Dicarbomethoxycarbene. A Laser Flash Photolysis Study

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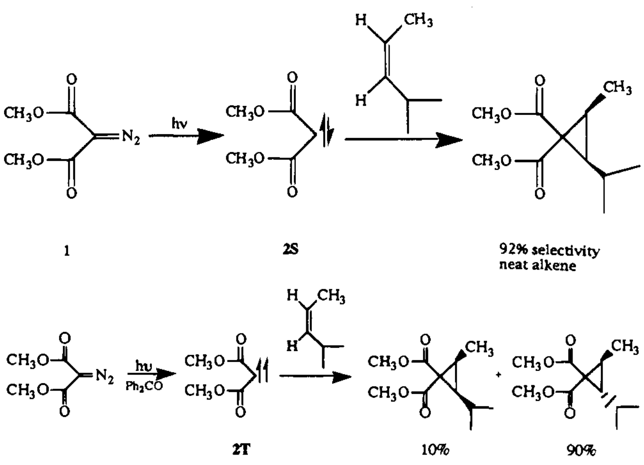
Abstract: Dimethyl diazomalonate (**1**) was studied by laser flash photolysis (LFP) techniques. LFP of **1** generates dicarbomethoxycarbene (**2**), which can be intercepted with pyridine to give a UV–vis active ylide. Analysis of the yield of ylide as a function of pyridine concentration provides estimates of the carbene lifetime in various solvents, of its rate constant for Wolff rearrangement, of its reaction with various quenchers, and of intersystem crossing.

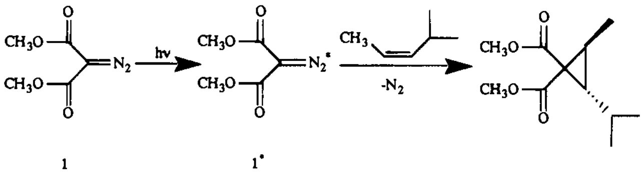
I. Introduction

Diazomalonates are easy to synthesize and handle. Consequently they have been frequently employed in both synthetic and mechanistic organic chemistry.[1] In fact, careful studies of dicarbomethoxycarbene (**2**) by chemical methods illustrate the principles and issues dominating contemporary carbene chemistry.[2]

Jones and co-workers[2] concluded that singlet **2S** likely adds stereospecifically to alkenes, and that the triplet carbene **2T** produced by benzophenone (Ph_2CO) sensitized photolysis of **1** reacts with alkenes to form cyclopropanes without maintenance of the stereochemistry present in the original alkene. These results demonstrated immediately that carbene intersystem crossing (ISC) is slow in neat alkene relative to chemical reactions of the carbene (Scheme 1). This is in marked contrast to simple arylcarbenes.[3]

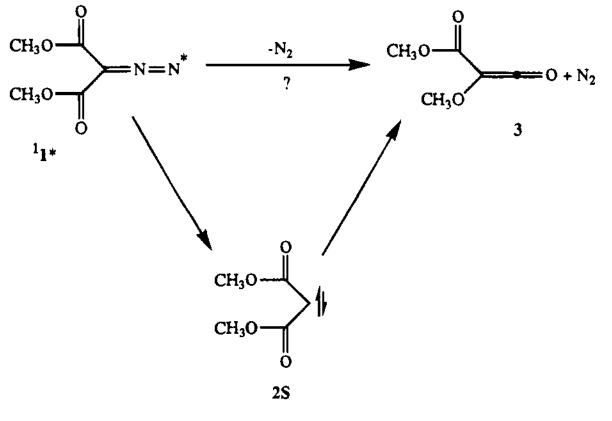


Perfect stereoselectivity was not observed in the cyclopropanation reaction; about 8% of the wrong isomer was formed. This was attributed to intermolecular reactions of a diazo excited state.



This view was supported by the observation that dilution of the alkene trap led to a slight increase in stereoselectivity (92% to 95%) due to decreased efficiency in trapping **1*** prior to deactivation. The stereoselectivity decreases slightly (92% to 87%) at very high dilution of alkene but does not approach the value realized upon triplet sensitization. This is further evidence that ISC (**2S** → **2T**) is slow even in dilute alkene in hexafluorobenzene.

The yield of cyclopropanes realized upon photolysis of **1** in neat alkene varies between 16% and 43% depending on the olefin.[2] Presumably the remainder of the material balance is derived from ketene **3** formed by Wolff rearrangement (WR)



in the excited state of the diazo compound ^{1}**1*** or in singlet carbene (**2S**), or in both species.[2] In fact many groups have by

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[1] (a) Regitz, M.; Maas, G. *Diazo Compounds*; Academic Press: Orlando, FL, 1986. (b) Patai, S. *The Chemistry of the Diazonium and Diazo Group*; Wiley: New York, 1978. (c) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I. (d) Moss, R. A.; Jones, M., Jr. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, p 61. (e) Moss, R. A.; Jones, M., Jr. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, p 95. (f) Marchand, A. P.; Brockway, N. M. *Chem. Rev.* **1974**, *74*, 431. (g) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. (h) Torres, M.; Lown, E. M.; Gunning, H. E.; Strausz, O. P. *Pure Appl. Chem.* **1980**, *52*, 1623. (i) Zeller, K.-P. *Tetrahedron Lett.* **1977**, *8*, 707. (j) Zeller, K.-P.; Meier, H.; Kolshorn, H.; Muller, E. *Chem. Ber.* **1972**, *105*, 1875. (k) Timm, U.; Zeller, K.-P.; Meier, H. *Tetrahedron* **1977**, *33*, 453.

[2] (a) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469. (b) Kammula, S. C.; Tracer, H. L.; Shevlin, P. B.; Jones, M., Jr. *J. Org. Chem.* **1977**, *42*, 293. It is possible that an oxirene intermediate is transiently formed in the rearrangement of **2S**. We have no data to support or discredit this possibility. Thus for the sake of simplicity it is not shown in any of the schemes.

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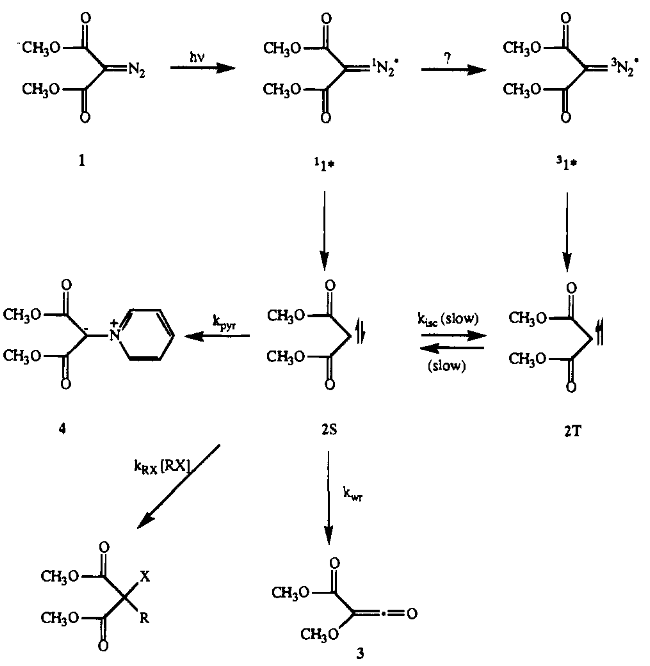
Scheme 1



now presented chemical evidence for the role of excited state diazo and diazirine precursors as mimics of the carbene processes.[4]

Thus, as part of our continuing interest in precursor excited states[5] and carbene rearrangements,[6] the diazomalonate–dicarbomethoxycarbene system appeared to be an ideal candidate for study by laser flash photolysis (LFP) methods.[7] Herein we are pleased to report the results of this study which reinforces and extends the ideas developed by previous researchers, especially Jones *et al.*[2]

II. Results and Discussion

II.1. Diazomalonate. LFP (XeF, 351 nm, 17 ns, 50 mJ) of dimethyl diazomalonate in cyclohexane, 1,1,2-trifluorotrichloroethane (Freon-113), benzene, and acetonitrile fails to produce a UV–vis active transient intermediate. However LFP of **1** in Freon-113 at ambient temperature in the presence of pyridine produces the transient spectrum of Figure 1. Weaker transient spectra of the same species were observed in cyclohexane and benzene but the transient could not be detected in acetonitrile.

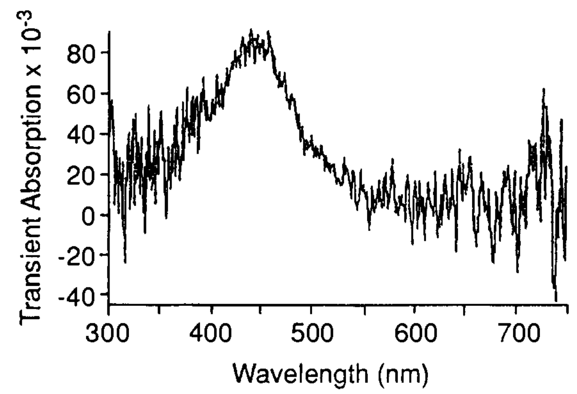
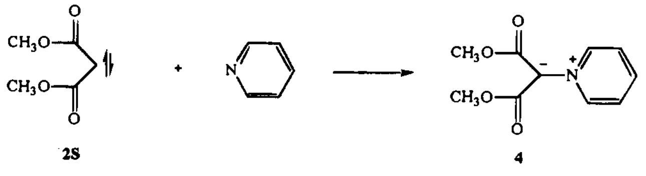
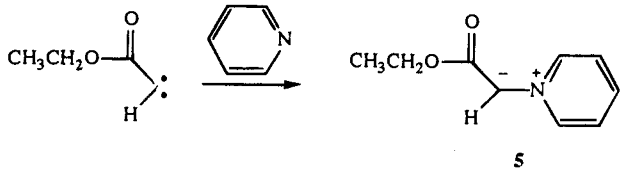


Figure 1. Transient spectrum of ylide **4** produced by LFP of **1** in Freon-113 containing 1.45 M pyridine at ambient temperature. The spectrum was recorded over a window of 175 ns, 50 ns following the laser pulse.

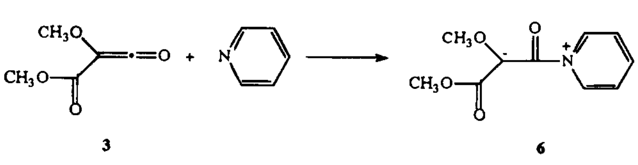
The transient is attributed to ylide **4** obtained by trapping of singlet carbene **2S**,



by analogy to the closely related carbethoxycarbene ylide **5** obtained by interception of carbethoxycarbene,[8]



and to many other carbene–pyridine ylides detected in recent years.[9] The possibilities that the ylide might be derived from reactions of an excited state of the diazo precursor **1*** or from ketene **3** will be considered but rejected (*vide infra*).



Pyridine ylide **4** is formed faster than the time resolution of our apparatus (Figure 2). However it is possible to measure the optical yield (A_y) of ylide as a function of pyridine concentration. Of course A_y is zero when pyridine is absent and increases steadily as the concentration of pyridine is increased. A plot of A_y versus [pyridine] (Figure 3) reveals that the yield of ylide is saturated (A_y^∞) when [pyridine] exceeds 0.4 M. Above this concentration of pyridine, every carbene generated in the laser pulse is captured prior to Wolff rearrangement or reaction with solvent.

The quantum yield of ylide formation ϕ_y is given in eq 1. Here ϕ_c is the quantum yield of carbene formation and the

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(3) (a) Gutsche, C. D.; Bachman, G. L.; Correy, R. S. *Tetrahedron* **1962**, *18*, 617. (b) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. (c) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153. (d) Baer, T. A.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 5180. (e) Moss, R. A.; Dolling, U.-H. *J. Am. Chem. Soc.* **1971**, *93*, 954. (f) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013.

(4) (a) Frey, H. M. *Adv. Photochem.* **1966**, *4*, 225. (b) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 3101. (c) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (d) Chang, K.-T.; Schecter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (e) Frey, H. M.; Stevens, I. D. R. *J. Am. Chem. Soc.* **1962**, *84*, 2647. (f) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1964**, 4700. (g) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072. (h) Wulfman, D. S.; Poling, B.; McDaniel, R. S., Jr. *Tetrahedron Lett.* **1975**, 4519. (i) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516. (j) LaVilla, J. A.; Goodman, J. L. *Tetrahedron Lett.* **1990**, *31*, 5109.

(5) (a) Platz, M. S.; White, W. R., III; Modarelli, D. A.; Celebi, S. A. *Res. Chem. Intermed.* **1994**, 175–193. (b) Chidester, W.; Modarelli, D. A.; White, W. R., III; Whitt, D. E.; Platz, M. S. *J. Phys. Org. Chem.* **1994**, *7*, 24–27. (c) Celebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8613. (d) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (e) White, W. R., III; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841.

(6) Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R., III; Mullins, M.; Celebi, S.; Toscano, J. P. *Prog. React. Kinet.* **1994**, *19*, 93. Our data are also consistent with limitation of the carbene lifetime due to cyclization to an oxirene rather than by Wolff rearrangement to a ketene. This view is not preferred because ketenes can be trapped upon decomposition of **1** but oxirenes cannot.

(7) Platz, M. S.; Maloney, V. M. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 239.

(8) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popic, V. *J. Am. Chem. Soc.* **1994**, *116*, 8146.

(9) Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 89–160.

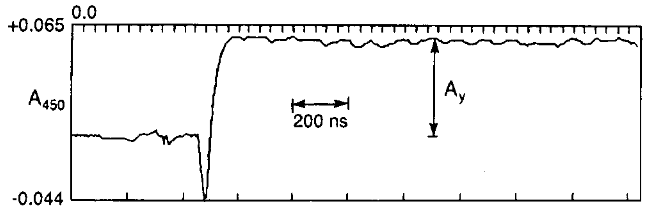

Figure 2. Rate of formation of ylide **4** in solvent containing 0.4 M pyridine.

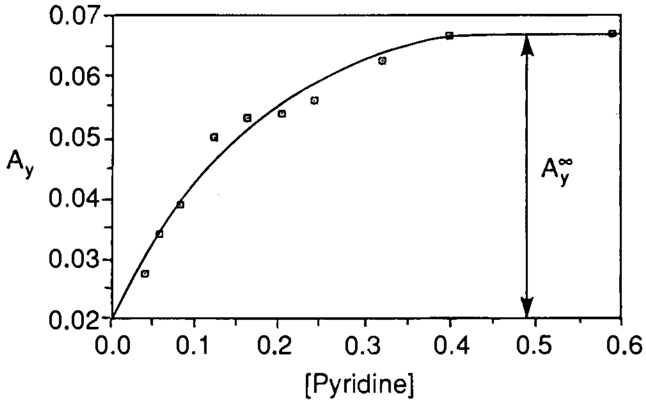

Figure 3. Plot of A_y versus [pyridine] in Freon-113.

$$\phi_y = \frac{\phi_c k_{pyr}[\text{pyridine}]}{k_{wr} + k_{rx}[\text{rx}] + k_{pyr}[\text{pyridine}]} \tag{1}$$

relevant rate constants are as defined in Scheme 1. The optical yield of ylide is related to ϕ_y by eq 2.

$$A_y = \phi_y A_y^\infty \tag{2}$$

Combining and rearranging eqs 1 and 2 leads to eq 3.[6]

$$\frac{1}{A_y} = \frac{k_{wr} + k_{rx}[\text{rx}]}{\phi_c A_y^\infty} \frac{1}{k_{pyr}[\text{pyridine}]} + \frac{1}{\phi_c A_y^\infty} \tag{3}$$

Thus a plot of ($1/A_y$) versus (1/[pyridine]) is predicted and found (Figure 4) to be linear. Division of the intercept by the slope of this plot gives the ratio $k_{pyr}/(k_{wr} + k_{rx}[\text{rx}]) = k_{pyr}\tau$ assuming that all of the decay processes of the carbene proceed through its singlet state and that relaxation to the triplet ground state[10] of the carbene is slow. These assumptions are dictated by the previously cited product study. These ratios are given in Table 1 as a function of solvent. Values of k_{pyr} are expected[6,9] to range between 1×10^9 and 5×10^9 $M^{-1}\ s^{-1}$ for singlet carbene **2S**, which indicates the very large values of $k_{wr} + k_{rx}[\text{rx}]$ of $>10^9\ s^{-1}$ in hydrocarbon solvents and of $>10^8\ s^{-1}$ in Freon-113.

The ISC rate of singlet diphenylcarbene is on the order of $10^{9-10}\ s^{-1}$.[11] ISC rates depend upon the magnitude of singlet–triplet gaps, the nature (open or closed shell) of the lowest electronic state of the singlet carbene, and the matching of vibrational levels of the singlet and triplet states.[12] The ISC rates of non-aryl carbenes are unknown, as are the values of the parameters which control these rates. However, our intuition suggests that ISC in dicarbomethoxycarbene is slower than in diarylcarbenes. We note that very large dilution of the alkene trap with hexafluorobenzene solvent is required for some singlet dicarbomthoxycarbene spin relaxation but that spin equilibration of diphenylcarbene is complete in neat alkene.[13]

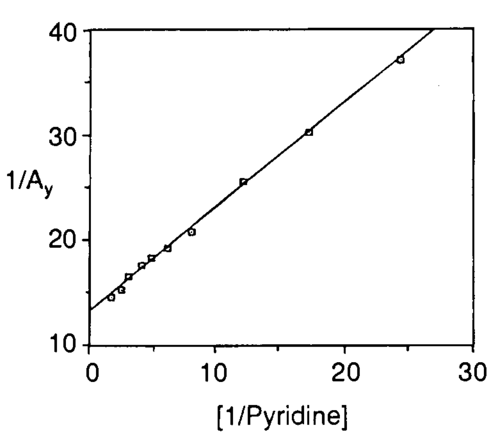

Figure 4. Double reciprocal treatment of the data of Figure 3.

Table 1. Values of $k_{pyr}\tau$ and Deduced Values of τ for Dicarbomethoxycarbene **2S**

solvent	$k_{pyr}/k_{wr} + k_{rx}[\text{rx}]$	τ^a (ns)	A_y^∞ (rel)
$CFCl_2CF_2Cl$	13.2	3–13	1.00[b]
C_6H_6	2.5	0.5–2.5	*c*
c-C_6H_{12}	3.4	0.7–3.5	0.625
c-C_6D_{12}	3.5	0.8–4.0	0.649

[a] Assuming $k_{pyr} = (1-5) \times 10^9\ M^{-1}\ s^{-1}$ and $\tau = 1/(k_{wr} + k_{rx}[\text{rx}])$. [b] By definition. [c] It is difficult to saturate the yield of ylide in benzene due to the very short lifetime of the carbene.

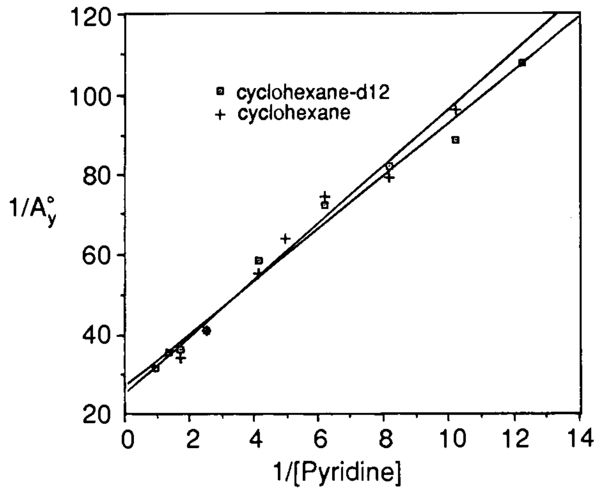

Figure 5. Double reciprocal treatment of ylide yield data in cyclohexane and cyclohexane-d_{12}.

The rather short lifetime of **2S** in benzene is undoubtedly due to the addition of the carbene to the aromatic, a reaction discovered by Jones and co-workers.[2]

There is essentially no solvent isotope effect on the carbene lifetime in cyclohexane (Figure 5). It is likely that the carbene lifetime in this solvent and at this temperature is largely limited by Wolff rearrangement such that $k_{wr} \approx 1/\tau$. There may be a small solvent effect on k_{wr} as τ is deduced to be about twice as long in freon as in cyclohexane. However, this may simply reflect a small solvent effect on k_{pyr}.[14] Jones *et al.*[2] discovered

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(10) Roth, H. D.; Hutton, R. S. *Tetrahedron* **1985**, *41*, 1567.

(11) (a) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

(12) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111. (b) Michl, J.; Bonacic-Koutecky, U. *Electronic Aspect of Organic Photochemistry*; Wiley: New York, 1990; Chapter 1.

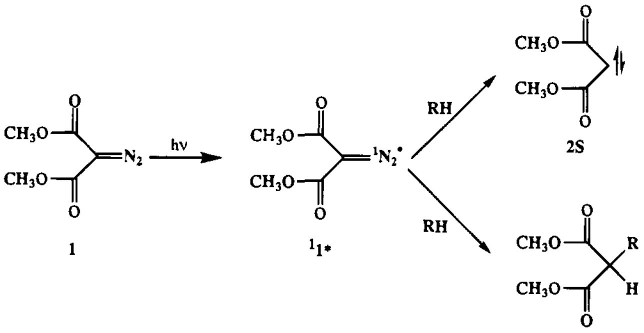
(13) Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193.

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

that photolysis of **2** in alkanes leads to C−H insertion adducts. In principle this may be due to capture of ^{1}**1*** or **2S** or both species. Recall, however, that the carbene lifetime is the same in cyclohexane and in cyclohexane-d_{12}. This immediately seems to exclude the carbene as the source of the formal C−H insertion adducts. A comparison of A_y^∞ in Freon-113 with that in cyclohexane is even more convincing. The data (Table 1) indicate that approximately twice as much carbene is produced in Freon-113 as in cyclohexane, per laser flash. This indicates that there is an invisible intermediate (^{1}**1***) which partitions between reaction with the C−H bonds of the solvent and decomposition to form carbene.

Further support for the ^{1}**1*** as the source of the formal C−H insertion adducts is provided by the observation that 4% more trappable carbene is produced in cyclohexane-d_{12} than in cyclohexane, per laser pulse.

We do not believe that ^{3}**1*** is the origin of the formal C−H insertion adducts because Jones *et al.*[2] have reported that the yield of these adducts is drastically reduced upon triplet sensitization. Furthermore, LFP of **1** in xylene fails to produce benzylic radicals as expected for hydrogen atom abstraction reactions of triplet diazomalonate.



Our conclusion that ^{1}**1*** forms C−H insertion adducts is simply the intermolecular variant of the belief that diazo excited states can suffer intramolecular C−H rearrangement concurrent with nitrogen extrusion.[5,6] We feel that this process requires more study, but at this preliminary stage, we are not prepared to speculate on the mechanistics details of the reaction of ^{1}**1*** with alkanes to form adducts. These results lead us to wonder whether ^{1}**1*** may react with alkenes to form cyclopropanes as suggested by Jones *et al.*[2] Our data does not exclude this possibility. Unfortunately, we cannot test this speculation at present because the carbene lifetime is very short in neat alkene (relative to alkanes) and thereby prevents the use of the pyridine ylide probe technique in concentrated solutions of alkenes.

Our failure to detect **4** in acetonitrile is worthy of note. This negative result may be due to a polar solvent effect on the mode of decomposition of ^{1}**1*** (the partitioning of ^{1}**1*** to carbene or ketene) or to a solvent effect on the carbene lifetime. It may even be due to the formation of a nitrile ylide with a poor or inaccessible chromophore.

II.2. Carbene, Ketene, or Diazo Excited State Reaction with Pyridine? Jones and co-workers were able to measure the relative reactivities of dicarbomethoxycarbene **2S** with various alkene traps in cyclopropanation reactions.[2] Singlet dicarbomethoxycarbene **2S** was found to be rather unselective as expected for a very short lived intermediate (Table 2).[2]

The yield of ylide (A_y) in Freon-113 is saturated (A_y^∞) when [pyridine] > 0.4 M. Under these conditions, every dicarbomethoxycarbene **2S** generated in a laser pulse is captured by pyridine and $1/\tau = k_{pyr}$[pyridine], with $k_{pyr} = (1-5) \times 10^9$ M^{-1} s^{-1} and $\tau = 3-13$ ns. In the presence of a second carbene quencher [Q] (Scheme 2), the yield of ylide is reduced such that eq 4 is valid when [pyridine] > 0.4 M.[6,9] Plots of A_y^∞/

$$\frac{A_y^\infty}{A_{\text{ylide}}} = \frac{1 + k_q[Q]}{k_{pyr}[\text{pyridine}]} \tag{4}$$

A_y versus [Q] are predicted and found (Figure 6) to be linear. Deduced values of k_q are listed in Table 2.

The excellent agreement between the relative reactivities determined chemically in concentrated mixtures of alkenes and by LFP in the presence of relatively dilute alkene demonstrates that the same intermediate is trapped to form cyclopropanes and pyridine ylides. As the cyclopropane-forming intermediate is stereospecific, it has been identified as singlet dicarbomethoxycarbene. This correspondence validates our assignment of the transient as carbene rather than ketene[15] derived. As the LFP work is performed with relatively dilute alkene, we do not expect that either pyridine or alkene has trapped ^{1}**1*** because very small dilution of neat alkene increases the stereospecificity

Scheme 2

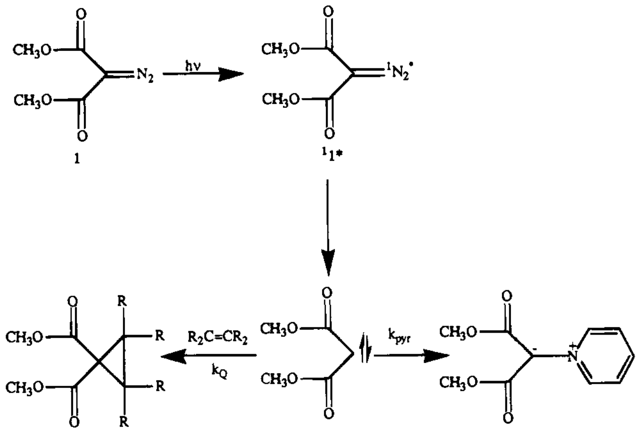
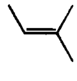
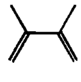
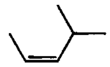
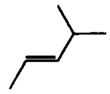
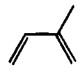
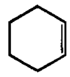


Table 2. Relative Rates of Addition of Singlet Dicarbomethoxycarbene to Olefins ([pyridine] = 0.62 M)

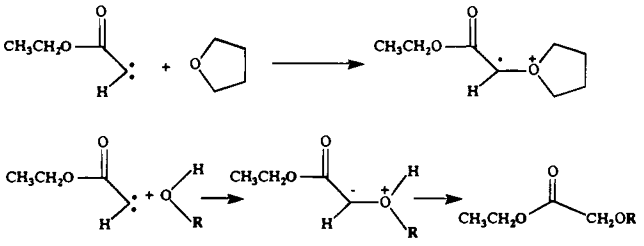
	k_q(M^{-1}s^{-1})^a	Relative Rates^b LFP	Relative Rates^c Chemical Analysis
	3.5 x 10^8	1.00^d	1.00^d
	5.2 x 10^8	1.47	1.30
	2.6 x 10^8	0.74	0.88
	3.1 x 10^8	0.88	0.55
	1.43 x 10^8	0.40	0.23
	4.3 x 10^8	1.23	------
	3.8 x 10^8	1.07	------

[a] Assuming $k_{pyr} = 1 \times 10^9$ M^{-1} s^{-1}. [b] This work. [c] Determined by Jones et al., ref 2. [d] By definition, relative rates should be compared down vertical columns and not across horizontal columns.

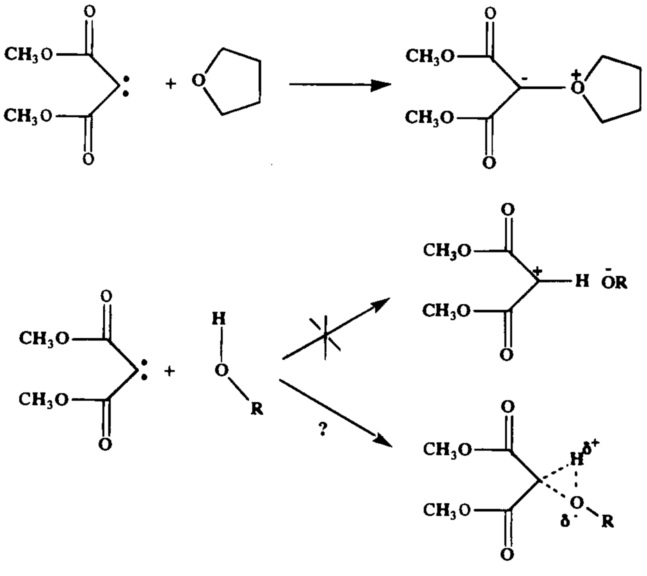
of cyclopropanation.[2] It also demonstrates that ISC in the singlet carbene is slow and that under LFP conditions it is reasonable to expect that all of the carbene decay proceeds through singlet state reactions.

The relative reactivities of various alcohols and ethers toward singlet dicarbomethoxycarbene were determined as with alkenes. The data are presented in Table 3.

It is immediately obvious that alcohols react slightly more rapidly than ethers with carbene **2S**. This is in contrast to carbethoxycarbene, which reacts more rapidly with ethers[8] than with alcohols. This was attributed to ylide formation with the carbene monoester, although the ylides could not be detected by transient UV–vis spectroscopy. These results were in accord with expectations.[16]



The lack of a THF/THF-d_8 isotope effect indicates that **2S** also reacts with ethers to form ylides, rather than by CH/D insertion. However, it seems clear that **2S** must react with alcohols by a different mechanism. A proton transfer mechanism seems unreasonable in this system, we prefer to think of the insertion into the O–H bonds of alcohols as concerted but with some charge development.



II.3. A Cyclic Diazodiester. In order to gain insight into the role that conformation plays in the photochemistry of α-diazodiketones, we have also examined a cyclic analogue (**5**) of dimethoxy diazomalonate by laser flash photolysis methods. Kaplan, Meloy, and Mitchell first suggested that the photochemistry of diazoketones could be strongly influenced by conformational factors.[17] They demonstrated that α-diazoketones exist in solution as a mixture of *syn* and *anti* conformers. Further experiments indicated that the photochemical Wolff rearrangement takes place preferentially from the *syn* conformer, where concerted backside displacement of nitrogen by the migrating R group is possible. Thus, it can be expected that, relative to dimethyl diazomalonate, Wolff rearrangement should be much more facile for **5**, which is locked in a *syn* conformation. Indeed Jones *et al.* found that photolysis of **5** in neat alkene gives very poor yields of cyclopropanes.[2]

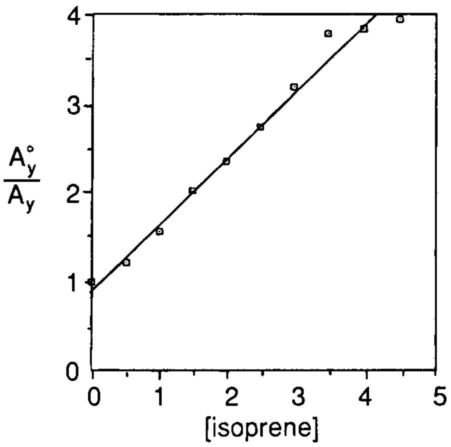
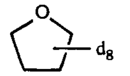


Figure 6. Plot of A_y^∞/A_y versus [isoprene] at constant [pyridine] = 0.62 M.

Table 3. Deduced Rate Constants for Reaction of Singlet Dicarbomethoxycarbene with Alcohols and Ethers

Quenchers	k_q(M^{-1} s^{-1})[a]	Relative Reactivity
CH3OH	1.5x10^9	1.00[b]
CH3OD	1.4x10^9	0.93
CF3CH2OH	2.2x10^9	1.47
CH3CH2OH	1.9x10^9	1.27
	4.3x10^8	0.35
 d$_8$	4.5x10^8	0.30

[a] Assuming k_{pyr} = 1 × 10^9 M^{-1} s^{-1} ([pyr] = 0.62 M). [b] By definition.

LFP (308 nm) of **5** in acetonitrile or Freon-113 fails to produce a UV–vis active transient intermediate. However, LFP

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[15] Cyclic aryl ketenes react with pyridine to form UV–vis active ylides: (a) Boate, D. R.; Johnston, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858. (b) Barra, M.; Fisher, T. A.; Cernigliaro, G. J.; Sinta, R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2630. (c) Andraos, J.; Chiang, Y.; Huang, C.-G.; Kresge, A. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 10605.

[16] Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 89–160.

[17] (a) Kaplan, F.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 950. (b) Kaplan, F.; Mitchell, M. L. *Tetrahedron Lett.* **1979**, 759.

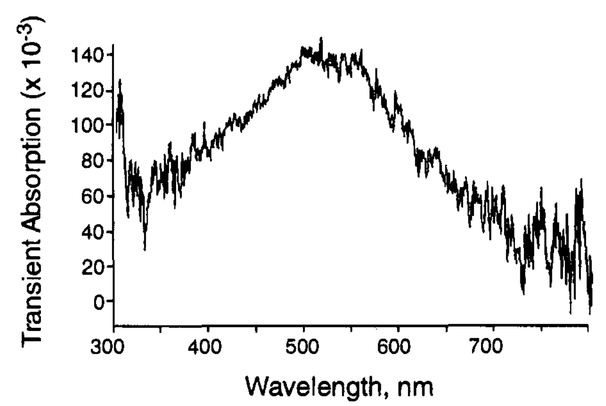


Figure 7. Transient spectrum of ylide **8** formed by LFP of **5** in Freon-113 containing 0.4 M pyridine.

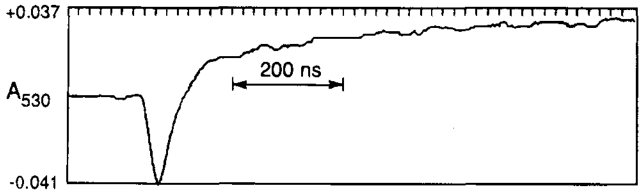


Figure 8. Formation of ylide **8** in acetonitrile containing 0.82 mM pyridine following LFP of **5**.

of **5** in these solvents in the presence of only millimolar concentrations of pyridine produces an intense transient signal (460 nm in acetonitrile, 530 nm in Freon-113) (Figure 7). The transient grows in over many hundreds of nanoseconds (Figure 8). Recall that dimethyl diazomalonate required fairly substantial concentrations of pyridine (0.1–0.4 M) to trap the carbene generated by LFP. Moreover, in this case, the carbene–pyridine ylide is formed within the 20 ns period of the laser pulse such that $k_{growth} > 5 \times 10^7$ s^{-1}. Thus, we attribute the transient formed upon LFP of **5** in the presence of small concentrations of pyridine to ketene–pyridine ylide **8** rather than carbene–pyridine ylide **9** as shown in Scheme 3.[15]

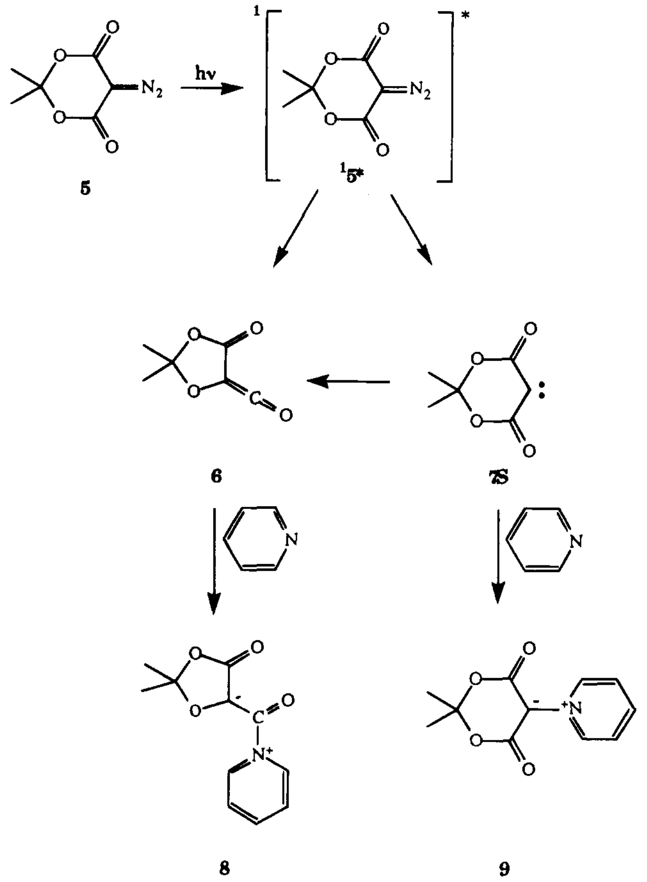
The lifetime of ketene **6** and the rate constant of its reaction with pyridine were determined by examining the growth of ylide **8** in acetonitrile as a function of pyridine concentration. Under these conditions, $k_{obs} = k_o + k_{pyr}$[pyridine], where k_o is the sum of all rate constants of all first-order and pseudo-first-order processes which consume the ketene in the absence of pyridine. Thus, a plot (Figure 9) of k_{obs} vs [pyridine] is predicted and found to be linear. From this plot, the lifetime of ketene **6** ($\tau = 1/k_o$) is calculated to be 2.4 μs with $k_{pyr} = 3.6 \times 10^9$ in acetonitrile. These values agree quite well with the previous work of Scaiano and co-workers,[15] who studied a series of 2-diazo-1,4-naphthoquinones and the ketenes and ketene–pyridine ylides derived from them.

III. Conclusions

Laser flash photolysis of dimethyl diazomalonate (**1**) produces a transient species which reacts with pyridine to form a UV–vis active ylide. The transient is identified as singlet dicarbomethoxycarbene because it displays the same selectivity for alkenes as determined by Jones *et al.*[2] by chemical analysis of cyclopropanes. The singlet carbene lifetime τ (which is equal to $1/(k_{wr} + k_{rx}[\mathrm{rx}])$, where k_{wr} and k_{rx} are rate constants for Wolff rearrangement and reaction with solvent) is deduced to be 1–4 ns in cyclohexane and cyclohexane-d_{12}. The lifetime values so deduced depend on the assumption that all of the carbene chemistry in these solvents proceeds through the singlet state of the carbene.

The lack of a solvent isotope effect on the carbene lifetime indicates that the carbene lifetime in alkanes at ambient

Scheme 3



temperature is controlled by Wolff rearrangement to form ketene.[2] The lack of a solvent isotope effect on the carbene lifetime indicates that the formal C–H insertion adducts formed on photolysis of dimethyl diazomalonate (**1**) in alkanes, discovered by Jones,[2] are produced from reactions of the diazo singlet excited state (^{1}**1***). This is confirmed by the observation that the yield of trappable carbene produced per laser pulse is much greater in freon solvent than in cyclohexane. Furthermore, the yield of trappable carbene produced per laser pulse in cyclohexane-d_{12} is slightly greater than that realized in cyclohexane. Very little carbene is produced in acetonitrile, which may indicate that the partitioning of ^{1}**1*** to form ketene and carbene may be subject to a polar solvent effect or that the carbene reacts in this solvent to form a nitrile ylide which is not UV–vis active.

A cyclic analogue of **1** was also studied by LFP. Flash photolysis in acetonitrile produces a long lived ketene which reacts with pyridine to form an ylide.

IV. Experimental Section

Materials. Dimethyl diazomalonate[18] and its cyclic derivative[19] were prepared according to literature procedures. Solvents (Aldrich) were used as received unless otherwise specified. Benzene and THF were distilled from sodium/benzophenone. Cyclohexane and methanol were distilled from sodium. Pyridine was distilled and stored over KOH. Isoprene, cyclohexene, 2,3-dimethyl-2-butene, 2,3-dimethyl-1,3-butadiene, 2-methyl-2-butene, *cis*-4-methyl-2-pentene, *trans*-4-methyl-2-pentene, and 1,1,2-trichlorotrifluoroethane were passed through an alumina column immediately before use.

Typical Procedure for Laser Flash Photolysis Experiments. The

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(18) Regitz, M. *Chem. Ber.* **1966**, *99*, 3128.

(19) (a) Eistert, B.; Geiss, F. *Chem. Ber.* **1961**, *94*, 929. (b) Korobitsyna, I. K.; Nikolaev, V. A. *Zh. Org. Khim.* **1976**, *12*, 1244.

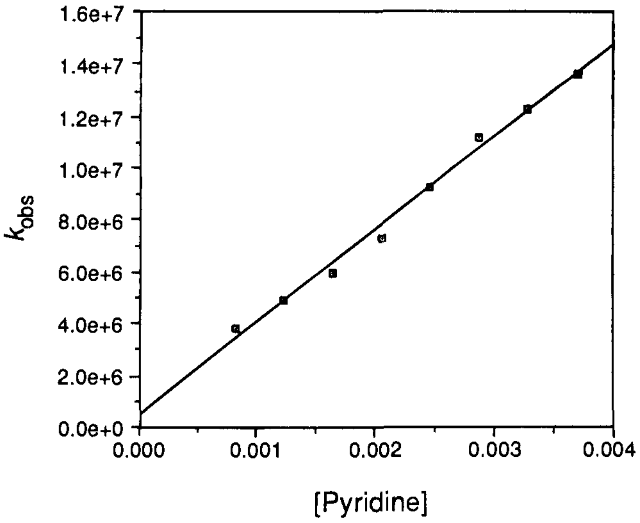

Figure 9. Plot of k_{obs} versus [pyridine] generated by LFP of **5**.

LFP apparatus in use at OSU has been described previously.[20] Stock solutions of the diazo compounds in dry solvents were typically prepared to an optical density ~1.0 at 308 or 351 nm for lifetime experiments. A constant volume of the stock solution was added to Suprasil quartz cuvettes. (Typically, 10 cuvettes were used per experiment.) To each cuvette was added varying amounts of pyridine until [pyridine] ≈ 0.8 M. Solvent was then added to each cuvette in order to maintain a constant volume of sample throughout the experiment. Samples were degassed by purging with dry, oxygen-free argon for 2−3 min. Three transient spectra were recorded for each cuvette, with an average value of A_y used in the data analysis.

Stern−Volmer quenching experiments were performed similarly. Here, stock solutions consisted of **1** in Freon-113 containing 0.62 M pyridine. Quencher concentrations were typically varied from 0 to between 2 and 4 M for a series of 8−10 cuvettes.

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(20) 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.