Rearrangement of Dimethylcarbene to Propene: Study by Laser Flash Photolysis and *ab Initio* Molecular Orbital Theory

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Abstract: Laser flash photolysis (Nd:YAG laser, 355 nm, 35 mJ, 150 ps) of dimethyldiazirine and dimethyldiazirine-d_6 produces dimethylcarbene (DMC) and dimethylcarbene-d_6 (DMC-d_6), respectively. The carbenes were trapped with pyridine to form ylides which absorb around 364 nm. It was possible to resolve the growth of the ylides as a function of pyridine concentration in Freon-113, α,α,α-trifluoromethylbenzene, and perfluorohexane as a function of temperature. The observed rate constant (k_{obs}) of ylide formation was linearly dependent on the concentration of pyridine in all solvents and at all temperatures. From plots of k_{obs} versus [pyridine] it was possible to extract values of k_{pyr} (the absolute rate constant of reaction of the carbene with pyridine) and τ, the carbene lifetime in the absence of pyridine, and their associated Arrhenius parameters. In Freon-113 and α,α,α-trifluoromethylbenzene the carbenes decay both by rearrangement and by reaction with solvent. In perfluorohexane the carbene decay appears to be predominantly unimolecular. The experimental results are compared with *ab initio* molecular orbital calculations. The experimentally determined barrier to disappearance of DMC in perfluorohexane (2.56 ± 0.05 kcal/mol) is much smaller than that calculated (7.4 ± 2 kcal/mol) using *ab initio* molecular orbital theory. The Arrhenius parameters and isotope effects indicate that the rearrangement of DMC in perfluorohexane has a large component of quantum mechanical tunneling. The activation energy for the disappearance of DMC-d_6 in perfluorohexane (5.63 ± 0.03 kcal/mol) is consistent with calculations which indicate that QMT makes only a minor contribution to the deuterated system under the conditions of this study.

I. Introduction

Methylene (CH_2) is the simplest carbene, and methylcarbene (MC) and dimethylcarbene (DMC) are the prototypical alkyl- and dialkylcarbenes. Methylene has been studied extensively by computational and experimental methods.[2] Experiment and theory are in good agreement as to the geometries of the singlet and triplet states of CH_2 and their energy separation.[2,3] Among the experimental methods which have been applied to the study of methylene are gas-phase spectroscopy,[2,4] solution-phase CIDNP[5] and nanosecond (ns) spectroscopy,[6] low-temperature matrix electron paramagnetic resonance (EPR) spectroscopy,[7] and chemical trapping studies in the gas phase and in solution.[8]

Theory predicts that the triplet state of methylene is 9 kcal/mol more stable than the singlet state.[2,3] Methylcarbene is also predicted to have a triplet ground state, but with a much smaller singlet−triplet gap.[9] Dimethylcarbene is predicted to have a singlet ground state.[10]

Triplet carbenes are often compared to free radicals and singlet carbenes are often compared to carbocations in terms of their electronic structure and reactivity.[8] The effects of alkylation on singlet−triplet gaps are easily understood as a consequence of the fact that alkyl groups afford more stabilization to cations than to radicals.[11]

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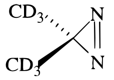
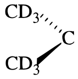
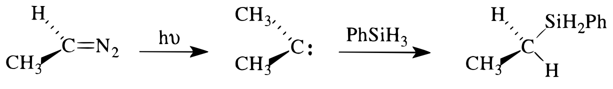
Experimental evidence for the existence of MC and DMC is quite meager. There is as yet no direct observation of MC or DMC in the gas phase or in cryogenic matrixes. Kramer and Wright were able to trap MC in solution with phenylsilane, but only in a very low yield (5%).[12]


DMD-d6


DMC-d6

$CD_3CD{=}CD_2$

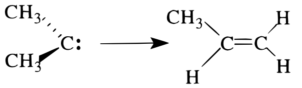
P-d6



DMC

McMahon and Seburg were able to trap methylcarbene in a cryogenic matrix with carbon monoxide to form a ketene, which was readily characterized by IR spectroscopy.[13]

The paucity of experimental data concerning DMC has historically been attributed to the expected ease of its rearrangement to propene (P)

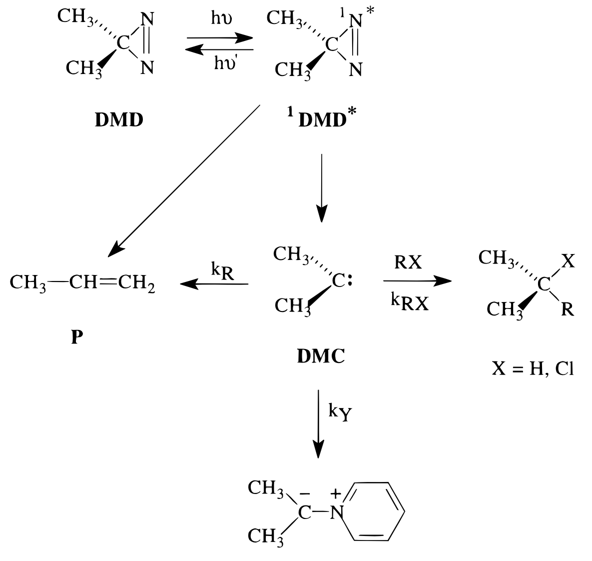

DMC **P**

a process which should be exothermic (on the basis of simple bond additivity arguments)[14] by more than 60 kcal/mol.

Nevertheless, we have previously trapped DMC with pyridine, in solution, and used laser flash photolysis methods to deduce that DMC has a lifetime of 20 ns in pentane at ambient temperature.[15] In this experiment (Scheme 1) dimethyldiazirine (DMD) was irradiated with a pulse of 351 nm light from a XeF excimer laser. Decomposition of the excited state of DMD (^{1}DMD*) leads to the formation of DMC which can, in principle, react with solvent (RX, X = H, hydrocarbons; X = Cl, Freons), rearrange (k_R), or react with pyridine (k_{pyr}) to form a UV−vis active ylide (Y, Scheme 1).[13]

The spectrometer in use in that work had a time resolution of ~20 ns which prevented the direct measurement of the growth of the ylide following the laser pulse.[15] This limitation did not permit the direct measurement of k_{pyr} and the carbene lifetime τ ($\tau = 1/(k_R + k_{RX}[RX])$). Instead, the lifetime was deduced by measuring the yield of ylide (A_Y) as a function of pyridine concentration. As expected[15] plots of $1/A_Y$ versus 1/[pyr] were linear. Dividing the intercept by the slope of this plot gave $k_{pyr}\tau$, where τ is the lifetime of DMC in the absence of pyridine. After assuming that DMC had a singlet ground state (which was subsequently justified by theory)[10] and that k_{pyr} was 1×10^9 M^{-1} s^{-1}, a value of $\tau = 20$ ns in alkane solvent at ambient temperature was deduced.[15] The lifetime of DMC in the hydrocarbon solvent was found to be limited, at least in part, by rearrangement to propene because the lifetime of DMC-d_6 was 3.2 times larger than that of DMC itself in a hydrocarbon solvent at ambient temperature.[15]

Scheme 1



Y

Herein we are pleased to report new experimental studies of DMC which allow the absolute measurement of both k_{pyr} and τ of DMC and DMC-d_6 as a function of temperature in $CF_2ClCFCl_2$ (Freon-113), perfluorohexane, and α,α,α-trifluoromethylbenzene. These studies will demonstrate that the lifetime of DMC is controlled by a mixture of rearrangement and reaction with solvent in the case of Freon-113 and α,α,α-trifluoromethylbenzene. The data in perfluorohexane are consistent with unimolecular decay of the carbene. The rearrangement of DMC is likely to proceed, at least in part, via quantum mechanical tunneling (QMT) in perfluorohexane because of the large isotope effects on Arrhenius parameters and because the observed barrier to rearrangement of DMC is much smaller than that predicted by calculations. The barrier to disappearance of DMC-d_6 in perfluorohexane is consistent with the calculated barrier. Thus, any contribution of QMT to the kinetics of DMC-d_6 must be relatively minor.

II. Results

II.1. Laser Flash Photolysis Studies. The LFP system used in this laboratory has been upgraded by incorporation of a frequency-tripled YAG laser which delivers 150 ps pulses (pretripling) at 355 nm with 30 mJ of energy, improved detection circuitry, and a monochromator.[16] The time resolution of the spectrometer was determined by measuring the apparent growth of triplet benzophenone, following a 355 nm laser pulse, at 525 nm. The apparent rise of the triplet benzophenone absorption was <1 ns.

LFP of DMD in Freon-113 fails to produce a detectable UV−vis active transient between 300 and 700 nm. Similar results are obtained upon LFP of pyridine in Freon-113. LFP (355 nm, 150 ps, 30 mJ, Nd:YAG) (Figure 1) of DMD and pyridine produces the same transient spectrum of ylide Y (Figure 1) observed previously with excimer laser pulses (351 nm, 55 mJ, 17 ns).[15] With the 150 ps pulsed laser it was possible to resolve the growth of the ylide (Figure 2). The growth is adequately

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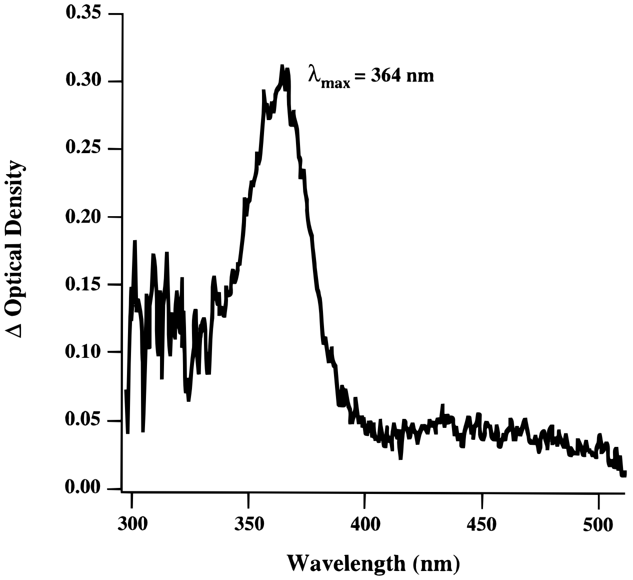


Figure 1. Transient spectra of ylide Y produced by LFP of DMD in Freon-113 at ambient temperature.

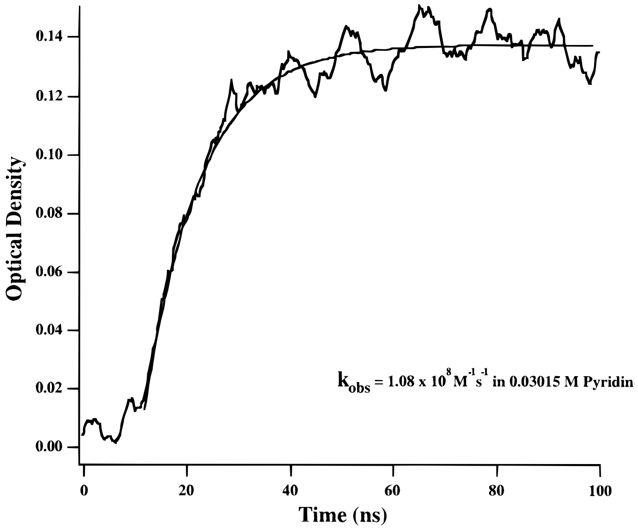


Figure 2. Formation of ylide (Y) monitored at 370 nm in α,α,α-trifluoromethylbenzene in the presence of 0.03 M pyridine at 243 K.

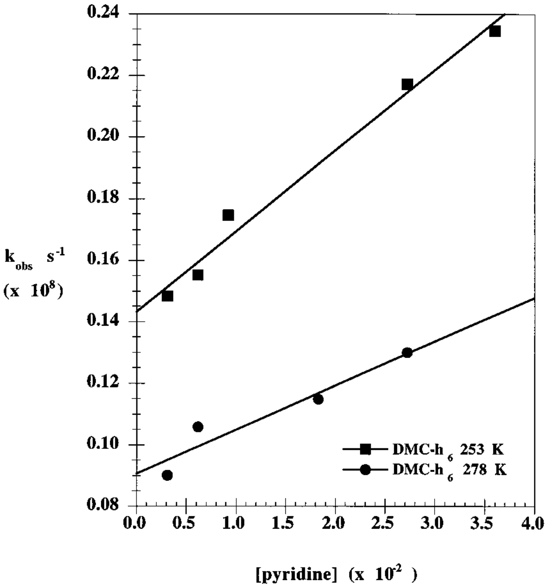


Figure 3. k_{obs} versus pyridine concentration obtained by LFP of DMD in α,α,α-trifluoromethylbenzene as a function of temperature.

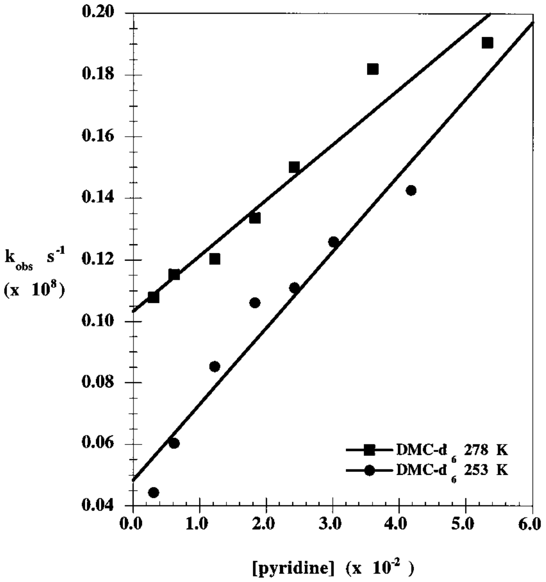


Figure 4. k_{obs} versus pyridine concentration obtained by LFP of DMD-d_6 in α,α,α-trifluoromethylbenzene as a function of temperature.

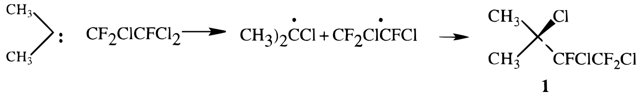
described by an exponential function with observed rate constant (k_{obs}), which is related to the absolute rate constants of Scheme 1 by eq 1.[17]

$$k_{\text{obs}} = k_{\text{R}} + k_{\text{RX}}[\text{RX}] + k_{\text{pyr}}[\text{pyr}] \qquad (1)$$

As predicted by eq 1, a plot of k_{obs} versus pyridine concentration is linear (Figures 3−5) with slope k_{pyr} and intercept ($k_{\text{R}} + k_{\text{RX}}[\text{RX}] = 1/\tau$). Results were obtained with DMD and DMD-d_6 over a temperature range of 243−273 K and in α,α,α-trifluoromethylbenzene and perfluorohexane solvent. Arrhenius treatment of the $1/\tau$ data is presented in Figures 6−8 and summarized in Table 1. The values of k_{pyr} show little systematic variation with temperature, consistent with $E_a \approx 0$ for this process, as observed with other carbenes.[18]

II.2. Reactions of Dimethylcarbene with Solvent. Dimethyldiazirine (DMD) was condensed into the solvents used to obtain absolute kinetic data. These solutions were then continuously irradiated with 350 nm radiation from a Ray-O-Net reactor. The products of photolysis were then characterized by gas chromatography−mass spectrometry to establish the importance of the $k_{\text{RX}}[\text{RX}]$ term to k_{T} in the solvents of interest.

Photolysis of DMD in Freon-113 led to the formation of a mixture of products. One reaction product has a molecular ion and fragmentation pattern consistent with that of **1**, formed by formal C−Cl bond insertion. This product likely derives from reaction of DMC with solvent via a radical pair intermediate.



1

Products with molecular ions and fragmentation patterns consistent with the formation of DMC−solvent adducts (e.g., **2**) were detected upon photolysis of DMD in α,α,α-trifluoromethylbenzene. We cannot rule out the possibility that DMC

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Table 1. Activation Parameters of the Reactions of DMC and DMC-d_6 Determined from the Intercepts ($k_R + k_{RX}$[RX]) of Plots of k_{obs} versus Pyridine Concentration

	DMC			DMC-D6		
solvent	E_a (kcal/mol)	$\Delta S^‡$ (298 K) (cal mol^{-1} K^{-1})	log *A*	E_a (kcal/mol)	$\Delta S^‡$ (298 K) (cal mol^{-1} K^{-1})	log *A*
$Cl_2CFCClF_2$	3.11 ± 0.05	−9.6 ± 0.7	10.7 ± 0.3	3.36 ± 0.05	−9.6 ± 0.7	10.7 ± 0.3
$C_6H_5CF_3$	2.90 ± 0.05	−11.0 ± 0.7	10.4 ± 0.3	3.85 ± 0.05	−8.2 ± 0.7	11.0 ± 0.3
C_6F_{14}	2.56 ± 0.05	−12.8 ± 0.7	10.0 ± 0.3	5.63 ± 0.03	−2.7 ± 0.7	12.2 ± 0.3

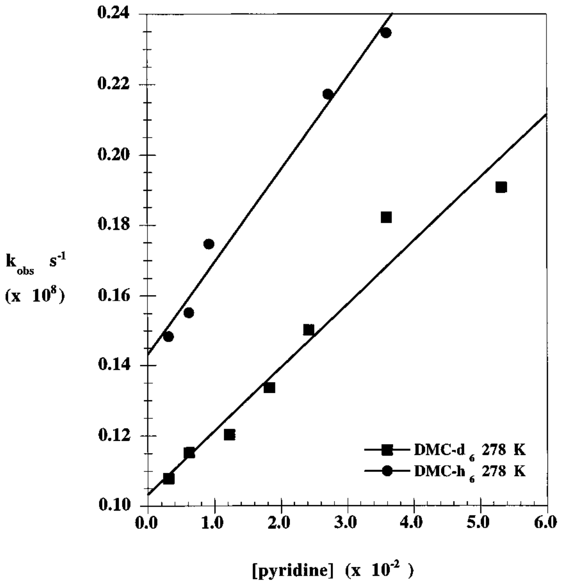


Figure 5. k_{obs} versus pyridine concentration obtained by LFP of DMD and DMD-d_6 in Freon-113 at 278 K.

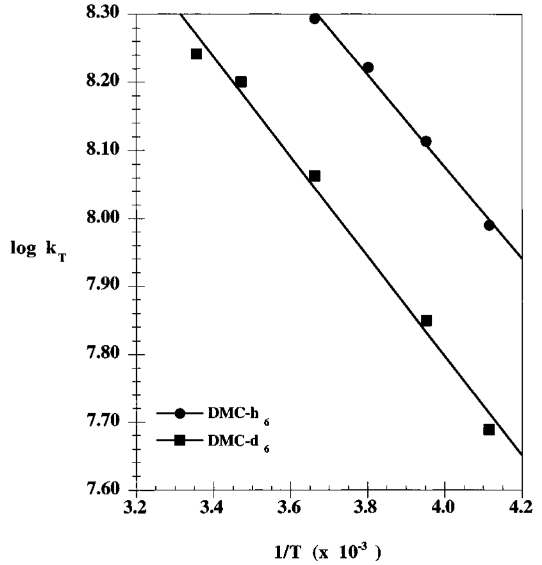
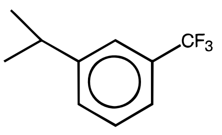


Figure 6. Arrhenius plots of the 1/τ data obtained in Freon-113.



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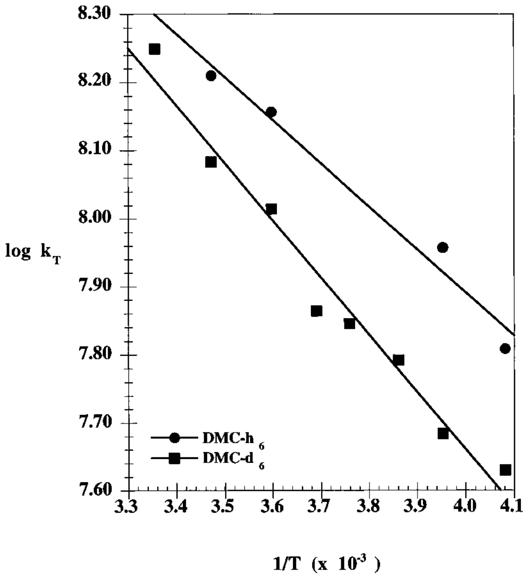

Figure 7. Arrhenius plots of the 1/τ data obtained in α,α,α-trifluoromethylbenzene.

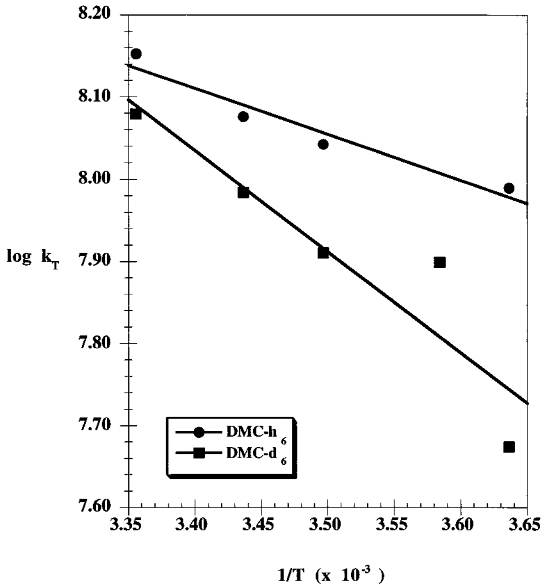

Figure 8. Arrhenius plots of the 1/τ data obtained in perfluorohexane.

forms a transient π complex with this aromatic solvent as postulated by Goodman,[20] Moss,[21] and Jones.[22] The GC traces and fragmentation patterns are available as Supporting Information. Suffice it to say that the k_{RX}[RX] term for the disappearance of DMC in Freon-113 and α,α,α-trifluoromethylbenzene is not trivial.

Finally, no adducts derived from reaction with DMC with solvent were observed upon photolysis of DMD in perfluorohexane. There is no evidence that the k_{RX}[RX] term is significant in perfluorohexane, and it will be neglected.

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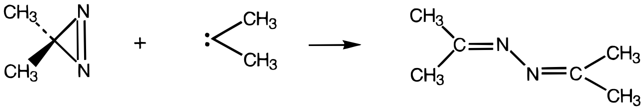
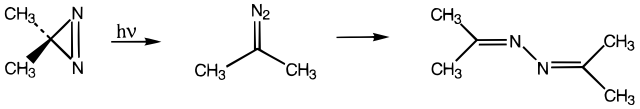
Azine (A) was formed on photolysis of DMD in all solvents. Azine can be formed by several mechanisms including the reaction of a carbene with its diazirine precursor. This reaction is very fast and complicates analysis of the kinetics of benzylchlorocarbene.[23]



DMD **DMC** **A**

It seems unlikely that azine is formed by reaction of DMD with DMC because the lifetime of DMC is very short and does not change upon doubling the concentration of precursor. We believe that DMC rearranges to its isomeric diazo compound and that this species forms azine by a non-carbenic mechanism.



III. Theory

To complement the experimental work we studied the 1,2-H-shift reaction of dimethylcarbene, as well as the cyano- and methyl-substituted analogues, by *ab initio* quantum chemical methods. To optimize the geometries of the reactants, products, and transition states, we used the second-order Møller−Plesset (MP2) method[24] in combination with analytic derivative methods and 6-31G(2p,d) basis sets.[25,26] Barrier heights and exothermicities were then determined by single-point calculations using the CCSD(T) method[27,28] and atomic natural orbital (ANO) type basis sets[29] contracted to (4s3p2d) and (3s2p) functions for carbon, nitrogen, and hydrogen, respectively.

To validate our approach, we performed calculations using the complete active space (CAS)SCF method[30] followed by second-order multireference configuration interaction (SD-MRCI),[31] including Davidson's correction,[32] and multireference second-order perturbation calculations, the so-called CASPT2 approach.[33] Due to the strong mixing of the orbitals describing the C−H and C−C bonds, the choice of an active space for the CASSCF method was particularly difficult, and it was necessary to use the smallest meaningful active space, two electrons in two orbitals. Thus, the CASSCF wave function of singlet dimethylcarbene as well as that of the transition state structure included the ...$(\sigma)^2(\pi)^0$ and ...$(\sigma)^0(\pi)^2$ configurations correlating the nonbonded electrons localized at the carbenoid center. For propene the active space includes the valence π space.

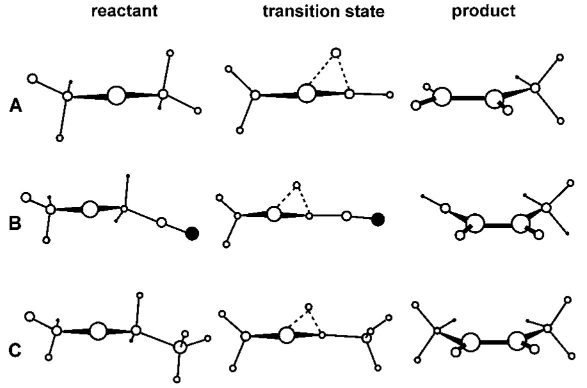


Figure 9. Calculated structures of the reactants, transition states, and products of the reactions dimethylcarbene → propene (A), (cyanomethyl)methylcarbene → 1-cyanopropene (B), and ethylmethylcarbene → 2-butene (C).

All multireference calculations have been performed using the MOLCAS-3 program systems.[33] Gaussian 94[34] was used to optimize the geometries, and the CCSD(T) calculations were performed with MOLPRO96.[35]

III.1. Results. III.1.1. Geometries. Recently, some of us (S.M., M.F.) have reported the singlet−triplet energy separation of methylated carbenes.[10a] This was the starting point of the present investigation. As the rearrangement reaction begins, one hydrogen atom moves in a plane that is almost perpendicular to the plane formed by the three carbon atoms, while the remaining two hydrogen atoms on the same methyl group swing very rapidly into a nearly planar position. Moreover, as the π-bond is formed, we observe a contraction of the C−C bond distance. In contrast, the "spectator" methyl group behaves almost perfectly like a rigid body. It rotates and bends by approximately 16° and 7°, respectively, such that the methyl group is placed in a conformation close to that in propene. At the transition state, the lengths of the breaking and forming C−H bonds are 125.1 and 132.6 pm, respectively. The length of the preformed C−C double bond is 140.2 pm. Focusing on the second half of the reaction, the moving hydrogen atom rotates into the plane of the carbon atoms to form the new C−H bond. This movement is followed by a further shortening of the forming C−C double bond and additional, rather small adjustments of the positions of the other atoms. The structures of the reactants, transitions states, and products are shown in Figure 9.

To optimize the geometries of the substituted systems, i.e., (cyanomethyl)methylcarbene and methylethylcarbene, the structures of dimethylcarbene, the transition state, and propene were used as templates to which the methyl or cyano group was attached. These structures were then used as starting points for geometry optimizations. The structures of all possible rotamers were optimized, but only the structures of lowest

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Table 2. Bond Distances (pm) and Bond Angles (deg)[a]

	b	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*
				Reactants					
A[l]	148.0	148.0	110.3	98.0	85.5	110.6		98.0	85.5
B[m]	147.5	149.4	109.2	97.1	83.6	110.6		98.5	93.3
C[n]	148.2	147.5	110.6	98.6	83.5	111.2		94.4	91.4
				Transition Structure					
A	150.9	140.2	112.3	105.1	69.2	125.1	132.6	59.6	77.7
B	150.4	140.9	111.5	104.4	70.4	125.2	134.1	60.2	78.8
C	151.1	140.8	112.1	104.9	70.6	124.1	134.0	60.4	82.6
				Products					
A	150.1	133.8	124.4	111.1	59.4				
B	149.6	134.5	125.3	110.4	59.0				
C	150.3	134.2	127.4	110.6	59.1				

[a] For convenience, we label the carbenoid center C1 and the carbon atom from which the hydrogen atom is removed C3. C2 denotes the carbon atom of the spectator group. The migrating hydrogen atom is labeled H32. Finally, H22 denotes the hydrogen atom attached to C2 and oriented almost perpendicular to the central plane. Because the cyano and methyl substituents can in good approximation be described as rigid bodies, we did not tabulate all geometrical parameters. The full set of coordinates can be obtained from the authors upon request. [b] Bond distance C1−C2. [c] Bond distance C1−C3. [d] Bond angle C2−C1−C3. [e] Bond angle C1−C2−H22. [f] Dihedral angle C3−C1−C2−H22. [g] Bond distance C3−H32. [h] Bond distance C1−H32. [i] Bond angle C1−C3−H32. [k] Dihedral angle C2−C1−C3−H32. [l] Reaction dimethylcarbene → propene. [m] Reaction (cyanomethyl)methylcarbene → cyanopropene. [n] Reaction ethylmethylcarbene → butene.

Table 3. Barrier Heights and Exothermicities (kcal/mol)

system	ΔE[a]	ZVPE[b]	ΔE[c]	ZPVE[b]
A[d]	8.5	−1.1	−68.6	2.4
B[e]	10.1	−1.3	−74.6	2.4
C[f]	5.5	−1.2	−68.9	2.3

[a] Barrier height. [b] Zero-point vibrational energy correction. [c] Exothermicity. [d] Reaction dimethylcarbene → propene. [e] Reaction (cyanomethyl)methylcarbene → cyanopropene. [f] Reaction ethylmethylcarbene → butene.

Table 4. Mulliken's Population Analysis

C3[a]	C1[a]	H32[a]	∑[b]	H31 + H33[c]	M[d]
		Dimethylcarbene			
−0.87	0.12	0.25	−0.50	0.56	−0.06
		Transition State Structure			
−0.53	−0.02	0.10	−0.45	0.48	−0.03
		Propene			
−0.50	−0.02	0.19	−0.33	0.40	−0.07

[a] Cf. footnote *a* in Table 2. [b] Sum of Mulliken charges at the centers of C3, C1, and H32. [c] Sum of Mulliken charges for the hydrogen atoms attached to C3 but not taking active part in the 1,2-H-shift reaction. [d] Sum of Mulliken charges for the spectator methyl group.

energy are reported because they were used to determine the energetics of the reaction.

Table 2 summarizes the bond distances and angles, focusing on the region of interest. We find that the effect of the cyano and methyl substituents on the geometry of the central region of the reactants, transition states, and products is rather small.

III.2.2. Reaction Barrier Heights and Exothermicities. The computed barrier heights and exothermicities of the rearrangement reactions are collected in Table 3 which also includes the zero-point vibrational energy corrections (ZVPE). The latter have been computed at the MP2 level of theory using the harmonic approximation.

Our best theoretical estimate for the barrier height in the 1,2-H-shift reaction in dimethylcarbene is 7.4 kcal/mol obtained at the CCSD(T)/ANO+ZPVE level of theory. The overall exothermicity for the rearrangement of dimethylcarbene to propene was calculated to be 66.2 kcal/mol. For (cyanomethyl)-methylcarbene the barrier height of the reaction and the overall exothermicity increase by 1.4 and 6.0 kcal/mol, respectively. In contrast, the effect of substituting a hydrogen atom by a methyl group on the energetics is opposite in sign; i.e., the reaction barrier is lowered by 3.1 kcal/mol, while the exothermicity increases by only 0.2 kcal/mol. This is consistent with our earlier report that the lifetime of ethylmethylcarbene is about 10 times shorter than that of DMC, under comparable conditions.[15]

To obtain a qualitative understanding of the substitution effects, we computed Mulliken populations for the rearrangement of dimethylcarbene to propene at the MRCI level. Mulliken charges are known to be strongly biased by the choice of basis sets. Nevertheless, if we analyze only *relative* charge differences during the course of the reaction, meaningful insight can be gained. Table 4 lists the partial charges at the carbenoid center, the hydrogen-donating carbon atom, the moving hydrogen, the "spectator" methyl group, and the remaining two hydrogen atoms.

The carbenoid C-atom has a partial positive charge in dimethylcarbene. During the hydrogen atom migration process negative charge flows from the hydrogen-donating carbon atom to the carbenoid center and the migrating proton. At the transition state the charge transfer to the carbenoid center is already completed. For the second half of the reaction a small back flow of positive charge occurs predominantly from the migrating hydrogen to the terminal, double-bonded carbon atom in propene. Charge development in the transition state is consistent with our finding that the lifetime of DMC is considerably shortened in polar solvents relative to nonpolar solvents.[15]

During the 1,2-H-shift reaction in dimethylcarbene a propene-like structure is achieved at an early stage while the migrating hydrogen atom remains in a position favoring the hyperconjugative interaction. The electron-withdrawing cyano group destabilizes the positive charge developing on the carbon α to the carbene center and reduces the amount of negative charge which flows to the carbene center. Thus, the charge population of the carbenoid center is reduced in (cyanomethyl)methylcarbene, leading to an increase of the reaction barrier, in accord with the principle of maximum overlap. In contrast, attaching a weak electron donor, such as a methyl group, to the hydrogen-donating carbon lowers the energy barrier of the reaction because the substituent cooperates with the charge transfer to the carbenoid center.

III.2. Validation, Error Estimates. In general, one expects the MP2 method to fail to properly describe bond formation. To validate the present approach, we also determined MCSCF wave functions for the 1,2-H-shift reaction of dimethylcarbene using the CASSCF method which was complemented by SD-MRCI and CASPT2 calculations. Table 5 summarizes the structures of the CASSCF and SD-MRCI wave functions.

By inspection we found that all CASSCF wave functions were dominated by the Hartree−Fock determinant. The second most important contribution for dimethylcarbene and the transition state is the $...(\sigma)^0(\pi)^2$ doubly excited configuration. For propene the $...(\pi)^0(\pi^*)^2$ excited configuration contributes with a weight of 4−5% to the total wave function. All remaining CI coefficients were small. Table 5 also includes the weight of the CASSCF reference function in the SD-MRCI and CASPT2 wave functions. They were very similar for both methods and all species. Finally, the last column of Table 5 reports the value of the so-called T_1-diagnostic for the CCSD(T) wave function.

Table 5. Structure of the Wave Functions[a]

CASSCF	MRCI	wMRCI[b]	wCASPT2[c]	T_1[d]
		Dimethylcarbene		
$(\sigma)^2(\pi)^0$ 96.8%	$(\sigma)^2(\pi)^0$ 85.5%	87.9	87.2	0.0133
$(\sigma)^0(\pi)^2$ 3.2%	$(\sigma)^0(\pi)^2$ 2.3%			
		Transition State Structure		
$(\sigma)^2(\pi)^0$ 98.1%	$(\sigma)^2(\pi)^0$ 86.2%	87.5	86.2	0.0144
$(\sigma)^0(\pi)^2$ 1.9%	$(\sigma)^0(\pi)^2$ 1.2%			
		Propene		
$(\pi)^2(\pi^*)^0$ 95.8%	$(\pi)^2(\pi^*)^0$ 85.3%	87.9	87.3	0.0104
$(\pi)^0(\pi^*)^2$ 4.1%	$(\pi)^0(\pi^*)^2$ 2.7%			

[a] The contributions of the individual configurations are given as relative weights. [b] Weight of the CASSCF reference function in the SD-MRCI wave function. [c] Weight of the CASSCF reference function in the CASPT2 wave function. [d] Value of the T_1-diagnostic of the CCSD(T) wave functions.

In summary, all these indicators support the initial assumption that the MP2 method is a suitable and economic choice to compute the geometries of the systems of this work and confirm earlier conclusions.[9a] However, there are indicators that the MP2 method may overestimate hyperconjugative effects.[34,35]

Another factor affecting the accuracy of the calculated reaction barriers and exothermicities is the selection of the correlation method (cf. Table 6). As the present systems are reasonably well described by a single determinant reference function, there is no doubt that the CCSD(T) method provides the most accurate results. Comparing the relative energies computed at various levels of theory, we observe that the CASPT2, SD-MRCI, and CCSD(T) methods all predict the barrier height to be within less than 0.7 kcal/mol. The correspondence is somewhat worse, about 2 kcal/mol, for the exothermicity. As the difference is largest for the CCSD(T) method we may conclude that triple and higher order excitations are needed to achieve a balanced correlation treatment, in particular with respect to the partially occupied π^* orbital at the carbenoid center. We also note that the relative MP2 energies appear to be shifted to lower values by 2 kcal/mol. This effect may be due to the overestimation of the hyperconjugation effect which appears to be strongest in dimethylcarbene.

There are a number of additional factors affecting the accuracy of the present calculations. Among these is the zero point vibrational energy correction which may be too large due to the harmonic approximation. Another aspect is the saturation of the one-particle basis space.

To summarize, the predicted barrier heights and exothermicities are computed with an accuracy of about 2 kcal/mol. The geometries are believed to be the largest source of error leading to an under- and overestimation of barrier height and exothermicity, respectively.

The rearrangement of dimethylcarbene to propene has been studied previously by Evanseck and Houk[38] who employed the MP2 method and somewhat smaller basis sets (6-31G*). Evanseck and Houk reported that the lowest energy structure of dimethylcarbene is of C_s symmetry, and their best theoretical estimate for the activation energy of the 1,2-H-shift reaction was 4.7 kcal/mol. This value is 2.4 kcal/mol smaller than our best estimate for two reasons: The lowest energy structure of singlet dimethylcarbene is of C_2 symmetry and is 0.98 kcal/mol lower in energy than the C_s structure favored by Evanseck and Houk,[38] in agreement with the recently reported value of 5.2 kcal/mol by Sulzbach et al.[39]

IV. Discussion

It is clear from Table 1 that the experimentally determined activation energies for the disappearance of DMC are much smaller than the value predicted by theory for the 1,2-hydrogen migration reaction of this carbene.

In Freon-113 the activation energies observed for the disappearance of DMC and DMC-d_6 are the same within experimental error (3.3−3.4 kcal/mol; see Table 1). The lack of any isotope effect is consistent with the GC−MS study which demonstrated that DMC reacts with Freon-113. There is no conflict with theory with the barrier measured in Freon-113, as DMC does not disappear in this solvent by a unimolecular reaction.

In α,α,α-trifluoromethylbenzene solvent, an isotope effect of 0.6 kcal/mol on the barrier to the disappearance of DMC is observed. This demonstrates that the lifetime of DMC is controlled, in part, by rearrangement to propylene. Nevertheless, photolysis of DMD in this solvent leads to the formation of dimethylcarbene−α,α,α-trifluoromethylbenzene adducts, detected by GC−MS. Thus, the measured activation barrier in this solvent cannot be associated with intramolecular hydrogen migration although the isotope effects indicate there is more rearrangement chemistry in α,α,α-trifluoromethylbenzene than in Freon-113.

It is possible that DMC forms a complex[20−22,40] with an aromatic solvent. Intuition suggests that complexation of DMC would lead to kinetic stabilization and to raising the barrier to rearrangment, a view supported by the calculations of Hadad and Sulzbach.[39] Our data do not argue for or against complexation of DMC with α,α,α-trifluoromethylbenzene, but complexation does not explain the small barrier measured in $C_6H_5CF_3$.

DMC is less likely to react with or complex to perfluorohexane than to α,α,α-trifluoromethylbenzene. Nevertheless, the enthalpic barrier to disappearance of DMC in perfluorohexane is actually *smaller* than that measured in the presumably more reactive solvents. However, the enthalpic advantage is offset by a more unfavorable entropic term. Thus, the rate of disappearance of DMC, in the absence of pyridine and at 298 K, is slowest in perfluorohexane and is fastest in Freon-113, as deduced from the Arrhenius parameters. This is consistent with increasing reaction of DMC with solvent upon changing the medium from C_6F_{14} to $C_6H_5CF_3$ to $CF_2ClCFCl_2$.

Quantum mechanical tunneling (QMT) can be invoked in hydrogen transfer reactions which overcome small apparent barriers. Indeed, Dix, Herman and Goodman[42] have proposed that the 1,2-rearrangement of hydrogen in methylchlorocarbene, in solution, has a contribution of quantum mechanical tunneling. Their data have been fit by theory,[43] which validates their conclusions. Tunneling “reduces” the barrier from 10.9 to 7.7 kcal/mol in methylchlorocarbene and by 2.2−2.6 kcal/mol in

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Table 6. Total and Relative Energies[a]

RHF	MP2	CASSCF	CASPT2	SD-MRCI	CCSD(T)
		Dimethylcarbene			
−117.020226	−117.459037	−117.039055	−117.465449	−117.510107	−117.522636
		Transition State Structure			
−116.995464	−117.450119	−117.010491	−117.452929	−117.496473	−117.509073
(15.54)	(5.60)	(17.92)	(7.85)	(8.55)	(8.51)
		Propene			
−117.118444	−117.575217	−117.145366	−117.577827	−117.622222	−117.631995
(−66.63)	(−72.90)	(−66.71)	(−70.52)	(−70.35)	(−68.62)

[a] The total energies are given in hartrees whereas the relative energies are given in kcal/mol and in parentheses.

cis- and *trans*-1,2-dichloroethylidene, respectively.[43] QMT explains the inter- and intramolecular transfer of hydrogen in carbenes prepared in low-temperature matrixes.[44] Typically, the case for QMT in matrix reactions at low temperature is much stronger than that which can be made at higher temperature in fluid solution because the measured kinetic isotope effects are very large at low temperature.

The isotope effects observed on the lifetime of DMC in perfluorohexane are large and dramatic ($\Delta E_a^D - \Delta E_a^H = 3.18$ kcal/mol, $A_D/A_H = 158$) and cannot be explained by transition structure theory. Thus, we conclude that the decay of DMC and DMC-d_6 in perfluorohexane is intramolecular and that the rearrangement of DMC proceeds by a quantum mechanical tunneling mechanism in this solvent. The barrier to disappearance of DMC-d_6 in perfluorohexane is close to that predicted by theory. Therefore, the decay of DMC under these conditions may not necessarily contain a component of QMT and is not altered by complexation with perfluorohexane.

V. Conclusions

Laser flash photolysis (Nd:YAG laser, 355 nm, 35 mJ, 150 ps) of dimethyldiazirine and dimethyldiazirine-d_6 produces dimethylcarbene (DMC) and dimethylcarbene-d_6 (DMC-d_6), respectively. The carbenes were trapped with pyridine to form ylides which absorb near 364 nm. It was possible to resolve the growth of the ylides as a function of pyridine concentration in Freon-113, α,α,α-trifluoromethylbenzene, and perfluorohexane as a function of temperature. The observed rate constant (k_{obs}) to ylide formation was linearly dependent on the concentration of pyridine. From plots of k_{obs} versus pyridine concentration it was possible to extract values of k_{pyr} (absolute rate constant of reaction of the carbene with pyridine) and τ, the carbene lifetime, and their associated Arrhenius parameters. In Freon-113 the carbenes decay by rearrangement and by reaction with solvent. In perfluorohexane the carbene decay appears to be predominantly unimolecular. The Arrhenius parameters indicate that the rearrangement of hydrogen has a strong tunneling component. The fact that the observed barrier to rearrangement of DMC is much smaller (2.56 kcal/mol) than that predicted by *ab initio* theory (7.4 ± 2 kcal/mol) also points to the involvement of tunneling in the rearrangement of DMC. The barrier to rearrangement of deuterium in DMC-d_6 in perfluorohexane (5.6 kcal/mol) is comparable to that predicted by theory. Tunneling and complexation with solvent may not be important in the deuterated system in perfluorohexane.

VI. Experimental Section

Laser Flash Photolysis Studies. Stock solutions of the 3,3-dimethyl-3*H*-diazirine and 3,3-bis(trideuteriomethyl)-3*H*-diazirines were prepared for each solvent of interest with an optical density of 0.35 ± 0.20 at 355 nm for lifetime and kinetic experiments. The solvents utilized were Freon-113, α,α,α-tifluoromethylbenzene, and perfluorohexane. A constant volume (1.5 mL) of the stock solution was added to Suprasil quartz fluorescence-free static cells and a varying amount of pyridine until the pyridine concentration reached approximately 1.12 M. A special sample holder for variable temperature work was used to avoid scattering the laser beam, and the temperature of the setup was regulated with a NESLAB RTE-110 variable temperature controller.

The LFP apparatus[16] consists of a Continuum PY62C-10 Nd:YAG laser (355 nm, 30 mJ, 2 ns). Samples were deoxygenated by bubbling with dry, oxygen free argon for 2 min. Each of the samples was placed in the appropriate sample cell fitted with a rubber septum. The sample cells were irradiated with Nd:YAG laser pulses that impinged on the sample at a right angle to a 150 W Xe arc lamp fitted with an aspherab beam collimator. The monitoring beam was focused on the slit of an Oriel monochromator, selected for the wavelength of interest, with both front and rear slits set between 0.2 and 0.4 mm. Signals were obtained with a photomultiplier tube detector and were digitized by a Tektronix 7912 A/D transient digitizer. The entire apparatus is controlled by a Macintosh IIx microcomputer which was used for storage of the digitized data. Data analysis was performed with IgorPro PPC (version 3.02) by Wavemetrics.

Preparation of 3,3-Dimethyl-3*H*-diazirine.[45] Ammonia was condensed in a solution of acetone (4.00 g, 0.07 mol) in methanol (20 mL) at −35 °C. Hydroxylamine-*O*-sulfonic acid was added (slowly) over a period of 45 min, and the reaction was allowed to stir for 4 h at −35 °C. The temperature was slowly raised to room temperature and the ammonia allowed to evaporate. The resulting solution was filtered, and the undissolved ammonium salts were washed with 2 × 50 mL of methanol. The methanol washes were collected, and the solvent was evaporated, leaving a residue which was dissolved in chloroform (50 mL), filtered, and dried over anhydrous sodium sulfate. Chloroform was evaporated, yielding an oil which solidified (mp 38−40 °C) upon standing.

Crude diaziridine (3.00 g, 0.04 mole) was dissolved in water (25 mL) in a modified three-necked flask. A tube (~15 cm) containing KOH and Drierite is attached to the side port of the reaction flask and the other side connected to a trap prepurged with argon-containing trap solvent (Freon-113, α,α,α-trifluoromethylbenzene, or perfluorohexane). Argon was circulated from the reaction flask exiting through the trap. The reaction flask was cooled to 0 °C, and a solution of potassium permanganate (6.48 g, 0.04 mol) in 75 mL of 10% aqueous NaOH was added over a period of 30 min. The volatile diazirine was eluted with the carrier gas into the trap cooled to −78 °C and identified by its characteristic UV spectrum ($\lambda_{max} = 365$ nm) and ^{1}H NMR (CDCl$_3$) δ (ppm) 0.99 (CH$_3$, 6H, s).

Preparation of 3,3-Bis(trideuteriomethyl)-3*H*-diazirine. A solution of acetone-d_6 (4.35 g, 0.068 mol) and ammonia-d_3 (10 mL, 0.34

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mol) was prepared at −35 °C under an argon atmosphere in anhydrous methanol-*d*. To this solution was added *tert*-butylhypochlorite (14.80 g, 0.136 mol) over a period of 1.5 h, and the resulting solution was stirred continuously for an additional 4 h. The temperature was slowly raised to room temperature and the ammonia allowed to evaporate. The resulting solution was filtered, and the undissolved ammonium salts were washed with 2 × 50 mL of methanol. The methanol washes were collected, and the solvent was evaporated, leaving a residue which was dissolved in chloroform (50 mL), filtered, and dried over anhydrous sodium sulfate. Chloroform was evaporated, yielding an oil. No further purification was attempted at this point.

Crude diaziridine (1.50 g, 0.02 mol) was dissolved in D_2O (25 mL) in a modified three-necked flask. A tube (∼15 cm) containing KOH and Drierite was attached to the side port of the reaction flask and the other side connected to a trap prepurged with argon-containing trap solvent (Freon-113, α,α,α-trifluorotoluene, or perfluorohexane). Argon was circulated from the reaction flask exiting through the trap. The reaction flask was cooled to 0 °C, and a solution of potassium permanganate (3.24 g, 0.02 mol) in 25 mL of 10% aqueous NaOH was added over a period of 30 min. The volatile diazirine was eluted with the carrier gas into the trap cooled to −78 °C and identified by its characteristic UV spectrum ($\lambda_{max} = 364$ nm) and ^{1}H NMR ($CDCl_3$) δ (ppm) 1.033 ($(CD_3)_2$), with % D = 100.

GC−MS Analysis. 3,3-Dimethyldiazirine was condensed into Freon-113, α,α,α-trifluoromethylbenzene, or perfluorohexane and the concentration adjusted to give ∼0.10 mol of diazirine (determined spectrophotometrically, $\epsilon_{360} = 1200$). Photolyses were conducted in quartz cuvettes with the solutions degassed by bubbling with Ar before photolysis using a Rayonet apparatus. The diazirine was photolyzed at 350 nm for 24 h at 5 °C.

GC−MSD mass spectral analyses were performed on a HP-5970B mass spectrometer, 5965A infrared detector, with a capillary direct interface connected to a HP-5890 gas chromatograph with a fused silica capillary column cross-linked with 5% phenyl methyl silicone (column i.d. 0.25 nm, column length 15 m). GC traces and fragmentation patterns in Freon-113, α,α,α-trifluoromethylbenzene, and perfluorohexane are provided as Supporting Information.

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Supporting Information Available: Results of GC−MS analysis on the photolysis of dimethyldiazirine as in Freon-113 and α,α,α-trifluoromethylbenzene (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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