reactivity data derived from the plot are relevant to the chemical trapping studies, in which oligomeric methanol was also used. The slope of the  $\phi^0/\phi$  plot of Figure 8 is 95.0 at a pyridine concentration of 0.0412 M. The ratio defined in eq 6 is as given in eq 7 (see Appendix 1):

$$(k_2 + k_3K)k_{\text{pyr}} = 3.9 \quad (7)$$

From eq 2 we know that  $k_3K = 0.2k_2$ , so **6** is 3.25 times as reactive toward  $\text{CH}_3\text{OD}$  as pyridine ( $k_2/k_{\text{pyr}} = 3.25$ ) at 20 °C (Table III).

It was also possible to study the effect of tetramethylethylene on the yield of ylide **16**. If we can assume that only carbene **6** reacts with alkenes, then eq 6 reduces to eq 8:

$$\phi^0/\phi = 1 + (k_{\text{alkene}}/k_{\text{pyr}}[\text{pyridine}])[\text{alkene}] \quad (8)$$

As seen in Figure 9, a plot of  $\phi^0/\phi$  vs  $[\text{TME}]$  is linear with a slope of 37.1 when  $[\text{pyridine}] = 0.0515 \text{ M}$ . Thus **6** is 1.91 times as reactive towards tetramethylethylene as pyridine ( $k_{\text{TME}}/k_{\text{pyr}} = 1.91$ ).

The relative reactivities of carbene **6** toward  $\text{CH}_3\text{OD}$ , tetramethylethylene, and pyridine are quite similar to those of another singlet carbene, chlorophenylcarbene (Table III). Moreover, the selectivities of **6** as determined by LFP and competition experiments in solution are very similar;  $k_2/k_{\text{TME}} = 2.2$  (solution), 1.7 (LFP). Accordingly, the selectivity of **6** appears unexceptional, and our previous assumption that the absolute reactivity of **6** toward  $\text{CH}_3\text{OD}$  is close to  $k_{\text{dif}}$  appears justified.

Similar experiments were performed with the *p*-cyanopyridine ylide **16b** as a probe. A plot of  $\phi$  vs  $[\text{p-cyanopyridine}]$  is shown in Figure 10. The saturation point is approached at a concentration of *p*-cyanopyridine of 0.08 M. Therefore **6** is trapped more rapidly by pyridine than by the *p*-cyano derivative. The yield of

(28) Scaiano, J. C. *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. III, p 73.

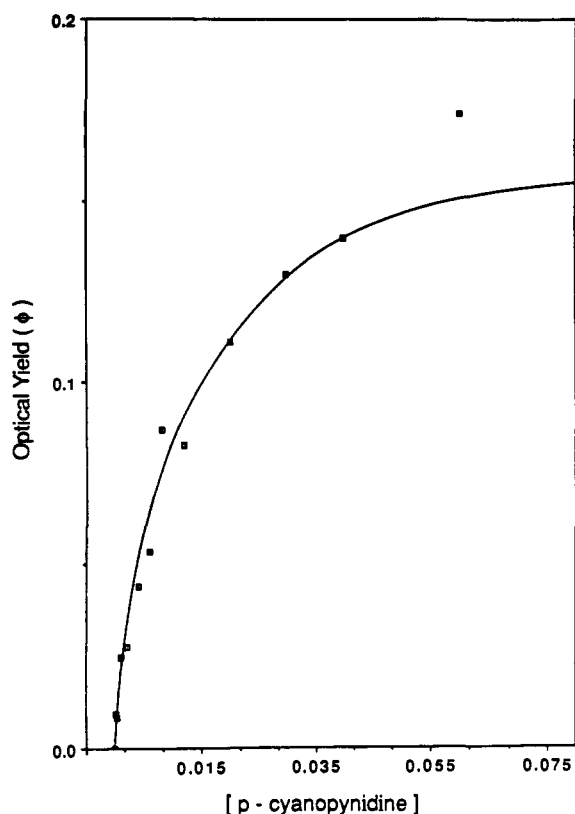


Figure 10. Optical yield ( $\phi$ ) of ylide **16b** produced by LFP of diazirine **15** in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  as a function of *p*-cyanopyridine concentration.

Table IV. The Relative Reactivity of Homocub-9-ylidene toward Various Quenchers Determined with the *p*-Cyanopyridinium Ylide Probe **16b**

quencher	rel reactivity	quencher	rel reactivity
$\text{CH}_3\text{OH}$	3.2	cyclohexene	0.95
$\text{CH}_3\text{OD}$	1.2	1-methylcyclohexene	0.6
TME (tetra-methylethylene)	1.0	styrene	0.6

**16b** is reduced in the presence of either alcohol or olefinic quenchers. The reciprocal quenching plots are linear (Figure 11). The relative reactivities of various alkenes and methanol determined by quenching of the *p*-cyanopyridinium ylide **16b** are given in Table IV.

If we assume that only carbene **6** reacts with pyridine, then Scheme II predicts eq 9, where  $A$  is a constant and  $\tau$  the time  $\phi[16a] = A - A \exp\{(-k_{\text{pyr}}[\text{pyridine}] - k_0)/(K + 1)\tau\} = A - A \exp(-k_{\text{obs}}\tau)$  (9)

constant for the exponential growth of ylide. When  $[\text{pyridine}] \geq 0.05 \text{ M}$ , the yield of ylide ( $\phi$ ) is saturated (see Figure 7). In the saturation region

$$k_{\text{pyr}}[\text{pyridine}] \gg k_0 \quad (10)$$

and (Appendix II):

$$k_{\text{pyr}}[\text{pyridine}]/(K + 1) = k_{\text{obs}} \geq 5 \times 10^7 \text{ s}^{-1} \quad (11)$$

or

$$K = \{k_{\text{pyr}}[\text{pyridine}]/k_{\text{obs}}\} - 1 \quad (12)$$

for  $[\text{pyridine}] \geq 0.05 \text{ M}$ . As the maximum value of  $k_{\text{pyr}}$  is  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (see Table II), and the minimum value of  $k_{\text{obs}}$  is  $5 \times 10^7 \text{ s}^{-1}$ , the upper bound for  $K$  is now defined (eq 13) and bracketed at room temperature (see also eq 3).

$$0.20 \leq K \leq 4 \quad (13)$$

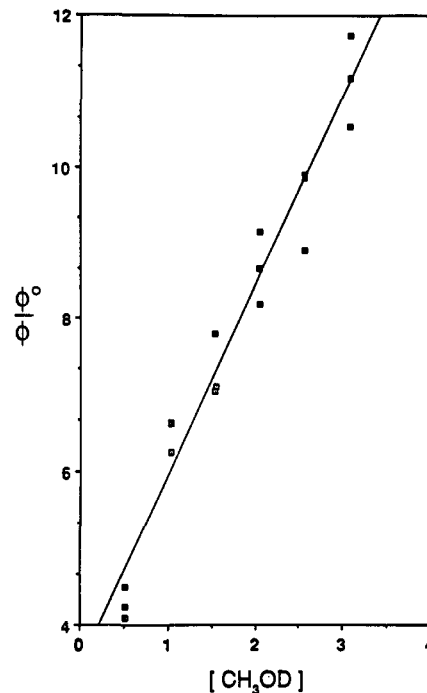


Figure 11. Stern-Volmer analysis of the quenching of **16b** by  $\text{CH}_3\text{OD}$  in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  with  $[\text{p-cyanopyridine}] = 1.07 \times 10^{-1} \text{ M}$ .

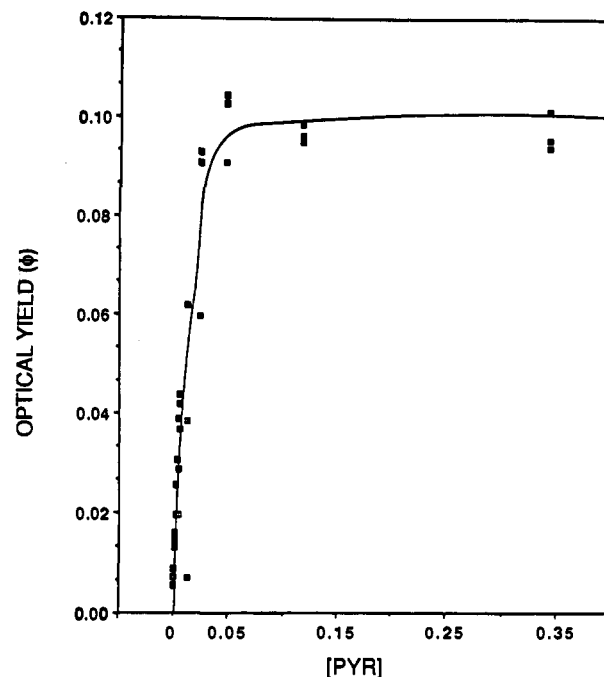


Figure 12. Optical yield ( $\phi$ ) of ylide **16a** produced by LFP of diazirine **15** in  $\text{CH}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  as a function of pyridine concentration.

**Low-Temperature Flash Photolysis.** The rate of formation and yield of **16a** was also studied at  $-60^\circ\text{C}$ . The yield of ylide **16a** ( $\phi$ ) as a function of pyridine concentration at this temperature (Figure 12) is virtually identical with that observed at  $+20^\circ\text{C}$  (Figure 7). The yield of ylide **16a** is saturated when  $[\text{pyridine}] \geq 0.05 \text{ M}$ . The rate of ylide formation still exceeds  $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  under these conditions.

The equilibrium constant  $K$  is close enough to unity to make it impossible to determine the ground state from our data. If the carbene were substantially ( $>2-3 \text{ kcal/mol}$ ) higher lying than the alkene, its equilibrium population would be very small at  $-60^\circ\text{C}$ . Accordingly, the rate of ylide formation would be quite slow at that temperature. Yet ylide formation is in fact too rapid to measure at  $-60^\circ\text{C}$  at reasonable concentrations of pyridine. The proportion of carbene present at equilibrium is substantial at all

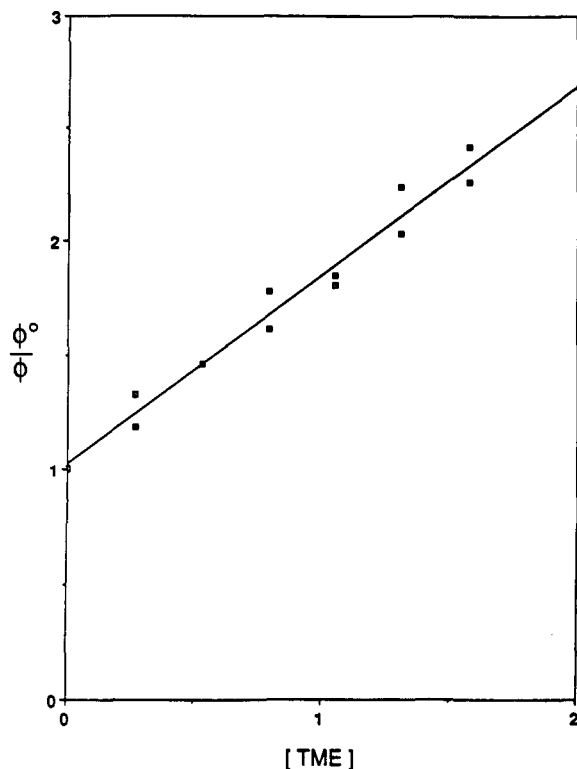


Figure 13. Stern-Volmer analysis of the quenching of **16a** by tetramethylethylene in  $\text{CH}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  with  $[\text{pyridine}] = 0.773\text{ M}$ .

temperatures used in this work. The carbene is either the ground state or only marginally higher in energy than the alkene.

It was possible to resolve  $k_{\text{obs}}$  at  $-60^\circ\text{C}$  at a pyridine concentration of  $0.00476\text{ M}$  ( $\tau = 55\text{--}74\text{ ns}$ ). Under these conditions  $k_{\text{obs}} = 1.5 \times 10^7\text{ s}^{-1}$ .

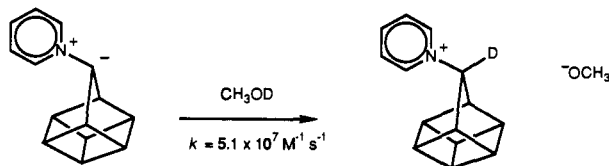
Figure 12 shows that a pyridine concentration of  $0.00476\text{ M}$  ( $\phi = 0.04$ ) corresponds to a  $\phi$  value about one-half the value of  $\phi$  at saturation. Under these conditions, and with the assumption that **6** and **8** still rapidly equilibrate, eq 4 applies, and eq 11, which holds for the saturation region, becomes eq 14 when  $\phi$  is half the saturation limit. If the upper limit of  $k_{\text{pyr}}$  is still  $5 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ , the upper limit of  $K$  is only 2.2 at this temperature.

$$2\{k_{\text{pyr}}[\text{pyridine}]/(K + 1)\} = k_{\text{obs}} \quad (14)$$

It was possible to repeat quenching of the equilibrium mixture of **6** and **8** at  $-60^\circ\text{C}$  (Figures 13 and 14). The relative reactivities of **6** at  $-60^\circ\text{C}$  are  $k_2/k_{\text{pyr}} = 6.5$  and  $k_{\text{tme}}/k_{\text{pyr}} = 0.64$ .

The selectivities of **6** vary only within a factor of 3 between  $+20$  and  $-60^\circ\text{C}$ . This is consistent with activation energies close to zero for the reactions of carbene **6** and with absolute rates that are close to diffusion controlled. In this sense the behavior of **6** mirrors that of chlorophenylcarbene.

The lifetime of ylide **16a** is reduced by the presence of  $\text{CH}_3\text{OD}$ . A plot of  $k_{\text{obs}}$  (ylide decay) vs  $[\text{CH}_3\text{OD}]$  is linear (Figure 15). The slope of this plot is the absolute rate constant for reaction of the ylide with  $\text{CH}_3\text{OD}$  ( $k = 5.1 \times 10^7\text{ M}^{-1}\text{ s}^{-1}$ ). We suspect that ylide **16a** is being trapped by  $\text{CH}_3\text{OD}$  through a simple transfer of deuterium.



**Sources of Error.** The bracketing of  $K$  required two assumptions. The lower limit of  $K$  relied upon the assumption that  $k_2 = k_{\text{dif}}$ . If this is in error, then  $k_2$  must be orders of magnitude smaller than almost every other rate constant for reaction of a

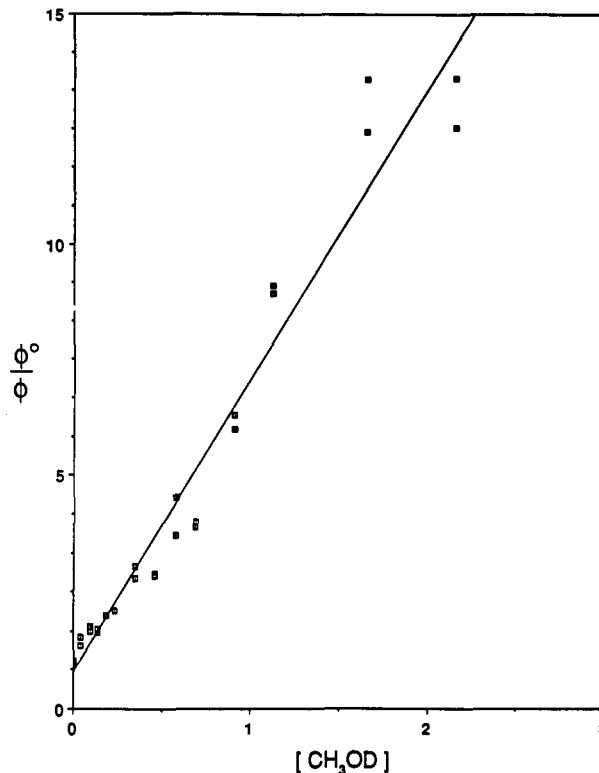


Figure 14. Stern-Volmer analysis of the quenching of **16a** by  $\text{CH}_3\text{OD}$  in  $\text{CH}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  with  $[\text{pyridine}] = 1.24\text{ M}$ .

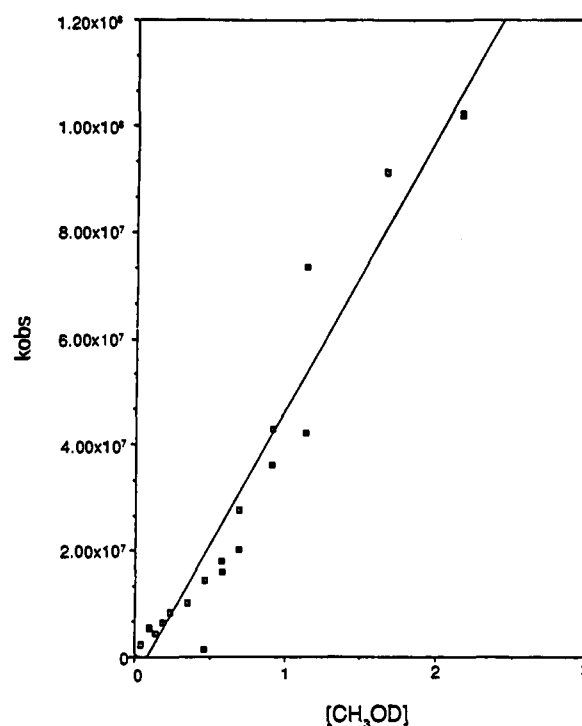


Figure 15. A plot of  $k_{\text{obs}}$  for the disappearance of **16a** as a function of  $[\text{CH}_3\text{OD}]$ .

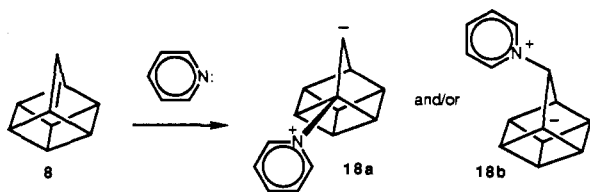
singlet carbene with an alcohol. We see no structural feature in **6** that would make this true.

The upper limit for  $K$  required the assumption that alkene **8** does not react with pyridine to give ylide **18a** and/or **18b**. In our hands *trans*-1-phenylcyclohexene, produced by photolysis of the *cis* isomer,<sup>29</sup> does not react with 1 M pyridine at a measurable

(29) Bonneau, R.; Jousset-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* 1976, 98, 4329.



rate and gives no detectable transient species.



Moreover, this assumption is neither unreasonable nor, in fact, crucial to our arguments. Putative compound **18** is an unconjugated 1,3 dipole, not a 1,2 dipole as is **16a**. Therefore **18** should not have a chromophore resembling those of ylides. We are confident that the spectrum of Figure 4 is that of **16a** not **18**. However let us assume for the moment that the pyridine derived transient is indeed **18a** or **18b**. If this is the case, then the upper limit of  $K$  cannot be defined and may in fact be a very large number. This requires that **8** reacts with the nucleophile pyridine at a rate that is close to diffusion control, but by eq 2 this transient assignment requires that strained alkene **8** must now be quite unreactive toward methanol. We feel that this is chemically unreasonable and strengthens our attribution of the carrier of the transient spectrum to **16a** rather than **18a,b**. But, perhaps both **16a** and **18** are formed in the presence of pyridine, and only **16a** is detectable by UV-vis spectroscopy. The transient spectrum of **16a** is very intense—as strong or stronger than the transients produced from adamantylidene or the alkylhalocarbenes of Table I. The formation of **16a** cannot be a minor process in the presence of 0.05 M pyridine!

For the sake of argument let us assume that the equilibrium mixture of **6** and **8** reacts with pyridine to give a 1:1 mixture of **16a** and **18**. Under these conditions eq 15 applies:

$$2k_{\text{py}}[\text{pyridine}]/(K + 1) = k_{\text{obs}} \quad (15)$$

This would have only a slight effect on the limits for  $K$  given in eq 13 ( $0.2 \leq K \leq 8$ ).

## Conclusions

Traditional product analysis experiments and LFP studies agree that the equilibrium constant for the **6**–**8** system is close to unity at +20 °C. It is not clear which species is favored at equilibrium. Both the carbene **6** and the bridgehead alkene **8** react with  $\text{CH}_3\text{OD}$  within an order of magnitude of a diffusion-controlled rate.

## Experimental Section

**General.** All chemicals were purchased from Aldrich Chemical Co. except as indicated elsewhere or were synthesized as described.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker WM-250, GE QE-300, and JEOL GSX-270 instruments in  $\text{CDCl}_3$ . The residual  $\text{CHCl}_3$  in  $\text{CDCl}_3$  was taken as internal standard. The chemical shift of the residual proton was set at 7.24 ppm.  $^2\text{H}$  NMR spectra were recorded on a Bruker WM-250 instrument in  $\text{CHCl}_3$ . GC-mass spectral analyses were carried out on a Hewlett-Packard 5992B gas chromatograph-mass spectrometer with a 2 mm i.d., 1.5 m glass column packed with 3% OV-17 silicone oil absorbed on 80/100 mesh Chromosorb W. Analytical GC separations were achieved by use of a Hewlett-Packard 5890 chromatograph equipped with a Hewlett-Packard 3390A integrator, using a 0.75 mm i.d., 60 m SPB-1 glass column. Preparative gas chromatographic separations were performed on a Varian Aerograph A90P chromatograph with helium as carrier gas. The 6 ft.  $\times$  1/4 in. and 2 ft.  $\times$  1/4 in. columns were constructed of 20% OV-101 or OV-17 silicon oil absorbed on 80/100 mesh Chromosorb WHP. IR spectra were taken on a Nicolet 5DBX spectrometer. Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected. All photoreactions were run in quartz tubes, using a 450-W medium-pressure Hanovia 679A46 mercury vapor lamp.

**General Procedure for the Preparation of Tosylhydrazone Sodium Salts.** Carbonyl compound [cubane-carboxaldehyde<sup>30</sup> (vide infra) or pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one,<sup>31</sup> 252 mg, 1.9 mmol] and to-

sylhydrazine (356.5 mg, 1.9 mmol) were mixed in 2 mL of pure pyridine. The exothermic reaction mixture was swirled and cooled to room temperature. The solution then was transferred to a refrigerator at –20 °C for 36 h. The mixture was filtered, and colorless crystals were recovered. The tosylhydrazones were dissolved in 2.5 mL of dry THF with stirring. To the solution was added sodium hydride (45.6 mg, 1.9 mmol) in one portion at room temperature under an atmosphere of argon. The solution was stirred at room temperature for 8 h. All solvent was evaporated with a stream of argon to yield a pale yellow solid. The solid salt was used for the next step without further purification.

**Preparation of Cubane-carboxaldehyde.**<sup>30</sup> To 1 mL of dichloromethane was slowly added oxalyl chloride (21  $\mu\text{L}$ , 0.24 mmol) at –78 °C. After the mixture was stirred for 5 min, DMSO (150  $\mu\text{L}$ , 2.12 mmol) in 100  $\mu\text{L}$  of dichloromethane was added. Cubylcarbinol (30 mg, 0.23 mmol) in 0.5 mL of dichloromethane was added dropwise. After the reaction mixture was stirred for 25 min, triethylamine (200  $\mu\text{L}$ , 1.43 mmol) was added. Stirring was continued for an additional 5 min, and the mixture was warmed to room temperature. The solution was quenched with 3 mL of water and the mixture was extracted three times with 10 mL of dichloromethane. The organic layer was washed sequentially with 5 mL of 10% hydrochloric acid, 5 mL of water, and 5 mL of brine and dried over  $\text{MgSO}_4$  overnight. The solvent was removed with use of a rotary evaporator to give a colorless oil (26.0 mg) which contained >95% cubane-carboxaldehyde as determined by  $^1\text{H}$  NMR analysis. The compound could be used without further purification. However, a portion was purified by TLC on silica gel with ether–pentane (7:40 v:v) as solvent ( $R_f$  = 0.47). Pure cubane-carboxaldehyde (8.4 mg, 75.7%) was recovered:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69 (s, 1 H), 4.36 (m, 3 H), 4.00 (m, 4 H).

**Preparation of the Tosylhydrazone Sodium Salt of Cubane-carboxaldehyde (1).** The general procedure was followed. Cubane-carboxaldehyde (15 mg, 0.11 mmol) and tosylhydrazine (21 mg, 0.11 mmol) yielded the tosylhydrazone (21 mg, 60%):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (br s, 1 H), 7.83 (d,  $J$  = 8.1 Hz), 7.37 (s, 1 H), 7.32 (d,  $J$  = 8.1 Hz), 4.11 (m, 3 H), 3.92 (m, 4 H), 2.44 (s, 3 H).

**Preparation of the Tosylhydrazone Sodium Salt of Pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one (2).** The general procedure was followed. The tosylhydrazone of pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one (451 mg, 78.5%) was recovered: mp 117–119 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (br s, 1 H), 7.83 (d,  $J$  = 9 Hz, 2 H), 7.30 (d,  $J$  = 9 Hz), 3.75 (m, 1 H), 3.52 (m, 4 H), 3.41 (m, 1 H), 3.28 (m, 2 H), 2.41 (s, 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.56, 143.92, 136.31, 129.64, 128.14, 44.59, 43.18, 43.00, 42.81, 42.42, 37.44, 21.73; IR (neat) 3212, 2983, 1674, 1598, 1442, 1340, 1165  $\text{cm}^{-1}$ ; MS,  $m/e$  (rel intensity) 300 ( $M^+$ , 0.4), 145 (100), 115 (62), 91 (54), 77 (11); HRMS calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  ( $M^+$ ) 300.0932, found 300.0933.

**Preparation of 3.** A 2  $\times$  30 cm quartz photolysis reaction tube equipped with a T-joint with a high-vacuum Teflon stopcock was charged with the aziridylimine (**5**) of pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one<sup>31</sup> (or **1** or **2** or **7**) (129.6 mg, 0.4 mmol) and 2 mL of *cis*-4-methyl-2-pentene. The solution was degassed by the freeze–pump–thaw method. The tube was irradiated with a 450-W medium-pressure Hanovia mercury vapor lamp in a water-cooled bath for 12 h. The solution was then poured into a round-bottom flask and the photoreaction tube rinsed twice with 3 mL of dichloromethane. The washings were combined with the original solution. Removal of the solvent on a rotary evaporator gave a yellow oil. Purification was carried out on preparative GC with use of a 3 ft.  $\times$  1/4 in. OV-101 column (He flow 40 mL/min, oven temperature 190 °C,  $t_R$  = 15.2 min). Compound **3** was collected as a colorless oil (30.4 mg, 38%):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.36 (m, 4 H), 3.16 (m, 2 H), 3.03 (m, 1 H), 2.53 (m, 1 H), 1.37 (m, 1 H), 0.99 (d,  $J$  = 6.1 Hz, 3 H), 0.91 (d,  $J$  = 6.6 Hz, 3 H), 0.89 (m, 1 H), 0.84 (d,  $J$  = 6.6 Hz, 3 H), 0.59 (dd,  $J$  = 8.6 Hz,  $J$  = 10.5 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  52.25, 48.56, 45.32, 44.62, 44.33, 43.98, 43.13, 42.23, 41.48, 30.90, 26.24, 23.85, 23.08, 14.28, 10.42; MS,  $m/e$  (rel intensity) 200 ( $M^+$ , 0.2), 185 (1), 157 (14.2), 142 (28.4), 129 (100), 115 (66), 91 (53), 77 (28); HRMS calcd for  $\text{C}_{15}\text{H}_{20}$  ( $M^+$ ) 200.1565, found 200.1560.

**Preparation of 4.** The same procedure as for **3** was used except that *trans*-methyl-2-pentene was employed as a trap.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.36 (m, 3 H), 3.35 (m, 1 H), 2.84 (m, 2 H), 1.02 (d,  $J$  = 6.1 Hz, 2 H), 0.97 (d,  $J$  = 5.7 Hz, 3 H), 0.89 (t,  $J$  = 6.7 Hz, 1 H), 0.81 (d,  $J$  = 6.1 Hz), 0.56 (m, 1 H), 0.34 (dd,  $J$  = 4.9, 9.4 Hz, 1 H); MS,  $m/e$  (rel intensity) 200 ( $M^+$ , <1), 185 (1), 157 (14.9), 142 (24), 129 (100), 115 (57), 91 (46), 77 (26); HRMS calcd for  $\text{C}_{15}\text{H}_{20}$  ( $M^+$ ) 200.1565, found 200.1558.

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(31) (a) Chapman, N. B.; Key, J. M.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 3865. (b) Hamlin, J. E.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2731.

**Preparation of 5.** To a solution of 132 mg (1 mmol) of pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one in 5 mL of benzene in a 25-mL flask was added in one portion 210 mg (1 mmol) of *trans*-1-amino-2,3-diphenylaziridine.<sup>9</sup> After brief swirling at room temperature, the reaction mixture was a colorless, homogeneous solution; however, it rapidly turned cloudy as water separated. After 2 h the benzene and water were removed as an azeotrope on a rotary evaporator with a bath at room temperature. The resulting crude hydrazone (usually a sticky liquid, only occasionally could a solid be recovered) was subjected to photolysis or pyrolysis without further purification. However, purification could be carried out with TLC on a silica gel with methanol-dichloromethane (1.8/100, v/v) as eluent,  $R_f = 0.63$ . Solvent was removed on a rotary evaporator to give a sticky liquid, which crystallized in a refrigerator: mp 71–73 °C; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 7.44–7.21 (m, 10 H), 3.70 (d,  $J = 5.7$  Hz), 3.54 (m, 4 H), 3.31 (m, 1 H), 3.19 (m, 1 H), 3.12 (m, 2 H), 2.30 (m, 1 H); <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>) δ 184.86, 138.90, 132.93, 129.84, 128.30, 127.48, 127.29, 127.18, 126.28, 56.03, 50.53, 43.94, 42.85, 42.64, 42.55, 42.28, 42.16, 42.03, 40.18; MS,  $m/e$  (rel intensity) 324 ( $M^+$ , 0.7), 194 (100), 129 (9), 115 (86), 91 (18); HRMS calcd for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub> ( $M^+$ ) 324.1626, found 324.1601.

**Preparation of 7.** The same procedure as for 5 was used. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.50 (s, 1 H), 7.34–7.28 (m, 10 H), 3.90 (m, 4 H), 3.86 (m, 3 H), 3.67 (br s, 1 H), 3.49 (br s, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) (aromatic signals are not included) δ 160.99, 56.98, 55.97, 51.64, 49.27, 48.43, 44.98; HRMS calcd for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub> ( $M^+$ ) 324.1626, found 324.1612.

**Preparation of 9 and 10.** To a 2 × 30 cm quartz photolysis reaction tube equipped with a T-joint with a high-vacuum Teflon stopcock was added a solution of the aziridylimine (5) of pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one (129.6 mg, 0.4 mmol) in 2 mL of methanol-*d*. The solution was degassed by the freeze-pump-thaw procedure and the tube was irradiated with a 450-W medium-pressure Hanovia 679A46 mercury vapor lamp in a water-cooled bath for 12 h. The solvent was removed with use of a rotary evaporator and the residue subjected to preparative GC separation with use of a 2 ft. × 1/4 in. OV-17 column (He flow 20 mL/min, temperature programmed in the range of 120–300 °C). A colorless liquid was collected which had exactly the same spectra as those of the authentic compound 10 (see below) except for the <sup>2</sup>H NMR spectrum and the ratios of peaks in the <sup>1</sup>H NMR spectrum. <sup>2</sup>H NMR (250 MHz, CHCl<sub>3</sub>) δ 3.94, 3.28.

**Preparation of 10.** A 25-mL three-necked flask equipped with a reflux condenser was charged with 25 mg of sodium hydride and 1.5 mL of THF. The mixture was heated to 45 °C with stirring and 0.3 mL of methyl iodide was added. Then 1-deuterio-9-hydroxypentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonane<sup>32</sup> (18 mg, 0.135 mmol) in 2 mL of THF was added over a period of 5 min. After the addition, the solution was heated for an additional 1 h. The mixture was cooled to room temperature and quenched with 1.5 mL of water. The mixture was then extracted twice with 20 mL ether, and the organic extractions were washed with 5 mL of brine and dried over MgSO<sub>4</sub>. The solvent was removed with use of a rotary evaporator to give a pale yellow liquid (15 mg, 75%): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.93 (s, 1 H), 3.52 (m, 2 H), 3.29 (s 3 H), 3.26 (m, 3 H), 3.22 (m, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 96.41, 58.08, 45.96, 43.79, 42.98, 41.69; <sup>2</sup>H NMR δ 3.28; HRMS calcd for C<sub>10</sub>H<sub>10</sub>DO ( $M^+ - 1$  H) 148.0872, found 148.0879.

**Preparation of Bicyclo[4.3.0]nona-3,6(1)-diene.**<sup>19</sup> Ammonia (600 mL) was condensed in a three-necked flask equipped with a mechanical stirrer and a cold finger condenser. A dry ice-ethanol bath was used to maintain the temperature at –78 °C. Lithium (10.5 g, 1.5 mol) was added to the flask in small pieces. A deep blue solution resulted. This solution was then stirred for an additional 2 h to make certain that the lithium was completely dissolved in the ammonia. A solution of 59 g (0.5 mol) of indan and 115 mL of absolute ethanol was then added dropwise to the ammonia-lithium solution over a period of 1 h. The mixture was stirred for 6 h at –78 °C after which time the mixture became a slurry containing a white precipitate. Methanol (200 mL) was added carefully to the mixture and then stirred overnight. The reaction mixture was quenched with 400 mL of water and the product extracted from the resulting mixture twice with 250 mL of petroleum ether. The organic layers were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed on a rotary evaporator to give 58.7 g of colorless liquid (almost quantitative yield, >98% purity): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.76 (s, 2 H), 2.65 (s, 4 H), 2.27 (t,  $J = 7.5$  Hz, 4 H), 1.87 (quintuplet,  $J = 7.1$  Hz, 2 H).

**Preparation of the *N*-(2-Phenylaziridyl)imine of Pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one.**<sup>9</sup> A similar procedure to that used for 5

was employed. The differences were that an equi-molar equivalent of 1-amino-2-phenylaziridine was used instead of 1-amino-2,3-diphenylaziridine and methanol-dichloromethane (2.4/100 v/v) employed as eluent,  $R_f = 0.25$ : <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 (m, 5 H), 4.04 (br s, 1 H), 3.63 (m, 4 H), 3.39 (m, 3 H), 2.88 (dd,  $J = 4.9, 7.6$  Hz, 1 H), 2.45 (d,  $J = 7.6$  Hz, 1 H), 2.32 (d,  $J = 4.9$  Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 186.36, 138.92, 128.44, 127.19, 126.38, 44.38, 44.26, 43.32, 43.08, 42.93, 42.53, 42.31, 40.65, 39.37, 39.15; HRMS calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub> ( $M^+$ ) 248.1313, found 248.1306.

**Preparation of Dihydro 13.** A 100-mL one-neck flask equipped with a reflux condenser was charged with the *N*-(2-phenylaziridyl)imine of pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one (1.19 g, 4.8 mmol) and 10 g of bicyclo[4.3.0]nona-3,6(1)-diene. The reaction flask was immersed in a oil bath which was preset at 190 °C and the mixture was vigorously stirred. The solution was refluxed and N<sub>2</sub> evolved. After 40 min, the solution was cooled and distilled at 70 °C (2 mmHg) to remove the excess dihydroindan. The residues were taken up in a minimum amount of dichloromethane and subjected to analytical GC (SPB-60 capillary column, temperature programmed from 100 to 250 °C, He flow 40 mL/min). Dihydro 13 ( $t_R = 16.1$  min, 16.7%) was collected by using preparative GC to give 66.5 mg (5.8%) of dihydro 13: a colorless liquid at room temperature and a white solid at –20 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.57 (s, 2 H), 3.31 (m, 2 H), 3.25 (m, 2 H), 3.10 (m, 2 H), 3.04 (t,  $J = 5.2$  Hz, 1 H), 2.99 (t,  $J = 5.2$  Hz, 1 H), 2.14 (s, 4 H), 1.93 (m, 2 H), 1.82–1.58 (m, 4 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 125.55 (d,  $J = 148.1$  Hz), 55.30, 45.41 (d,  $J = 152.1$  Hz), 45.27 (d,  $J = 152.1$  Hz), 45.19 (d,  $J = 152.1$  Hz), 43.01 (d,  $J = 156.1$  Hz), 42.30 (d,  $J = 156.1$  Hz), 36.87 (t,  $J = 128.2$  Hz), 30.40, 29.56 (t,  $J = 128.2$  Hz), 26.51 (t,  $J = 131.2$  Hz); MS,  $m/e$  (rel intensity) 236 ( $M^+$ ) (1), 165 (22), 142 (57), 129 (39), 91 (100), 115 (86.9). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>: C, 91.47; H, 8.52. Found: C, 91.27; H, 8.65.

**Preparation of 13.** To a solution of dihydro 13 (66.5 mg, 0.28 mmol) in 20 mL of dry toluene with magnetic stirring was added 171 mg (0.75 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in one portion at room temperature. After the addition, the scarlet solution was stirred under reflux for 39 h. The progress of the oxidation was followed by <sup>1</sup>H NMR. After the solution was cooled to room temperature, the mixture was filtered through Celite and the solid washed with 2 × 5 mL of toluene. The toluene was evaporated with use of a rotary evaporator to leave a pale brown solid. Two methods could be used to purify the crude product: (1) the brown residue was distilled with use of a Kugelrohr apparatus at 105–107 °C (1 mmHg); (2) the brown solid was taken up in a minimum amount of dichloromethane and passed through a 1 × 5 cm neutral alumina column with petroleum ether as eluent. Pure product was collected with use of about 150 mL of petroleum ether. After the solvent was removed on a rotary evaporator, 32.6 mg of a colorless solid was recovered, which contained, by <sup>1</sup>H NMR analysis, 85% 13 and 15% starting material (photoinert). The yield of the reaction was 42% based on a calibration of the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.03 (dd,  $J = 7.2, 2.6$  Hz, 2 H), 5.87 (dd,  $J = 7.2, 2.6$  Hz, 2 H), 3.57 (m, 2 H), 3.23 (m, 2 H), 3.17 (m, 2 H), 3.08 (m, 2 H), 2.24 (t,  $J = 5.0$  Hz, 1 H), 2.01 (m, 2 H), 1.81 (m, 2 H), 1.59 (m, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 127.64 (d,  $J = 158.1$  Hz), 119.23 (d,  $J = 159.1$  Hz), 50.08, 46.27, 45.66 (d,  $J = 150.1$  Hz), 43.54 (d,  $J = 146.1$  Hz), 43.49 (d,  $J = 146.1$  Hz), 42.85 (d,  $J = 149.1$  Hz), 41.91 (d,  $J = 154.1$  Hz), 41.53 (d,  $J = 156.1$  Hz), 33.97 (t,  $J = 128.2$  Hz), 26.84 (t,  $J = 132.2$  Hz).

**Spiro[homocubane-9,9'-diaziridine].** The general procedure of Bayley and Knowles<sup>33</sup> was followed. Pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one (1.87 g, 14.16 mmol) was stirred with NH<sub>3</sub> (25% w/v) in CH<sub>3</sub>OH for 50 min at –10 °C. A solution of hydroxylamine-*O*-sulfonic acid (Aldrich, 95% purity, dried overnight in a desiccator over P<sub>2</sub>O<sub>5</sub>) in CH<sub>3</sub>OH (20 mL) was added dropwise. The mixture was stirred at 2 °C for 19 h. The resulting slurry was concentrated with use of a rotary evaporator. The solid residue was triturated with 2 × 40 mL of dichloromethane. The combined dichloromethane extracts were extracted with 2 × 50 mL of 2 N H<sub>2</sub>SO<sub>4</sub>, which was precooled to 2 °C. The aqueous extracts were combined and made alkaline with 2 N NaOH at 0 °C, and the product was extracted back with dichloromethane (3 × 50 mL). The combined extracts were dried over K<sub>2</sub>CO<sub>3</sub> at 4 °C for 8 h. The solution was filtered and the solvent was evaporated on a rotary evaporator at room temperature to give the diaziridine (0.65 g, 31.4%) as a sticky yellow solid. Purification was achieved by a silica gel TLC with methanol-dichloromethane (15:100) as eluent,  $R_f = 0.5$ . Pure diaziridine was a white solid, which decomposed before melting: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 3.63 (m, 4 H), 3.31 (m, 2 H), 2.74 (m, 2 H), 2.04 (br s, 2 H, disappeared when D<sub>2</sub>O was added); <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>) δ 103.69, 47.22 (d,  $J = 150.10$  Hz), 43.11 (d,  $J = 155.08$  Hz), 42.58 (d,  $J = 156.06$  Hz);

(32) 1-Deuterio-9-hydroxypentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonane was made by the reduction of 1-deuteriopentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one<sup>31b</sup> with lithium aluminum hydride in dry ether.

(33) Bayley, H.; Knowles, R. *Biochemistry* 1980, 19, 3883.

IR (neat) 3187, 3156, 2990, 1237, 1187  $\text{cm}^{-1}$ . HRMS calcd for  $\text{C}_9\text{H}_9\text{N}_2$  ( $M^+ - 1\text{H}$ ) 145.0766; found 145.0778; calcd for  $\text{C}_9\text{H}_9\text{N}_2$  ( $M^+ - 2\text{H}$ ) 144.0688, found 144.0697.

**Spiro[homocubane-9,9'-diazirine].** (Caution! This compound is extremely explosive and must be treated with the greatest care.<sup>33</sup> All operations were conducted under dim light. Diaziridine (100 mg, 0.68 mmol) was partly dissolved in 4 mL of acetone. A solution of  $\text{CrO}_3$  (104 mg, 1.04 mmol) in 1.04 mL of 2 N  $\text{H}_2\text{SO}_4$  was added dropwise at 0 °C with vigorous stirring. The solution was stirred at room temperature for 35 min and then poured onto 50 g of ice. The precipitated product was extracted into 5 × 15 mL of pentane. The combined pentane extracts were washed with 10 mL of 5%  $\text{K}_2\text{CO}_3$  and 10 mL of water and then dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent on a rotary evaporator at room temperature yielded the diazirine (53 mg, 53%) which was a colorless liquid which solidified at -20 °C:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.62 (m, 4 H), 3.25 (m, 2 H), 2.36 (m, 2 H).

**Photolysis of 5 in Tetramethylethylene.** The procedure was similar to that for making compound 9. A mixture of methanol-tetramethylethylene was used as solvent instead of methanol-*d*-benzene. The adduct of 6 and tetramethylethylene 17 was collected on a 2 ft. × 1/4 in. OV-17 preparative GC column (He flow 20 mL/min, temperature programmed in the range 130–250 °C).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.32 (m, 4 H), 3.15 (m, 2 H), 3.01 (m, 2 H), 1.04 (s, 12 H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  45.88, 45.53, 42.69, 22.91, 20.53; MS, *m/e* (rel intensity) 185 (15), 157 (28), 147 (30), 143 (42), 129 (48), 128 (100), 115 (64), 103 (29), 91 (57), 78 (52), 65 (27); HRMS calcd for  $\text{C}_{15}\text{H}_{20}$  ( $M^+ - 1\text{Me}$ ): 185.1330, found: 185.1332.

**Dependence of 10/9 on  $[\text{CH}_3\text{OD}]$ .** (a) **Compound 5 as Precursor.** The procedure used in forming 9 and 10 was followed. Compound 5 (129.6 mg, 0.4 mmol) was dissolved in benzene solution (6 mL) which contained  $\text{CH}_3\text{OD}$  in the following concentrations: 0.1, 0.2, 0.4, 0.8, 2.2, 6.2, 12.3 M. The ratio of 10/9 for each corresponding solvent was determined by  $^2\text{H NMR}$  as follows: 0.10, 0.13, 0.14, 0.35, 0.44, 0.53, 0.56. See Figure 1.

(b) **Compound 13 as Precursor.** The same procedure as above was followed. Compound 13 (26 mg, 0.116 mmol) was dissolved in 1.7 mL of benzene which contained  $\text{CH}_3\text{OD}$  in the following concentrations: 0.5, 10.5, 14.8, 18.5 M. The ratio of 10/9 for each corresponding solvent was determined by  $^2\text{H NMR}$  as follows: 0.22, 0.18, 0.16, 0.14. See Figure 2.

(c) **Compound 15 as Precursor.** The same procedure as above was followed. Compound 15 (20 mg, 0.139 mmol) was dissolved in 2 mL of benzene which contained  $\text{CH}_3\text{OD}$  in the following concentrations: 0.5, 0.7, 3.5, 10.5, 14.8, 18.56 M. The ratio of 10/9 for each corresponding solvent was determined by  $^2\text{H NMR}$  as follows: 0.19, 0.26, 0.30, 0.38, 0.47, 0.73. See Figure 3.

**Preparation of the Adduct of 6 and *trans*-Stilbene.** The same general procedure as for making 9 and 10 was used. Compound 5 (129.6 mg, 0.4 mmol) was dissolved in 3 mL of benzene containing *trans*-stilbene (216.8 mg, 1.2 mmol) and  $\text{CH}_3\text{OD}$  (52.8 mg, 1.6 mmol). After 12 h of irradiation, the crude product contained 9 and the product of addition of 6 to stilbene. Pure material was prepared through preparative GC (2 ft. × 1/4 in. OV-17 column, He flow 20 mL/min, temperature programmed in the range 120–300 °C,  $t_R = 45$  min).  $^1\text{H NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27–7.16 (m, 10 H), 3.47 (m, 2 H), 3.27 (m, 2 H), 3.10 (m, 2 H), 2.75 (s, 2 H), 2.72 (m, 2 H); MS, *m/e* (rel intensity) 231 (33), 217 (40), 205 (100), 179 (83), 129 (59), 115 (63), 91 (54); HRMS calcd for  $\text{C}_{23}\text{H}_{20}$  ( $M^+$ ) 296.1565, found 296.1552.

**Laser Flash Photolysis.** (a) **General.** The LFP apparatus in use at Ohio State has been described previously.<sup>34</sup> UV absorbance readings were measured on either a Perkin-Elmer Lambda 3B UV-vis spectrophotometer or a Hewlett Packard 7912 diode array spectrophotometer. Dichloromethane was refluxed for 2 h over 4 Å molecular sieves, distilled, and stored over molecular sieves. Stock solutions of diazirine were prepared by isolation of the diazirine from pentane solution as a colorless oil and subsequent solution in purified dichloromethane. The concentrations of all of the solutions were adjusted so that the absorbance at 351 nm was between 0.006 and 0.01. Photolysis at 351 nm was accomplished by using a Lumonics eximer laser TE 861 M-T (XeF) with a pulse duration of 17 ns and an average energy of 60 mJ/pulse.

(b) **Optical Yield Experiments.** Stock solutions of diazirine were prepared as previously described in dichloromethane which had been distilled and stored over molecular sieves. *p*-Cyanopyridine was recrystallized from xylene and a 0.1 M stock solution prepared in dichloromethane. Aliquots (1.5 mL) of the stock diazirine solution were placed in multiple sample tubes and the heterocycle concentration adjusted by addition of varying amounts of the *p*-cyanopyridine stock so-

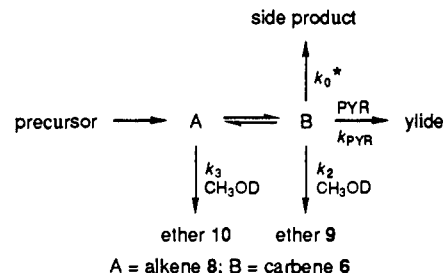
lution or neat pyridine. The total volume of all samples was kept constant by the addition of  $\text{CH}_2\text{Cl}_2$ . Pyridine was distilled from barium oxide and stored over potassium hydroxide pellets. Experiments performed with pyridine employed concentrations ranging from  $1.24 \times 10^{-4}$  to  $4.76 \times 10^{-1}$  M at 20 °C and from  $1.24 \times 10^{-4}$  to 1.48 M at -60 °C.

(c) **Time Constant Studies.** Aliquots of stock solutions of diazirine in  $\text{CH}_2\text{Cl}_2$  were used and pyridine was added to adjust the concentrations of pyridine which ranged from 0.0083 to 3.09 M. The lifetime of the growth of the ylide varied between 17 and 25 ns as calculated by the Marquadt algorithm on the Macintosh Iix. These numbers correspond to the time resolution of the flash photolysis apparatus. At -60 °C it was possible to resolve the growth when the pyridine concentration was 0.00476 M with  $t = 55$ –74 ns.

(d) **Stern-Volmer Rates.** Multiple samples with fixed concentration of pyridine or *p*-cyanopyridine were employed. Various concentrations of olefinic quenchers were generated by addition of neat olefin to the samples and the total volume kept constant by addition of  $\text{CH}_2\text{Cl}_2$ . TME, styrene, 1-methyl-1-cyclohexene, and cyclohexene were purified by distillation and collected and stored over 4 Å molecular sieves. Methanol, spectral grade (Aldrich), was purified by distillation from sodium methoxide and stored over 4 Å molecular sieves. Methanol-*d* gold label was obtained from Aldrich and used as received. The *p*-cyanopyridinium ylide was quenched with styrene, cyclohexene, 1-methyl-1-cyclohexene, and tetramethylethylene in the presence of *p*-cyanopyridine concentrations of  $9.61 \times 10^{-1}$  M. A second quenching study with TME was performed with a concentration of *p*-cyanopyridine of  $1.92 \times 10^{-1}$  M. Quenching of the same ylide with methanol and methanol-*d* was performed with [*p*-cyanopyridine] =  $1.07 \times 10^{-1}$  M. Stern-Volmer quenching studies of the pyridinium ylide were performed in the same manner with TME and methanol-*d* at 20 and -60 °C. Quenching with TME was performed in the presence of  $5.15 \times 10^{-2}$  M pyridine at 20 °C and  $7.73 \times 10^{-1}$  M pyridine at -60 °C. Quenching of the pyridinium ylide with methanol-*d* at 20 °C was performed in the presence of  $4.12 \times 10^{-2}$  M pyridine and at 1.24 M pyridine at -60 °C.

## Appendix 1

The equations that follow refer to the mechanism



$$\phi^0 = \{k_{\text{PYR}}[\text{PYR}][\text{B}]\} / \{k_{\text{PYR}}[\text{PYR}][\text{B}] + k_0[\text{B}]\} \quad (1)$$

$$\phi = \{k_{\text{PYR}}[\text{PYR}][\text{B}]\} / \{k_{\text{PYR}}[\text{PYR}][\text{B}] + k_2[\text{CH}_3\text{OD}][\text{B}] + k_3[\text{CH}_3\text{OD}][\text{A}] + k_0[\text{B}]\} \quad (2)$$

$$[\text{A}] = [\text{B}]K$$

$$\phi = \{k_{\text{PYR}}[\text{PYR}][\text{B}]\} / \{k_{\text{PYR}}[\text{PYR}][\text{B}] + k_2[\text{CH}_3\text{OD}][\text{B}] + k_3[\text{CH}_3\text{OD}][\text{B}]K + k_0[\text{B}]\} \quad (3)$$

$$\frac{\phi^0}{\phi} = \frac{k_{\text{PYR}}[\text{PYR}] + k_2[\text{CH}_3\text{OD}] + k_3K[\text{CH}_3\text{OD}] + k_0}{k_{\text{PYR}}[\text{PYR}] + k_0} \quad (4)$$

$$\frac{\phi^0}{\phi} = \frac{(k_{\text{PYR}}[\text{PYR}] + k_0) + (k_2 + k_3K)[\text{CH}_3\text{OD}]}{k_{\text{PYR}}[\text{PYR}] + k_0} \quad (5)$$

$$\frac{\phi^0}{\phi} = 1 + \frac{k_2 + k_3K}{k_{\text{PYR}}[\text{PYR}] + k_0} [\text{CH}_3\text{OD}] \quad (6)$$

When  $[\text{PYR}] > 0.04$  M,  $k_{\text{PYR}}[\text{PYR}] \gg k_0$ . The slope of a plot of  $\phi^0/\phi$  versus  $\text{CH}_3\text{OD}$  is given by eq 7

$$\text{slope} = (k_2 + k_3K) / k_{\text{PYR}}[\text{PYR}] \quad (7)$$

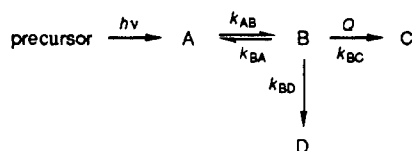
If only carbene 1 reacts with quencher as with tetramethylethylene (TME) the slope of a plot of  $\phi^0/\phi$  versus alkene quencher is given by eq 8

$$\text{slope} = k_{\text{TME}} / k_{\text{PYR}}[\text{PYR}] \quad (8)$$

(34) Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* 1988, 110, 7143.

**Appendix 2**

The postulated mechanism is consistent with the simple form shown below



where C is the species monitored by LFP. C corresponds to a pyridinium ylide. D corresponds to the product of reaction of carbene with solvent, precursor, or impurities.

$$dC/dt = k_{BC}[Q][B] \quad (1)$$

At time = 0,  $A = A_0$ ,  $B = 0$ ,  $C = 0$ , and  $D = 0$ , where  $A_0$  is the concentration of intermediate A formed in the laser flash. At time =  $t$ ,  $A_0 = A + B + C + D$  where A, B, C, and D are the concentrations of these species at time  $t$ . As

$$K = A/B \quad (2)$$

then

$$A_0 = BK + B + C + D$$

and as

$$C/D = k_{BC}[Q]/k_{BD}$$

then

$$A_0 = BK + B + C + [k_{BD}/(k_{BC}[Q])]C \quad (3)$$

$$B(K+1) = A_0 - C \left( 1 + \frac{k_{BD}}{k_{BC}[Q]} \right) \quad (4)$$

$$B = \frac{A_0 - k'C}{K+1} \quad (5)$$

where  $k' = 1 + k_{BD}/(k_{BC}[Q])$ .

Substitution for the value of B of eq 5 into eq 1 yields

$$\frac{dC}{dt} = k_{BC}[Q] \left( \frac{A_0 - k'C}{K+1} \right) \quad (6)$$

$$\frac{dC}{dt} = -k_{BC}[Q] \left( \frac{k'C - A_0}{K+1} \right) \quad (7)$$

$$\int_0^C \frac{dC}{k'C - A_0} = \int_0^t -\frac{k_{BC}[Q]}{K+1} dt \quad (8)$$

Integration of eq 8 yields eq 9

$$\left( \frac{1}{k'} \right) [\ln (k'C - A_0)] = -\frac{k_{BC}[Q]}{K+1} t + \ln I \quad (9)$$

where  $I$  is a constant of integration

$$\ln (k'C - A_0) = -\left[ \frac{k'k_{BC}[Q]}{K+1} \right] t + \ln I \quad (10)$$

Recall that

$$k' = 1 + \frac{k_{BD}}{k_{BC}[Q]} = \frac{k_{BC}[Q] + k_{BD}}{k_{BC}[Q]}$$

from eq 5, then

$$\ln [k'C - A_0] = -\left[ \frac{(k_{BC}[Q] + k_{BD})}{K+1} \right] t + \ln I \quad (11)$$

$$(k'C - A_0) = I \exp \left[ \frac{(-k_{BC}[Q] - k_{BD})}{K+1} t \right] \quad (12)$$

$$C = \frac{A_0}{k'} + \left( \frac{I}{k'} \right) \exp \left[ \frac{(-k_{BC}[Q] - k_{BD})}{K+1} t \right] \quad (13)$$

The boundary condition that  $C = 0$  at  $t = 0$  and that  $C = A_0/k'$  at  $t = \infty$  requires that  $I = -A_0$ . Then at  $t = \infty$  eq 14 is valid

$$C = A_0 \left( \frac{k_{BC}[Q]}{k_{BC}[Q] + k_{BD}} \right) \quad (14)$$

and as  $Q \rightarrow \infty$  then  $C = A_0$  at time =  $\infty$ . Recasting (14) in terms of the postulated mechanism yields eq 15

$$[16a] = \frac{A_0}{k'} - \frac{A_0}{k'} \exp \left[ \frac{(-k_{PYR}[PYR] - k_0)}{K+1} t \right] \quad (15)$$

where  $A_0$  is now the initial concentration of alkene **2** formed after the laser flash. When  $[PYR] \geq 0.04$  M the ylide yield is saturated and  $k_{PYR}[PYR] \gg k_0$  and  $k_{obs} = k_{PYR}[PYR]/(K+1)$ .