of the filtrate revealed it to contain *cis*- and *trans*-**6** in a ratio of 85:15, which could not be improved by extending the reaction time or performing the epimerization reaction with sodium methoxide in methanol. Following evaporation of the solvent, the 85:15 mixture was enriched in the trans isomer by column chromatography using Merck 60 silica gel and cyclohexane–diethyl ether, 9:1 v/v, as the eluant. The fraction most enriched in *trans*-**6** contained *cis*- and *trans*-**6** in a 1:1 ratio; further enrichment proved to be impossible because silica gel catalyzes the epimerization of *trans*-**6** into its cis isomer. From the ^{13}C NMR spectra ($CDCl_3$) of pure *cis*-**6** and of the 1:1 mixture of the cis and trans isomers, the following resonances could be assigned to *trans*-**6**: 211.93 (C-2), 58.06 (C-1), 49.64 (C-6), 41.46 (C-3), 32.22, 30.79, 27.91, 22.50, 21.45. EIMS (70 eV), *m/z* (rel intensity): 138 (M^+, 11), 110 ($M^+ - CO$, 7), 97 (12), 96 (13), 95 (100), 82 (7), 81 (11), 80 (5), 79 (20), 68 (15), 67 (71). CIMS (CH_4), *m/z* (rel intensity): 139 ($M^+ + 1$, 62), 121 ($M^+ - H_2O$, 100).

Bicyclo[4.3.0]non-1(6)-en-2-ol (8). This compound was prepared by reduction of BNEN according to the method of Luche.[19] BNEN (136 mg, 1 mmol) was dissolved in 2.5 mL of a methanol solution of 0.4 M $CeCl_3{\cdot}7H_2O$. To this was slowly added 1 mmol of $NaBH_4$ over a 2-min period with constant stirring. The mixture was allowed to react at room temperature for 20 min, followed by addition of water and extraction with ether. The ether extracts, after being dried over sodium sulfate, were concentrated to give a yellow oil, which was purified on a silica gel column using 10:1 petroleum ether–diethyl ether as the eluant. The resulting material gave only a single peak at 2.72 min on GC analysis under our standard set of conditions. Coinjection with a sample of the 2-propanol photolysate of BNEN on the GC capillary column showed enhancement of the product peak present at 2.718 min relative to that of residual BNEN at 2.975 min. On GC/MS analysis, allylic alcohol **8** showed major peaks at 138 (M^+, 33), 120 ($M^+ - H_2O$, 19), 110 ($M^+ - C_2H_4$, 100), 95 (75), 92 (36) 91 (67), 79 (60), 77 (37), 67 (64), 66 (33), and 41 (58). The CI (CH_4) mass spectrum of **8** exhibits a weak parent peak at the correct mass (*m/z* 139 ($M^+ + 1$, 6)) and an intense peak at *m/z* 121 ($M^+ - H_2O$, 100), but lacks the fragmentation peak at *m/z* 110 ($M^+ - 28$). The EIMS spectrum of **8** shows *m/z* (rel intensity) 120 ($M^+ - H_2O$, 22), 94 (37), 91 (12), 81 (13), 80 (12), 79 (100), 77 (14), 67 (55). ^{13}C NMR ($CDCl_3$): 139.87 (C-1), 136.10 (C-6), 66.48 (C-2), 36.48 (C-3), 33.05 (C-9), 32.85 (C-7), 26.17 (C-5), 22.00 (C-4), and 19.60 (C-8). ^1H NMR ($CDCl_3$): 4.15 (br s, C*H*OH), and unresolved multiplets at 2.5, 2.3, and 1.0–2.0 ppm.

(*Z*-(1,6))-Bicyclo[4.3.0]nonan-2-ol (9). Compound **9** was prepared by exhaustive hydrogenation ($p(H_2)$ = 4.8 bar, 5 days) of a solution of BNEN (200 mg) in ethyl acetate with 100 mg of Adams' catalyst (hydrated PtO_2). After evaporation of the solvent, the crude product was separated from **6** by column chromatography. This afforded 45 mg of pure **9**. ^1H NMR ($CDCl_3$): δ 3.94 (m, 1 H, H2), 2.22 (m, 1 H, H1), 1.93 (m, 1 H, H6), 1.75–0.89 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ 71.49 (C-2), 46.34 (C-1), 40.10 (C-6), 31.52, 29.43, 27.04, 23.94, 21.35, 21.05. CIMS (NH_3), *m/z* (rel intensity): 157 ($M^+ + NH_3$, 1), 141 (M^+, 2), 140 (1), 139 (8), 124 (10), 123 ($M^+ - H_2O$, 100), 121 (25).

BNEN–Cyclopentene Adducts. The stoichiometries of the 1:1 and 2:1 BNEN–cyclopentene adducts were inferred from their CI and EIMS spectra. The EI and CIMS spectra of the 1:1 and 1:2 BNEN–cyclopentene adducts display molecular ion peaks at the correct mass and strong peaks due to fragmentation of one or both cyclopentenyl groups from the parent ion.

Acknowledgment. D.I.S. and the NYU group are indebted to the National Science Foundation (CHE-8900099) for financial support. We thank Professor Richard A. Caldwell (University of Texas at Dallas), Professor Silvia E. Braslavsky and Mrs. Sigi Griebenow (Max-Planck Institut für Strahlenchemie, Mülheim, FRG) for their help in obtaining the photoacoustic calorimetry data, and Laura Cerruti and Robert D. Hudson (Hewlett Packard Company, Paramus, NJ) for some GC/MS analyses. Finally, we are grateful to Dr. V. C. Scaiano for allowing us to use the nanosecond laser flash photolysis apparatus in his laboratory at the National Research Council in Ottawa, where much of the kinetic studies were performed, and for his advice and encouragement.

Carbene Formation, Hydrogen Migration, and Fluorescence in the Excited States of Dialkyldiazirines†

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Contribution from the Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210. *Received March 9, 1992*

Abstract: Photolysis of 3,3-dimethyldiazirine produces an electronically excited singlet state which decays by at least three competitive pathways: (1) fluorescence, (2) nitrogen extrusion and carbene formation, and (3) α-hydrogen migration and propylene formation concurrent with nitrogen extrusion. The temperature dependence of the fluorescence intensity was determined.

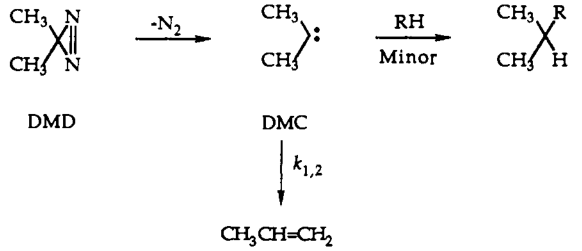
I. Introduction

Methylene (CH_2) is by now a rather well-understood compound.[1] The geometries of singlet and triplet CH_2 have been determined by gas-phase spectroscopy, and the singlet–triplet energy separation between these states has been determined experimentally.[2]

The intermolecular chemistry of $^1CH_2$ and $^3CH_2$ in the gas phase and in solution is also well documented.[3] The reactions of methylene in solution have been studied by CIDNP spectroscopy,[4] and Turro has analyzed the dynamics of these processes using nanosecond laser flash photolysis techniques.[5]

Progress in the study of alkylcarbenes and dialkylcarbenes has evolved more slowly. It is difficult to intercept dialkylcarbenes with chemical traps in better than very low yields presumably because of the facility of their intramolecular rearrangements (Scheme I), particularly 1,2 hydrogen or carbon migrations.[3,6]

Scheme I



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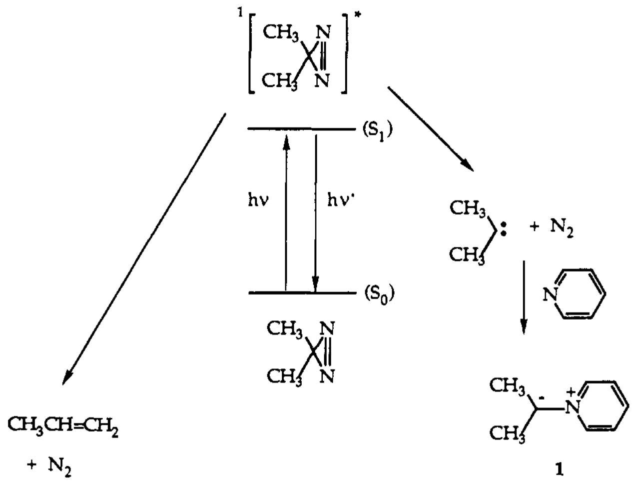
† This paper is dedicated to the memory of Professor Gerhard L. Closs.

(1) For a review, see: Shavitt, I.; *Tetrahedron* **1985,** *41,* 1531.

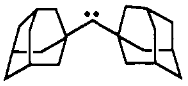
0002-7863/92/1514-7034$03.00/0 © 1992 American Chemical Society

Scheme II



Exceptions to this rule are 2,3-diphenylcyclopropanylidene,[7] diadamantylcarbene,[8] adamantanylidene,[9] and 9-phenyl-[10] and desphenylhomocubanylidene,[11] which exhibit plentiful intermolecular chemistry. In all of these cases intramolecular rearrangement leads to a very highly strained reaction product. This retards the rate of intramolecular reactions, which allows successful intermolecular capture of the carbene.

To our knowledge, simple alkyl- and dialkylcarbenes such as dimethylcarbene (DMC) cannot be generated as *persistent* species in rigid cryogenic media and characterized by spectroscopic methods.[12] The only dialkylcarbenes that have been successfully studied by matrix techniques are di-*tert*-butylcarbene[13] and diadamantylcarbene,[8] carbenes which both lack an α-CH bond.



Perfluoroalkylcarbenes have been detected by matrix EPR spectroscopy.[14] In this case the exceptional strength of the α-CF bonds inhibits intramolecular 1,2 fluorine rearrangement. This results in a very long lifetime of the perfluorinated carbene in a cryogenic matrix.

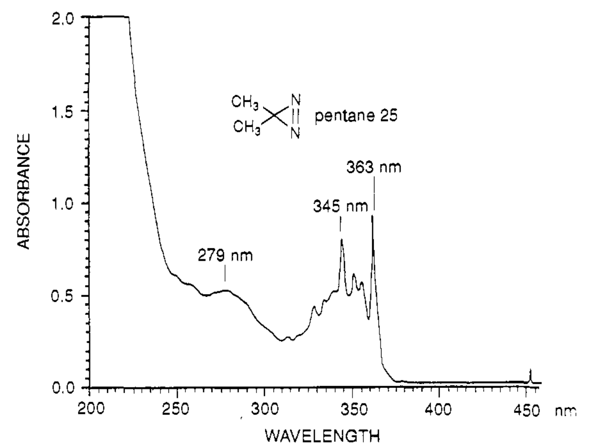


Figure 1. The absorption spectrum of DMD in pentane at ambient temperature.

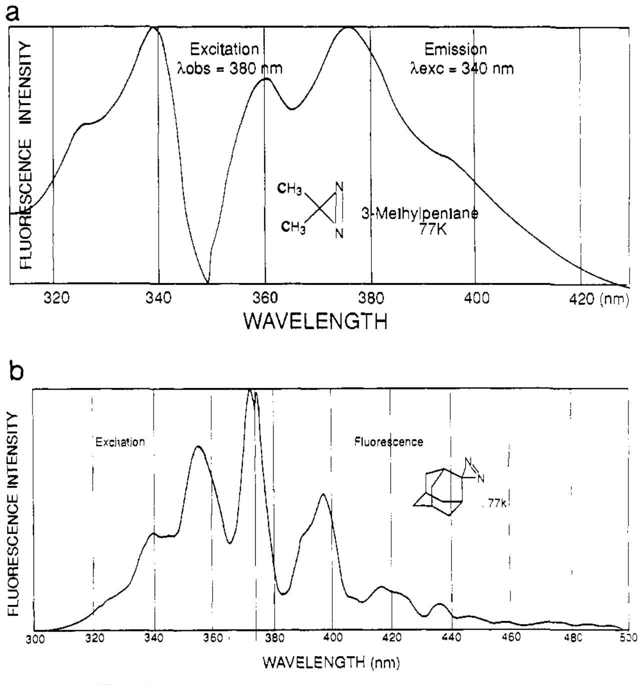
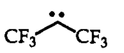
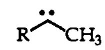


Figure 2. The fluorescence and fluorescence excitation spectra of (a) DMD and (b) adamantyldiazirine in 3-methylpentane at 77 K.





R = phenyl, Cl, OCH_3

Certain alkyl-substituted carbenes are persistent in matrices because they are stabilized by phenyl[15] or heteroatom substitution of the carbene center.[12]

The lack of success in chemical trapping of simple dialkylcarbenes in reasonable yields[6] and in detecting these intermediates by spectroscopic methods[12] has been attributed to the rapid rate of intramolecular rearrangement processes. Presumably the 1,2 hydrogen shift is faster than the rate of bimolecular trapping and cannot be frozen out at low temperature.

However, it has also been long appreciated that some of the rearrangement products can, in principle, arise from reactions of the excited state of the carbene[16a–e] or of an excited state of the

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(2) (a) Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *83*, 4849. (b) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251.

(3) For reviews, see: Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes Vol. I*; Jones, M. B., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; pp 2–19.

(4) (a) Roth, H. D. *J. Am. Chem. Soc.* **1972**, *94*, 1761. (b) Roth, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 1527. (c) Roth, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4935. (d) Roth, H. D. *J. Am. Chem. Soc.* **1972**, *94*, 1400.

(5) (a) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4417. (b) Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 2101.

(6) (a) Kramer, K. A. W.; Wright, A. N. *Tetrahedron Lett.* **1962**, 1095. (b) Frey, H. M. *J. Chem. Soc.* **1962**, 2293.

(7) (a) Jones, W. M.; Grasley, M. H.; Baarda, D. G. *J. Am. Chem. Soc.* **1964**, *86*, 912. (b) Jones, W. M.; Walbrick, J. M. *J. Org. Chem.* **1969**, *34*, 2217.

(8) (a) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232. (b) Morgan, S.; Platz, M. S.; Jones, M., Jr.; Myers, D. R. *J. Org. Chem.* **1991**, *56*, 1351.

(9) (a) Moss, R. A.; Chang, M. J. *Tetrahedron Lett.* **1981**, *22*, 349. (b) Adding, A. C.; Strating, J.; Wynberg, H.; Schlatmann, J. L. M. A. *Chem. Commun.* **1966**, 657. (c) Isaeu, S. D.; Yuchenko, A. G.; Stepanov, F. N.; Kolyada, G. G.; Novikov, S.; Karpentko, N. F. *J. Org. Chem. USSR* (*Engl. Transl.*) **1973**, *9*, 724. (d) Bayley, H.; Knowles, J. R. *Biochemistry* **1978**, *17*, 2420; **1980**, *19*, 3883. (e) Morgan, S. C.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2783.

(10) (a) Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285. (b) Eaton, P. E.; Appell, R. B. *J. Am. Chem. Soc.* **1990**, *112*, 4053.

(11) (a) Chen, N.; Jones, M. B., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305. (b) Chen, N.; Jones, M. B., Jr. *Tetrahedron Lett.* **1989**, *30*, 6969. (c) Chen, N.; Jones, M. B., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981.

(12) (a) Sheridan, R. S. *Organic Photochemistry Vol. 8*; Dekker: New York, 1987; p 159. (b) Recently, however, McMahon has trapped ethylidene with carbon monoxide in a cryogenic matrix: McMahon, R. J. Personal communication.

(13) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326.

(14) Wasserman, E.; Barash, L.; Yager, N. A. *J. Am. Chem. Soc.* **1965**, *87*, 4974.

(15) (a) Trozzolo, A. M.; Wasserman, E. In *Carbenes Vol. II*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; p 185. (b) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683. (c) Chapman, O. L.; Johnson, J. N.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 50. (d) Haider, K. W.; Platz, M. S.; Despres, A.; Migirdicyan, E. *Chem. Phys. Lett.* **1989**, *164*, 443.

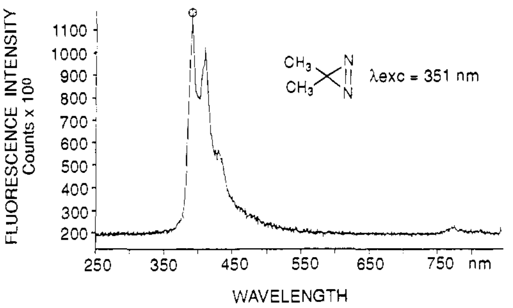


Figure 3. Laser induced fluorescence spectrum of 3,3-dimethyldiazirine in pentane at ambient temperature.

carbene precursor.[16f,g] These interpretations were prompted by the observatioin that different mixtures of rearrangement products are produced upon thermal- and light-induced decomposition of nitrogenous precursors of dialkylcarbenes.[16]

This has prompted this study of the decomposition of 3,3-dialkyldiazirines using laser flash photolysis and fluorescence techniques. Our data demonstrate that the photoexcited state of 3,3-dimethyldiazirine decays by at least three processes: (1) fluorescence, (2) nitrogen extrusion and carbene formation, and (3) 1,2 hydrogen migration and alkene formation concurrent with nitrogen extrusion (Scheme II). The relative importance of the various excited state decay pathways depends upon the nature of the alkyl group and on temperature.

II. Results

IIA. Fluorescence Spectroscopy. The absorption spectrum of 3,3-dimethyldiazirine (DMD) is given in Figure 1. The fluorescence spectrum of DMD and the fluorescence excitation spectrum of DMD are given in Figure 2a. There is a reasonable mirror-image relationship between the emission and fluorescence excitation spectra. The absorption and the fluorescence excitation spectra of dimethyldiazirine are also similar, which demonstrates that the emission is from DMD and not from an impurity. Further support for this interpretation comes from the observation that the vibrational spacing present in the fluorescence spectrum of DMD (1190 cm^{-1}) corresponds to an IR active mode of the diazirine (1239 cm^{-1}). Diazirine fluorescence appears to be a general phenomenon but is quite weak. The mirror-image relationship between the fluorescence and fluorescence excitation spectra of adamantyldiazirine (Figure 2b) is in fact more clearly evident than that of dimethyldiazirine. To our knowledge there are only a few reports in the literature[16g,17] of diazirine fluorescence. The fluorescence and absorption bands have been assigned to the diazirine nπ^* singlet excited state.[17d] The laser-induced fluorescence of dimethyldiazirine in pentane at ambient temperature is given in Figure 3. The LIF spectrum of DMD (Figure 3) is better resolved than the classically obtained spectrum of Figure 2a and is more clearly related to the absorption spectrum of Figure 1.

The fluorescence of DMD at ambient temperature is rather weak. However, the fluorescence intensity of DMD increases substantially as the temperature is decreased. In fact an Arrhenius treatment of the data is linear (Figure 4). There is precedent for this observation as Mirbach et al. have reported similar effects with cyclic azo compounds.[18]

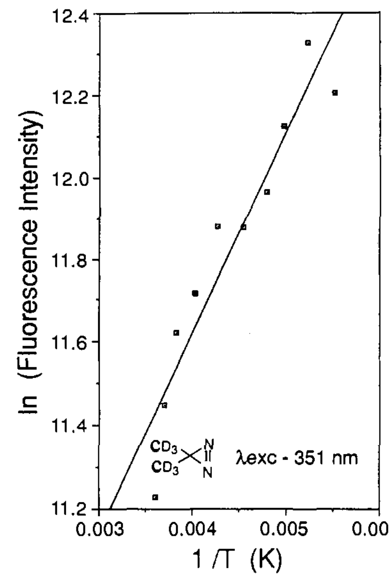
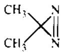
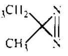
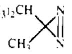
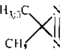
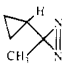
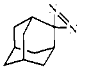


Figure 4. Arrhenius treatment of the fluorescence intensity of DMD-d_6 as a function of temperature.

Table I. Fluorescence and Absorption Spectral Data of Dialkyldiazirines in Pentane at Ambient Temperature (λ_{ex} = 351 nm)

Diazirine	Absorption λ_{max}(nm)	Emission λ_{max}(nm)
 DMD	328, 334, 339, 344, 352, 355, 364	386, 404
 DMD-d_6	338, 344, 352, 355, 362	386, 403
	330, 336, 346, 352, 357, 364	386, 404
	330, 336, 346, 353, 357, 364	386, 404
	330, 345, 353, 357, 364	386, 404
	330, 344, 352, 363	381, 403
	332, 348, 354, 362, 366	380, 404
	342, 352, 372, 372	380, 392, 400

3,3-Dimethyldiazirine-d_6. The spectroscopic properties of DMD-d_6 generally recapitulate the DMD observations but with one important exception. The intensity of the fluorescence obtained from DMD-d_6 is 1.55 ± 0.20 times larger than that observed from DMD under identical conditions, at ambient temperature.

The fluorescence of neither DMD nor DMD-d_6 is quenched to an appreciable extent by methanol, tetramethylethylene, or pyridine (8 M). Diazirine fluorescence is quenched, however, by molecular oxygen.

The fluorescence of dialkyldiazirines appears to be a general phenomenon. All of the dialkyldiazirines of Table I fluoresce and have excitation spectra which closely match the absorption spectra. The fluorescence intensities of all of the diazirines of Table I increase upon cooling. The differential activation energies of these diazirines obtained by Arrhenius treatment of the data are presented in Table II.

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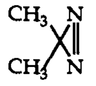
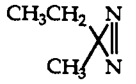
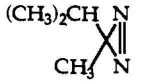
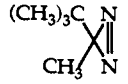
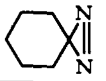
[16] (a) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (b) Kirmse, W.; Buschoff, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 692. (c) Frey, H. M.; Scaplehorn, W. *J. Chem. Soc. A* **1966**, 968. (d) Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (e) One can also argue that these differences arise from a common intermediate subject to dynamical effects; see: Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695. (f) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 1700. (g) Figuera, J. M.; Pérez, J. M.; Tobar, A. *J. Chem. Soc. Faraday Trans. I* **1978**, *74*, 809. (h) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512.

[17] (a) Hepburn, P. H.; Hollas, J. M.; Thakur, S. N. *J. Mol. Spectrosc.* **1925**, *54*, 483. (b) Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122. (c) Sieber, H.; Moomaw, W. R.; Neusser, H. J.; Schlag, E. W. *J. Phys. Chem.* **1991**, *95*, 6958. (d) Merritt, J. A. *Can. J. Phys.* **1962**, *40*, 1683.

[18] Mirbach, M. F.; Mirbach, M. J.; Liu, K.-C.; Turro, N. J. *J. Photochem.* **1978**, *8*, 299.

Table II. The Observed Activation Energy Parameters Associated with the Temperature Dependence of the Intensity of Dialkyldiazirine Fluorescence in Pentane

Diazirine	ΔEa (Kcal/mol)	Temp Range (K)
 DMD	-0.964 ± 0.117	182-279
 DMD-d_6	-1.509 ± 0.139	176-273
	-0.970 ± 0.088	140-260
	-0.629 ± 0.050	123-223
	-0.160 ± 0.018	113-263
	-0.0219 ± 0.0015	125-233

Scheme III

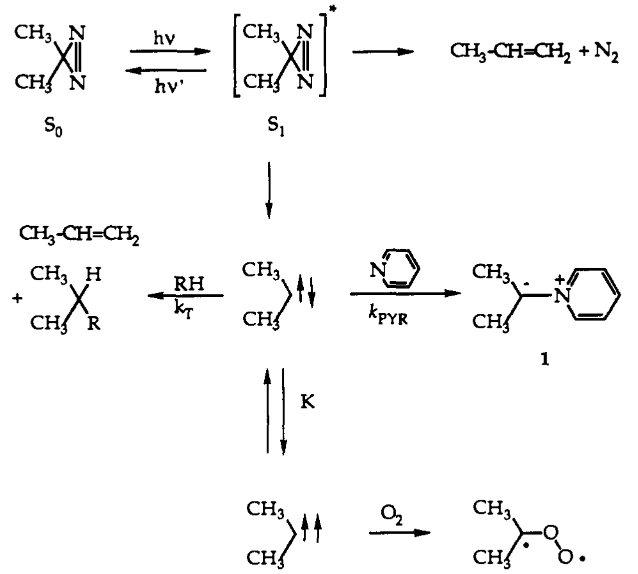
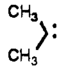
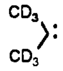
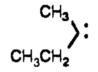


Table III. Dialkylcarbene Lifetimes at Ambient Temperature

carbene	solvent	lifetime, ns[a]	k_D/k_H
	pentane	21	
	α,α,α-trifluorotoluene	27	
	acetonitrile	8	
	acetonitrile-d_3	9	1.07
	chloroform	6.8	
	chloroform-d	7.3	1.08
	pentane	67	$\tau_D/\tau_H = 3.2$
	pentane	2	

[a] Assuming $k_{PYR} = 1 \times 10^9$ M^{-1} s^{-} $\tau = 1/k_T$.

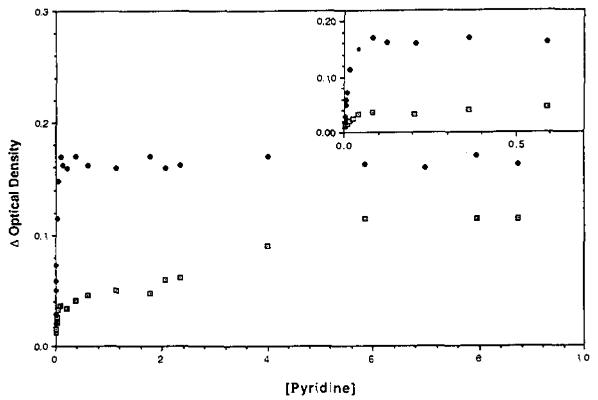
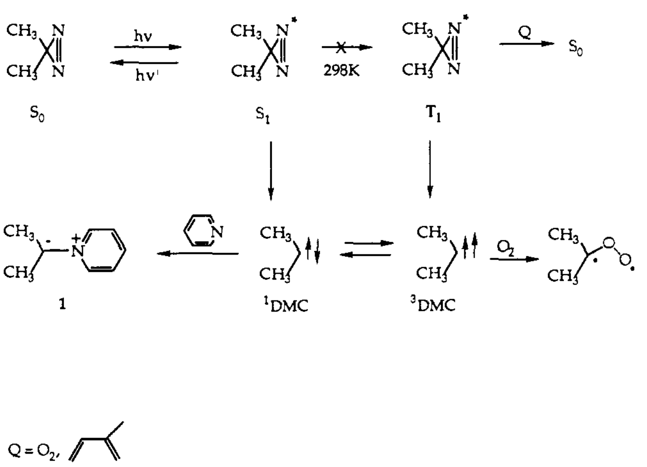


Figure 5. The yield of ylide 1 and 1-d_6 produced by LFP of DMD and DMD-d_6, respectively, in pentane at ambient temperature as a function of pyridine concentration, at identical diazirine concentrations (A_{351} = 0.15) (DMD, squares; DMD-d_6, diamonds).

Scheme IV



IIB. Carbene and Ylide Formation. Laser flash photolysis (LFP, XeF, 50 mJ, 17 ns) of DMD in pentane fails to produce a detectable transient intermediate in the 230–700-nm regime. There is no compelling evidence for intersystem crossing ($S_1 \rightarrow T_1$) in the excited state of dimethyldiazirine at ambient temperature; we cannot detect triplet–triplet transient absorption of T_1 upon LFP of DMD in pentane. Thus the triplet state of DMD either is not formed on direct photolysis of dimethyldiazirine in solution or has an exceptionally short lifetime. However, Frey has been able to interpret gas-phase photolysis data of methyldiazirine in terms of ISC to an excited triplet state of a diazirine, followed by loss of nitrogen to form triplet ethylidene as per Scheme IV.[19]

LFP of DMD in pentane containing pyridine produces an intense transient spectrum with λ_{max} = 364 nm. The transient is attributed to ylide 1 (Scheme II) by analogy to many previous observations of pyridine ylides obtained by the trapping of carbenes with pyridine.[20] The ylide cannot be formed from the reaction

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[19] Frey, H. M. *Adv. Photochem.* **1966**, *4*, 225.

[20] (a) Jackson, J. E.; Platz, M. S. *Advances in Chemical Applications of Lasers*; Brinker, H., Ed.; JAI Press: Greenwich, CT, in press. (b) Jackson, J. E.; Soundararajan, N.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 5595. (c) Jackson, J. R.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874. (e) Morgan, S. C. M.S. Thesis, The Ohio State University, 1989. (f) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (g) Ho, G. J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875. (h) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7298. (i) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638. (j) Chateauneuf, J. E.; Johnson, R. P.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217. (k) Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* **1990**, *112*, 5642. (l) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (m) Our preliminary work with dimethylcarbene has been communicated previously. Modarelli, D.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8985.

of the fluorescent excited state of diazirine **1** because pyridine does not quench the fluorescence of the diazirine.

Unfortunately there is severe spectral overlap between the diazirine fluorescence and the absorption spectrum of the ylide. Thus it is impossible to resolve the growth of the ylide absorption with confidence. We can say that ylide formation is complete within $\approx$150 ns of the laser pulse when the pyridine concentration = 0.004 M.

It is possible to measure the yield of ylide ϕ_y, produced in a laser pulse as a function of pyridine concentration. Of course, $\phi_y = 0$ when pyridine concentration = 0, and ϕ_y grows as pyridine concentration increases. However, with DMD the yield of ylide is saturated when the pyridine concentration > 8 M. In the presence of >8 M pyridine every dimethylcarbene molecule generated from dimethyldiazirine in a laser pulse is captured by pyridine to form the ylide (Figure 5). The yield of ylide obtained from dimethyldiazirine-d_6 in the presence of saturating concentrations of pyridine is 1.50 ± 0.22 (three measurements) times larger than the yield of ylide obtained from dimethyldiazirine. Assuming that ylides **1** and **1**-d_6 have identical extinction coefficients, we deduce that the yield of dimethylcarbene-d_6 produced from dimethyldiazirine-d_6, per laser pulse, is 50% larger than the yield of dimethylcarbene produced from dimethyldiazirine. Significantly, the isotope effect on the yield of diazirine fluorescence is, within experimental error, exactly equal to the isotope effect on the yield of carbene.

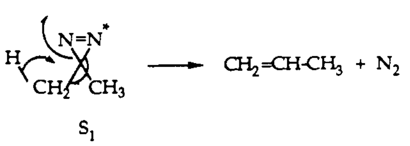
Quenching Studies of Ylide 1. The yield of ylide **1** is decreased by 20% upon LFP of DMD in the presence of oxygen, at constant pyridine concentration. However, the yield of ylide **1** is *not decreased* upon LFP of DMD in the presence of 1.0 M isoprene, at constant pyridine concentration. The latter observation demonstrates that dimethylcarbene is not generated by decomposition of the excited triplet state of dimethyldiazirine (T_1, Scheme IV). This is further evidence that intersystem crossing in the excited singlet state of dimethyldiazirine is insignificant in solution at ambient temperature. Oxygen quenching of the yield of ylide is consistent with the interconversion of singlet and triplet dimethylcarbene prior to rearrangement and reaction with pyridine and/or solvent. However, oxygen quenching of the yield of ylide also results from quenching of the fluorescent excited state of the diazirine precursor.

The yield of ylide **1** is decreased upon LFP of DMD in the presence of CH_3OH, a competitive trap of the carbene, at constant pyridine concentration.

III. Discussion

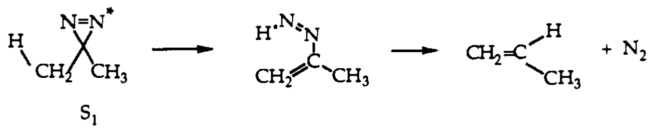
An electronically excited singlet state (S_1) can in general decay by fluorescence,[17] by internal conversion, by chemical reaction, or by intersystem crossing to T_1.[19]

The intensity of the fluorescence of 3,3-dimethyldiazirine-d_6 is significantly larger than that of 3,3-dimethyldiazirine. We think it unlikely that isotopic substitution that is remote from the diazirine chromophore will *increase* the rate constant of fluorescence[21] or *decrease* the rate constant of internal conversion, intersystem crossing, or carbene formation. Furthermore, it is known that isotopic substitution *remote* from the chromophore leads to no change in the lifetime of the $n\pi^*$ triplet states of acetophenone and benzophenone at 77 K.[22] The most likely interpretation of the data is that deuteration reduces the yield of chemical reaction (rearrangement) of the excited state. The data is consistent with 1,2 hydrogen migration concurrent with nitrogen extrusion in the diazirine excited state.



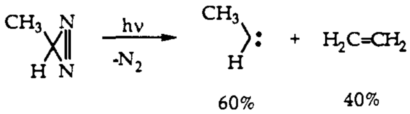
S_1

However, Curran[23] has pointed out that our data is also consistent with the following rearrangement:



S_1

At the present time we cannot distinguish between these alternatives. The direct photochemical formation of alkene from an alkyldiazirine excited state was first proposed by Frey.[16f] In fact, Frey deduced that upon photolysis in the gas phase methyldiazirine decomposes to give ethylidene (methylcarbene) in 60% yield and a 40% yield of ethylene upon extrusion of nitrogen.[16f]



In 1965 Mansoor and Stevens[16a] noticed that the distributions of products formed on pyrolysis and photolysis of ethylmethyldiazirine are considerably different. Pyrolysis of the diazirine yields a mixture of alkenes that is very similar to that obtained by Friedman and Shechter upon pyrolysis of the tosylhydrazone salt.[16h]

Many other observations of this type were reported subsequently from several laboratories.[16b–e] These observations were taken as evidence that a single intermediate cannot be common to both the heat- and light-initiated decomposition of the precursor(s). The mixture of rearrangement products formed on photolysis of the diazirine is typically less regioselective than the mixture of products formed upon thermolysis. This demonstrated that a more reactive, less selective intermediate is generated with light than upon thermal decomposition of the diazirine. Frey and Stevens[16a] and others[16b–e] postulated that photolysis of diazirines produces the carbene in an excited singlet state whereas pyrolysis of the carbene generates the carbene in its lowest singlet state.

The data of this work demonstrates that the excited state of dimethyldiazirine is an intermediate with a finite lifetime in solution. The increase in fluorescence intensity upon deuteration of DMD demonstrates that 1,2 hydrogen (deuterium) migration occurs in the excited state of the diazirine. This provides a more economical interpretation of the product studies reported earlier than postulation of a carbene excited state.

Ylide Formation. As mentioned earlier, LFP of DMD in the presence of pyridine produces the transient spectrum of pyridinium ylide **1**. The transient spectrum is very similar to those of other dialkyl and alkyl chloro carbene–pyridine ylides.[20] The ylide cannot be formed by reaction of pyridine with the excited singlet state of the diazirine (S_1) because pyridine does not quench the fluorescence of dimethyldiazirine.

Oxygen does quench the yield of ylide **1** produced by LFP of DMD in pentane. This result is consistent with oxygen scavenging of the fluorescent excited state of the diazirine and of the triplet state of dimethylcarbene (Scheme III). Alternatively one could imagine that carbene formation proceeds through the triplet state, T_1, of the diazirine precursor (Scheme IV). If this interpretation is correct, the triplet state of the diazirine is also quenched with oxygen, which thereby reduces the yield of ylide (ϕ_y). However, we can rule out this mechanism because isoprene,[24,25] a diffu-

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[21] Swenton, J. S. *Isotope Effects in Organic Chemistry Vol. 1*; Bunsell, Lee, Eds.;

[22] Miller, J. C.; Borkman, R. F. *J. Chem. Phys.* **1972**, *56*, 3727.

[23] We are grateful to Professor Curran for pointing out the possibility of this mechanism.

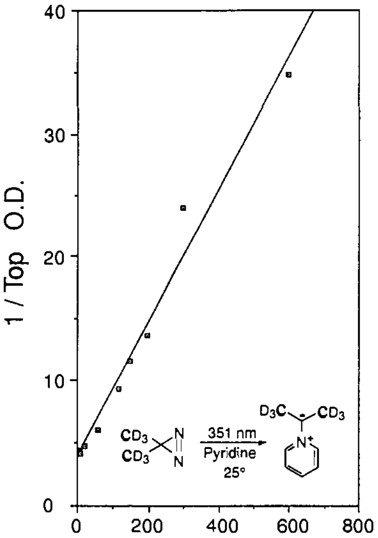
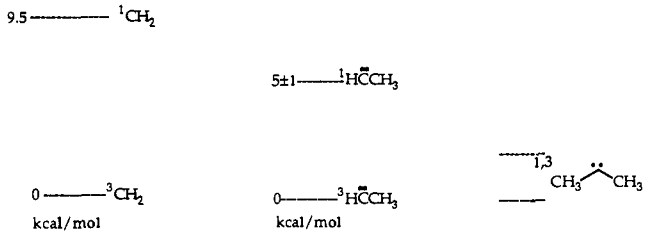


Figure 6. A plot of the inverse of ylide yield ($1/\phi_y$) versus the inverse of pyridine concentration for DMC-d_6 in pentane at ambient temperature.

sion-controlled quencher of triplet excited states with triplet energies in excess of 60 kcal/mol, does not reduce the yield of ylide **1**.

Lineberger[2] has determined that the singlet–triplet energy separation of CH_2 is 9.5 kcal/mol. This value is in good agreement with high-level ab initio molecular orbital calculations.[1] Recently, very high level calculations of methylcarbene have been reported by Gallo and Schaeffer,[26] which predict that the singlet–triplet separation in this system is 5 ± 1 kcal/mol, or about half of that of methylene. Significantly, these calculations are at a level (CISD(DVD)/TZ+2P+f11CISD/DZP) which correctly reproduces the singlet–triplet energy separation of CH_2.



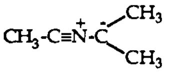
Calculations of a comparable quality are not yet available for dimethylcarbene. If we are allowed to extrapolate from the methylcarbene calculation, we estimate that the singlet–triplet separation of DMC is not significantly different from 0. Thus we expect that singlet and triplet DMC are both accessible species at ambient temperature (Scheme III).

Decomposition of dimethyldiazirine is expected to produce dimethylcarbene in the singlet state. The fact that oxygen, a triplet carbene trap, reduces the yield of ylide **1** is consistent with the idea that carbene intersystem crossing in both directions is competitive with the kinetics of inter- and intramolecular reactions of singlet and triplet dimethylcarbene. The rate constant of 1,2 hydrogen shift is not so large as to preclude intersystem crossing. Intersystem crossing (ISC) of diarylcarbenes is complete within about 0.1–0.25 ns.[27] If we guess that the ISC rate of singlet DMC is comparable, then the rate constant to hydrogen migration in singlet DMC is substantially less than 10^{10} s^{-1}.

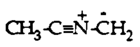
Plots (Figure 6) of the inverse of the yield of ylide (ϕ_y^{-1}) versus the inverse of pyridine concentration are linear as predicted by Scheme III. The ratios of the slopes to the intercepts of these plots are equal to the ratio of k_T/k_{PYR} where k_{PYR} is the absolute rate constant for reaction of ^{1}DMC with pyridine (Scheme III) and k_T is the sum total of all first-order and pseudo-first-order processes (hydrogen migration $k_{1,2}$, reaction with solvent k_{SH}, etc.) which consume DMC in the *absence* of pyridine.

Typical[20] values of k_{PYR} for singlet carbenes are 10^9 M^{-1} s^{-1}, and with chlorophenylcarbene k_{PYR} does not vary significantly with solvent.[28] If we assume that $k_{PYR} = 10^9$ M^{-1} s^{-1} for the reaction of ^{1}DMC with pyridine, we deduce that the lifetime ($\tau = 1/k_T$) of DMC in pentane (pyridine concentration = 0) is about 21 ns. There is a significant isotope effect on the lifetime of DMC in pentane, $\tau_D/\tau_H = 3.2$. The carbene isotope effect is larger than we anticipated but is nevertheless strong evidence that the lifetime of DMC in pentane at ambient temperature is substantially controlled by 1,2 hydrogen (deuterium) migration to form product. The large isotope effect may be due to a contribution of quantum mechanical tunneling to the hydrogen migration reaction.

A small solvent isotope effect on the lifetime of DMC is observed in acetonitrile and chloroform and their deuterated modifications. The solvent isotope effect of 1.07–1.08 is much smaller than that observed for the singlet states of phenylcarbene, 1-naphthylcarbene, and fluorenylidene in cyclohexane, which are close to 2.[29] The data demonstrate that DMC is reacting with solvent but that solvent CH insertion is probably only a minor process in acetonitrile and chloroform. LFP of DMD in acetonitrile does not produce the transient spectrum of nitrile ylide **2**. The absorption maximum of **2** is expected to be near 280 nm as per ylide **3**, which has been studied by Turro.[5] Thus there is no evidence that the lifetime of DMC in acetonitrile is controlled by reaction of the carbene with the nitrile nitrogen.



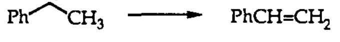
2



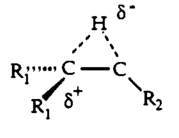
$CH_3\text{-}C\equiv\overset{+}{N}\text{-}\overset{-}{C}H_2$

3

The lifetime of DMC is much shorter in acetonitrile and chloroform than in pentane. We have previously found that the rate constant of 1,2 hydrogen migration of singlet 1-phenylethylidene increases by roughly a factor of 10 upon increasing solvent polarity.[30]



We[30] and others[31] have also found that alkyl substitution on the carbon bearing the migrating hydrogen accelerates the 1,2 rearrangement of hydrogen. The lifetime of ethylmethylcarbene in pentane at 25 °C is 10 times shorter than that of dimethylcarbene under the same conditions. Thus the dialkylcarbene kinetic data correlates exactly with that obtained with arylalkylcarbenes[30] and alkylchlorocarbenes[31] and is indicative of charge development in the hydrogen migration transition state.



R_1 = H or CH_3,

R_2 = CH_3 or phenyl

Alcohol Trapping of Dimethylcarbene. Dimethyldiazirine-d_6 and benzene-d_6 (as an internal standard) in neat methanol were photolyzed in an NMR tube. Deuterium NMR analysis revealed

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(24) Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973; Section 4, p 55-66.

(25) Kellog, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4320.

(26) Gallo, M. M.; Schaefer, H. F., Ill. *J. Phys. Chem.* **1992**, *96*, 1515.

(27) (a) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Sitzmann, E. V.; Eisenthal, K. B. *Applications of Picosecond Spectroscopy to Chemistry*; Reidell: Dordrecht, 1985; p 41. (c) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

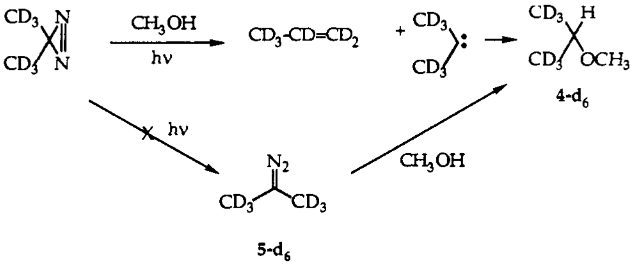
(28) Jones, M. B.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 1694.

(29) (a) Baer, T. A.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 954. (b) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305. (c) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

(30) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966.

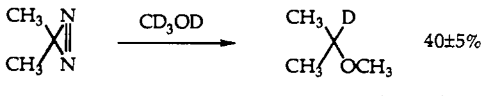
(31) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

that isopropyl-d_6 methyl ether (**4**-d_6) was formed in 52% yield.



As 8 M pyridine completely traps DMC, we expect that neat methanol (23 M) will capture all of the carbene produced from the diazirine as well. Thus we calculate that DMD-d_6 produces a 52% yield of DMC-d_6 and that the excited state of DMC-d_6 yields propylene in as much as 48% yield. Thus the excited state of dimethyldiazirine decomposes to form propylene and carbene with about equal efficiency. One can worry that photolysis of DMD-d_6 might produce diazo compound **5**-d_6 and give an artificially high yield of **4**-d_6. Some support of this view is provided by the observation of a weak diazo IR band at 2050 cm^{-1} upon very low temperature photolysis of DMD in 3-methylpentane. However, we do not feel that diazo formation is important in solution because LFP of DMD in pentane at ambient temperature fails to produce transient absorption in the region (≈250 nm) where dialkyl diazo compounds absorb significantly.

We also studied the photolysis of DMD-d_6 in CH_3OH. The yield of *trapable* carbene produced from DMD-d_6 is 30 ± 15% larger than from DMD, which is consistent with our previously mentioned isotope effects on diazirine fluorescence and ylide yield.



Temperature Effects. The fluorescence intensity of every diazirine of this study increases with decreasing temperature. This demonstrates that the fluorescence rate constant increases relative to the rate constants of other decay processes of the excited state (carbene formation and 1,2 hydrogen migration and alkene formation) as the temperature is lowered. This is not surprising because fluorescence is not an activated process. The data does demonstrate that there must be a barrier to nitrogen extrusion in the excited state (Figure 6). The presence of an orbital symmetry barrier to the loss of nitrogen in diazirine excited states was predicted by Jug and Müller-Remmers.[32] We do not know if there is concerted alkene formation–nitrogen extrusion upon *thermolysis* of dimethyldiazirine. This process is marked with a question mark in Figure 7. The product studies discussed earlier[16] indicate that hydrogen migration is not as serious a concern in thermal as opposed to photochemical decomposition of the nitrogenous precursors.

Conclusions. Photolysis of 3,3-dimethyldiazirine produces an electronically excited singlet state which decays by fluorescence, by nitrogen extrusion and carbene formation, and by α-hydrogen migration and propylene formation concurrent with nitrogen extrusion. The direct formation of alkene in the excited state of the diazirine results in a low yield of carbene that is trapable with external reagents. 1,2 hydrogen migration is not so fast as to preclude interception with external traps such as pyridine. These results are consistent with the work of Evanseck and Houk which predicts a barrier to 1,2 hydrogen migration in singlet dimethylcarbene.[33] The low yield of the carbene–pyridine ylide is readily measured because of the large extinction coefficient of the ylide. The rate of 1,2 hydrogen migration is accelerated by polar solvents and by branching of the alkyl group adjacent to the diazirine moiety. Direct formation of alkene in dialkyldiazirine excited states explains the different mixture of products formed in the thermal and photochemical decomposition of dialkyldiazirines reported by earlier researchers and the failure[12] to generate high concentrations of dialkylcarbenes as persistent species in cryogenic matrices.

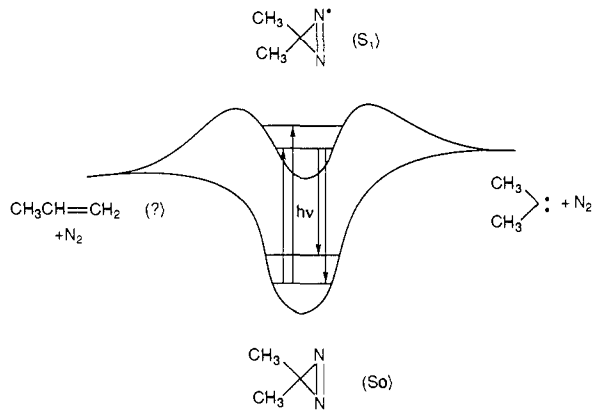


Figure 7. The dimethyldiazirine ground- and excited-state surfaces.

IV. Experimental Section

The LFP system and protocols in use at Ohio State have been described elsewhere;[34] DMD,[35] ethylmethyldiazirine,[36] pentamethylenediazirine,[37] and adamantyldiazirine[38] were prepared by literature procedures. Isopropylmethyldiazirine, *tert*-butylmethyldiazirine, dimethyldiazirine-d_6, and cyclopropylmethyldiazirine were prepared from diaziridines as per the following method.

General Synthesis of Dialkyldiaziridines. The appropriate ketone (0.15 mol) is stirred at −70 °C for 30 min under an argon atmoshere in 50 mL of anhydrous methanol. Ammonia (~55 mL) in 30 mL of methanol is slowly cannulated in, and the solution is stirred for 30 min at −70 °C. (Note: If the ammonia is wet, it may be dried by passage through a column of Drierite.) To this solution was added (over the course of 1 h) a freshly prepared[37a] solution of *tert*-butyl hypochlorite (25.18 g, 0.23 mol) in 25 mL of *tert*-butyl alcohol. **CAUTION!** This addition should be made *very slowly*, as a white gas/precipitate is violently formed. The temperature is maintained at −70 °C throughout the addition. After the addition is completed, the reaction mixture is slowly warmed to 0 °C and stirred for 15 min. The reaction mixture is then stirred at room temperature for another 15 min to boil off some of the excess ammonia, after which the solution is poured over ice and carefully acidified with 25% sulfuric acid. The ketone is removed by extraction with 4 × 50 mL ether, and the aqueous layer is then made alkaline with 2 M NaOH. The diaziridine is extracted from the aqueous layer with ether, dried over $MgSO_4$, and carefully evaporated under reduced pressure to yield the diaziridine as a clear/yellow liquid, which can be used without further purification.

Cyclopropylmethyldiaziridine: IR (neat) 1685 cm^{-1}; NMR ($CDCl_3$, 200 MHz, ppm) 3.47 (br s, 2 H), 1.72 (m, 4 H), 1.35 (s, 3 H), 1.26 (m, 1 H).

Isopropylmethyldiaziridine: IR (neat) 1651 cm^{-1}; NMR (acetone-d_6, 200 MHz, ppm) 3.10 (br s, 2 H), 1.19 (s, 6 H), 1.17 (s, 3 H).

***tert*-Butylmethyldiaziridine**: IR (neat) 1657 cm^{-1}; NMR (acetone-d_6, 200 MHz, ppm) 3.07 (s, 2 H), 1.19 (s, 9 H), 0.95 (s, 3 H).

Dimethyldiaziridine-d_6: IR (neat) 1660 cm^{-1}.

General Synthesis of Dialkyldiazirines. Into a modified three-necked flask (a side neck is attached parallel to the lab bench) is dissolved the diaziridine (0.01 g, 0.0102 mol) in 70 mL of DMSO. A tube (~15 cm long) containing first KOH pellets and then indicating Drierite is attached to the side port of the reaction flask, and to the other side of this is attached a large trap, prepurged with argon and containing 40 mL of pentane (dried over basic alumina). Argon is circulated from the reaction flask, exiting through the trap containing the pentane. The trap is cooled to −70 °C, and the reaction flask is cooled to 0 °C. Jones reagent

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[32] Müller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* **1985**, *107*, 7275.

[33] Evenseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 9148.

[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.

[35] Schmitz, E.; Ohme, R. *Chem. Ber.* **1961**, *94*, 2166.

[36] Paulsen, S. R. *Angew. Chem.* **1960**, *72*, 781.

[37] (a) Mintz, M. J.; Walling, C. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 184. (b) Schmitz, E.; Ohme, R. *Organic Syntheses*; Wiley: New York, 1973; Collect Vol. V, p 897.

[38] (a) Isaev, S. D.; Yurchenko, A. G.; Stepanov, F. N.; Kolyada, G. G.; Novikov, S. S.; Karpenko, N. F. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 1338. (b) Bayley, H.; Knowles, J. R. *Biochemistry* **1978**, *17*, 2420; **1980**, *19*, 3883.

(chromium trioxide, 0.022 mol, and sulfuric acid, 30 mL, 4 M) is added dropwise to the reaction flask (in the case of cyclopropylmethyldiazirine, 0.022 mol of freshly prepared silver oxide is substituted). After 30 min the cooling bath is removed from the reaction flask, allowing the volatile diazirine to be eluted with the carrier gas (Ar), and the diazirine is collected into the pentane. The diazirines are identified by their characteristic UV spectrum: All diazirines synthesized had λ_{max} = 364 nm in pentane except dimethyldiazirine-d_6, for which λ_{max} = 362 nm.

NMR Analysis of Photolyzed Diazirine–Methanol Solutions. The yields of dimethylcarbene-d_6 and dimethylcarbene were measured by analyzing the products of photolysis of methanolic solutions of the diazirines, by NMR spectroscopy. The diazirines were prepared in methanol and methanol-d_4, respectively; a small amount of benzene-d_6 (or benzene) was added as an internal standard. Two peaks are found in the initial ^{2}H-NMR spectrum of dimethyldiazirine-d_6; benzene-d_6 (δ 7.15), and dimethyldiazirine-d_6 (δ 0.749). A third peak appears after 12 h of photolysis at 350 nm (Rayonet) at 4 °C, which is attributed to the insertion product (δ 0.880). When integration against the benzene standard is carried out, we find an ~52 ± 8% yield of carbene insertion product (isopropyl-d_6 methyl ether). The spectra for dimethyldiazirine can be analyzed in the same manner, showing a 40 ± 5% yield of carbene insertion product (isopropyl methyl-d_3 ether).

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Registry No. 1, 136863-30-4; D_2, 7782-39-0; 3,3-dimethyldiaziridine, 5161-49-9; dimethylcarbene, 40852-89-9; cyclopropyl(methyl)diaziridine, 141784-28-3; isopropyl(methyl)diaziridine, 141784-29-4; *tert*-butyl(methyl)diaziridine, 141784-30-7; dimethyldiaziridine, 20686-76-4.

Stabilization of Zero-Valent Hydrazido Complexes by Phosphine Ligands. Crystal Structure of *fac*-$(CO)_3(DPPE)W{=}NNMe_2$, a Nitrene Analogue to Fischer Carbenes

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Abstract: The zero-valent tungsten hydrazido complex $(CO)_5W{=}NNMe_2$ (**2**) reacts with phosphines or phosphites to form *cis*-$(CO)_n(PR_3)_{5-n}W{=}NNMe_2$ (**3**, **8**, and **10**). Spectroscopic data show that these complexes contain bent hydrazido ligands, as does **2**. Kinetics are consistent with substitution of CO by PR_3 via a dissociative process. Complexes **3**, **8**, and **10** are significantly more stable than **2**, with *fac*-$(CO)_3(DPPE)W{=}NNMe_2$ (**10b**) [DPPE = 1,2-bis(diphenylphosphino)ethane] being isolable as a crystalline solid. Complex **10b** was characterized by X-ray crystallography: $P2_1/n$; a = 8.4406 (20) Å, b = 23.9747 (57) Å, c = 16.5073 (41) Å, β = 92.36 (2)°, V = 3337.6 (25) Å^3, Z = 4, $R(F)$ = 6.3%, $R(wF)$ = 7.2%, for 3025 reflections, $F_o > 3\sigma(F_o)$.

Introduction

The generation of zero-valent transition metal nitrene[1,2] (or imido) and hydrazido[3] complexes of the form $L_5M{=}NR$ (**1**) has been the subject of several reports in recent years, but in all cases these compounds have proven too labile for isolation.[1-3] Interest in the preparation of such complexes arises to an extent from their potential to serve as nitrene (NR) transfer agents. Their carbon analogues, Fischer carbenes [$(CO)_5M{=}CRR'$, M = Cr, W], have been observed to undergo a rich variety of transformations involving the incorporation of the carbene moiety into various organic products. Examples include ring annelations,[4] olefin cyclopropanation,[5] and various metathesis reactions.[6]

Systems in which metal nitrene complexes exhibit reactivity parallel to that of Fischer carbenes are rare. Bergman has shown that the imido ligand of Cp*IrN^{t}Bu undergoes a variety of cyclization reactions with unsaturated substrates, including incorporation of the N^{t}Bu fragment into a substituted pyrrole upon reaction with dimethyl acetylenedicarboxylate.[7] There are also several reports in which transition metal nitrene complexes have been proposed to be the reactive species for the transformation of olefins into *N*-tosyl- or *N*-triflylaziridines.[8] In addition to these, many high oxidation state imido complexes undergo metathesis with aldehydes to form imines, a reaction driven by the stability

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(1) (a) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007–8009. (c) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871–4876.

(2) (a) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263–1267. (b) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194–9198. (c) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665–3668. (d) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83–101. (e) Fourquet, J. L.; Leblanc, M.; Saravanamuthu, A.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1991**, *30*, 3241–3243.

(3) Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* **1991**, *10*, 541–543.

(4) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587–608. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *24*, 5813–5832. (c) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433–445.

(5) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411–432. (b) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *60*, 137–144.

(6) (a) Schubert, U. *Advances in Metal Carbene Chemistry*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (b) Weiss, K. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; pp 227–246. (c) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983.

(7) Glueck, D. S.; Jianxin, W.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041–2054.

(8) (a) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517–1524. (b) Mansuy, D.; Mahy, J. P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161–1163. (c) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074. (d) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744–6746. (e) O'Connor, K. J.; Wey, S. I.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001–1004.

0002-7863/92/1514-7041$03.00/0