11-cis Schiff bases in solution (the value is highly solvent dependent). All of the data can be rationalized by using the theoretical models presented in ref 19–21.

Finally, it should be noted that solvent can play an important role in determining level ordering. Onsager reaction field calculations[33] based on solute properties predicted by using INDO-PSDCI theory predict that the $^1B_u{}^{*+}$-like state in protonated Schiff bases and Schiff base salts will be stabilized preferentially by increasing solvent polarity, hydrogen bonding capability, or refractive index. It may be possible to invert the level ordering in ATRSBS by using highly polar and/or dispersive solvents. An attempt to induce level ordering reversal by using the mixed solvent, EPA, however, failed apparently to induce a lowest lying $^1B_u{}^{*+}$-like state (see Figure 3 and above discussion). Further studies in this area are needed to clarify the role of solvent and protein environment on excited state level ordering of solvated and protein bound retinyl Schiff base and protonated Schiff base polyenes.

Acknowledgment. This work was supported in part by grants to RRB from the National Institutes of Health (GM-34548) and the National Science Foundation (CHE-8518155). We gratefully acknowledge use of the Southern California Regional NMR Facility, which is funded by Grants CHE-7916324 and CHE-8440137 from the National Science Foundation. We thank Professor R. L. Christensen for interesting and helpful discussions.

Registry No. ATRSBS, 23369-82-6; ATRPSB, 61769-46-8; ATR, 116-31-4; ATRSB, 61769-47-9.

Reactivity and Intersystem Crossing of Singlet Methylene in Solution

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received September 2, 1986*

Abstract: Evidence is reported which demonstrates that singlet methylene, produced from the photolysis of diazomethane or diazirine, undergoes intersystem crossing to form triplet methylene in perfluorohexane solvent. The results of triplet sensitized photolysis and of direct photolysis experiments with dilute concentrations of substrate (*cis*- and *trans*-2-pentene and chloroform) appear to be essentially identical. Stern–Volmer analyses of the competition kinetics between acetonitrile and 2-pentenes or chloroform for singlet methylene are consistent with the near diffusion controlled reactivity of singlet methylene. With the assumption of diffusion-controlled reactions for singlet methylene, plots of the quantum yield for singlet vs. triplet reaction for methylene allow the first estimate ($\leq 8 \times 10^8$ s^{-1}) of the rate of intersystem crossing of singlet methylene in the condensed phase. This value is considerably smaller than the value that is extrapolated to the solution phase from results in the gas phase. The possible reasons for this difference are discussed.

Methylene (CH_2), the parent of the carbene family, has attracted the attention of organic chemists,[1] theorists,[2] spectroscopists,[3] and chemical physicists.[4,5] Almost all of the quantitative information concerning this species is derived from gas-phase investigations,[6] from which it has been concluded that CH_2 is a ground state triplet ($^3CH_2$) and that a low-lying singlet state ($^1CH_2$) exists at about 9 kcal/mol[7] above the ground state (Figure 1). Methylene possesses one carbon atom, two hydrogen atoms, and two nonbonding electrons. The two nonbonding electrons occupy the σ and π orbitals with their spins parallel for the more linear $^3CH_2$ ($\delta = 136°$), while they occupy the σ orbital paired spins for the lowest energy singlet methylene ($\theta = 102°$) (Figure 1). Both states have been observed spectroscopically in the gas phase,[3] and from kinetic investigations[4,5] it has been concluded that $^1CH_2$ is quenched by all additives, even inert gases, with high efficiency. Indeed, extrapolation of the gas-phase quenching data to the solution phase leads to the expectation that the lifetime of $^1CH_2$ will be of the order of picoseconds in the condensed phase. For example, $^1CH_2$ is quenched by He in the gas phase[4] with a rate constant of ca. 4×10^{-12} cm^3 molecule^{-1} s^{-1}, which translates into a bimolecular rate constant of ca. 2×10^9 M^{-1} s^{-1}. For an organic solvent concentration of 5 M, the rate of quenching for a completely inert solvent (such as helium!) would be 1×10^{10} s^{-1}, implying a lifetime of the order of 50 ps or less for $^1CH_2$ in solution. This expectation is based on the assumption that the rate of the $^1CH_2$ deactivation is a linear function of pressure even at high pressure (or in the solution phase). Since quenching must involve either reaction or intersystem crossing to $^3CH_2$, one is led to expect either the absence of the latter in solution upon direct production of $^1CH_2$ (in the case of reaction) or essentially immediate production of $^3CH_2$ (in the case of rapid intersystem crossing). Since distinct chemistries on $^1CH_2$ (direct photoexcitation of diazomethane)[8] and $^3CH_2$ (triplet sensitized excitation of diazomethane)[9] have been demonstrated in solution, *a "dilution effect" on the products of* $^1CH_2$ *is not expected from extrapolation of the gas-phase results because both intersystem crossing or reaction of this species are expected to occur at near collision controlled rates.* Indeed, the results in the literature[10] strongly support the thesis that $^1CH_2$ reacts with all substrates at the diffusion-controlled rate, since it is found to react with the CH bonds of even saturated hydrocarbons in a rather indiscriminate manner.[11] However, a qualitative investigation of the dilution

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(1) For a review see: Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press, Inc.: New York, 1971; Chapters 5–11.

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(11) Doering, W. v. E.; Buttery, R. G.; Laughlin, R. G.; Chaudhuri, N. *J. Am. Chem. Soc.* **1956**, *78*, 3224.

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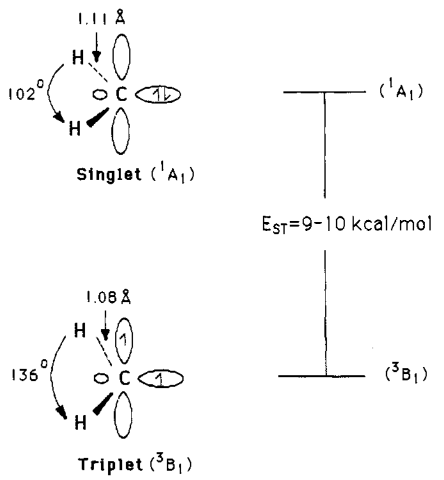
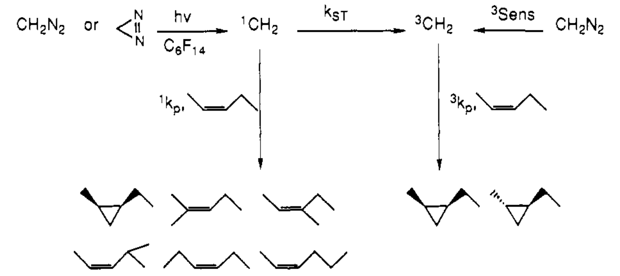


Figure 1. The electronic structures and the energy splitting of the two low-lying states of methylene.

Scheme I



effect in a perfluorinated solvent suggested that indeed $^1CH_2$ does undergo intersystem crossing in solution.[12] In this report we have systematically and quantitatively investigated the effect of dilution with perfluorohexane on the reactions of methylene with the cis and trans isomers of 2-pentene and with chloroform. We have also applied the Stern–Volmer analysis to determine the relative reactivity of $^1CH_2$ toward 2-pentenes and chloroform. The data obtained from the dilution studies and Stern–Volmer analysis allow the first estimation to be made of the rate of intersystem crossing of $^1CH_2$ to $^3CH_2$ in the condensed phase, and the rate is found to be much slower than that extrapolated from gas-phase experiments.

Experimental Strategy for Establishing Intersystem Crossing of $^1CH_2$

The experimental strategy for establishing the occurrence of intersystem crossing of $^1CH_2$ in solution depends on the existence of characteristic and differentiable reactions of $^1CH_2$ and $^3CH_2$ with a given substrate, and the existence of a solvent that is sufficiently inert to chemical reaction with singlet methylene in the presence of the substrate that intersystem crossing can occur. The basic idea is that dilution with the inert solvent will slow down the bimolecular reaction of $^1CH_2$ with the substrate and allow intersystem crossing to $^3CH_2$ to occur. The latter will then undergo its characteristic reaction with the substrate and thereby signal the occurrence of intersystem crossing of $^1CH_2$. The extreme reactivity of $^1CH_2$ precludes the use of common solvents. Perfluoro solvents provide the most likely candidates to resist reaction with $^1CH_2$ but generally do not possess desirable solubility characteristics for dilution experiments. Nonetheless, we found that perfluorohexane comes closest to meeting our desired requirements. We selected the reaction of methylene with *cis*- and *trans*-2-pentene and with chloroform because these reactions have been well characterized in the literature as being able to differentiate $^1CH_2$ and $^3CH_2$.[13,14] In the case of the 2-pentenes[13] as substrates, $^1CH_2$ undergoes stereospecific addition to the C=C double bond and undergoes net insertion into the CH bonds, while $^3CH_2$ undergoes nonstereospecific addition to the C=C bond and does not undergo any appreciable reaction with the CH bonds (Scheme I). In the case of chloroform[14] as substrate, $^1CH_2$ undergoes mainly *net* CCl bond insertion, while $^3CH_2$ undergoes mainly CH bond insertion (Scheme II).

Scheme II

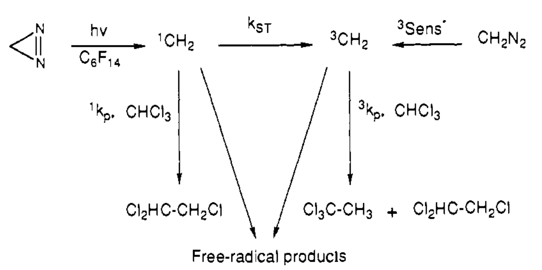
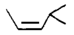
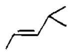
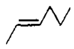
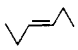
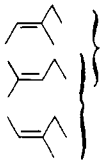


Table I. Product Yields (%) from the Reaction of CH_2 with *cis*- and *trans*-2-Pentene at 273 K

	cis-2-pentene		*trans*-2-pentene	
product	direct $h\nu$[a]	^{3}Sens*[b]	direct $h\nu$[a]	^{3}Sens*[b]
	40 ± 3	44 ± 3	<1	18 ± 1
	<1	51 ± 3	38 ± 4	79 ± 1
	11 ± 2			
	18 ± 3			
	18 ± 3			
			13 ± 2	
			18 ± 2	
			20 ± 3	
	13 ± 2[c]		11 ± 3[c]	

[a] Photolysis (>300 nm) of diazirine (ca. 0.01 M) or diazomethane (ca. 0.01 m) in 2-pentene. [b] Photolysis at 313 nm of a solution of diazomethane (ca. 0.01 M) and benzophenone (ca. 0.01 M) in 2-pentene. [c] These compounds cannot be separated by VPC.

Results

Product Analyses and Dilution Studies with 2-Pentene. Photolysis (λ > 300 nm) of diazomethane or of diazirine in deaerated neat *cis*-2-pentene or neat *trans*-2-pentene at 0 °C resulted in the formation of the products shown in eq 1 and 2, respectively. The cyclopropane products were formed with greater than 99% stereospecificity, and the mass balances were over 90%. The product distributions are summarized in Table I and are in agreement with results reported in the literature.[8,9,12] The results obtained were independent of the methylene precursor.

The product distributions were investigated as a function of dilution of the 2-pentenes in perfluorohexane. The results of these investigations are summarized in several figures: Figure 2 shows the percent cis cyclopropane formed from addition of methylene to *cis*-2-pentene as a function of [*cis*-2-pentene]; Figure 3 shows the percent *trans*-cyclopropane formed from addition of methylene to *trans*-2-pentene; Figure 4 shows the percent CH insertion

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(12) Ring, D. F.; Rabinovitch, B. S. *Int. J. Chem. Kinetics* **1971**, *1*, 11.

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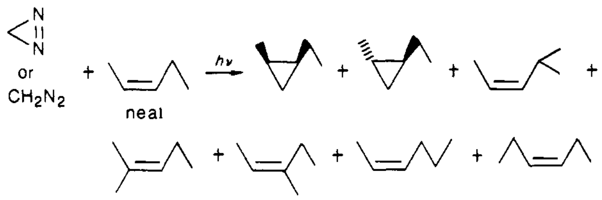

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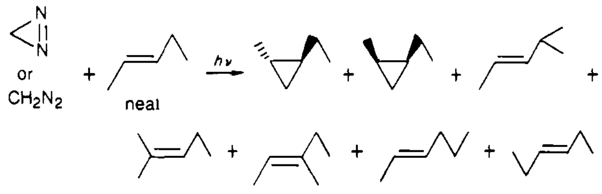


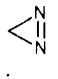
(2)

products (i.e., C_6 alkenes) formed from reaction of methylene with *cis*-2-pentene; and Figure 5 shows the percent CH insertion products (i.e., C_6 alkenes) formed from reaction of methylene with *trans*-2-pentene. The mass balance in all cases is over 47%, depending on the concentration of 2-pentene. In general, the mass balances are better at high concentrations of 2-pentene than at low concentrations.

The product distributions were also investigated for the triplet photosensitized (benzophenone) decomposition of diazomethane[15] in *neat 2-pentenes*. The results are listed in Table I and in the Figures 2–5. The results for triplet sensitized systems are similar to those obtained from direct photolysis of diazirine or diazomethane in very dilute 2-pentenes (Table II). The mass balances were lower for triplet sensitization in neat 2-pentenes, as was the case for the dilution experiments with direct excitation. For example, for triplet sensitization in *cis*-2-pentene the mass balance is ca. 41%.

The effect of isotopic substituion on the product distribution was investigated by employing ${}^{13}CH_2N_2$ and CD_2N_2 as methylene precursors. The product distributions in all cases investigated were independent of the isotopic content of the precursor (Figures 2–5).

Product Analyses and Dilution Studies with Chloroform. Direct irradiation of diazirine[16] in argon-purged chloroform ($CHCl_3$) at 0 °C produces mainly two products shown in eq 3 in ca. 80% yield.



$$+ CHCl_3 \xrightarrow{h\nu} Cl_2HC—CH_2Cl + Cl_3C—CH_3 \qquad (3)$$

The major product is a CCl insertion product, 1,1,2-trichloroethane (>90%), and the minor product is a CH insertion product, 1,1,1-trichloroethane. Dilution of the system with perfluorohexane causes a reduction of the CCl insertion product and an increase in the CH insertion product (Figure 6). The mass balance decreases as the system is diluted, and it is ca. 32% when the concentration of $CHCl_3$ is 0.3 M. The photolysis of diazirine in $CDCl_3$ leads to results which appear to be essentially identical with those found for $CHCl_3$ (Figure 6).

The triplet-sensitized (benzophenone) photolysis of diazomethane[15] in degassed $CHCl_3$ or $CDCl_3$ results in the same products as the direct photolysis, but in a strikingly different proportion. For the reaction in $CDCl_3$, the CD insertion product is now the major product (Table II, Figure 6). The ratio of CCl to CD insertion products for the triplet sensitized system is slightly different from that produced from direct photolysis of diazirine in very dilute $CDCl_3$. The small difference is attributed to the solvent change from neat $CDCl_3$ to perfluorohexane. The mass balance for sensitization in $CDCl_3$, however, is only ca. 24%.

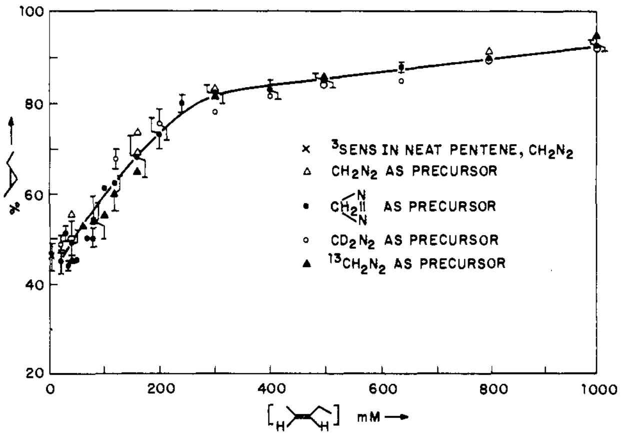


Figure 2. The yield of *cis*-1-ethyl-2-methylcyclopropane as percentage of total cyclopropanes formed by reaction of diazirine (●), diazomethane (△) diazomethane-d_2 (○), and diazomethane-${}^{13}C$ (▲) with *cis*-2-pentene in C_6F_{14} solvent at 0 °C. (×) = benzophenone triplet sensitized decomposition of diazomethane in *cis*-2-pentene at 0 °C.

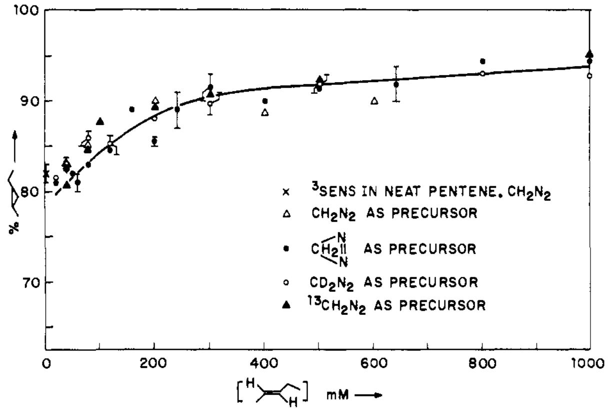


Figure 3. The yield of *trans*-1-ethyl-2-methylcyclopropane as percentage of total cyclopropanes formed by reaction of diazirine (●),diazomethane (△), diazomethane-d_2 (○), and diazomethane-${}^{13}C$ (▲) with *trans*-2-pentene in C_6F_{14} solvent at 0 °C. (×) = benzophenone triplet sensitized decomposition of diazomethane in *trans*-2-pentene at 0 °C.

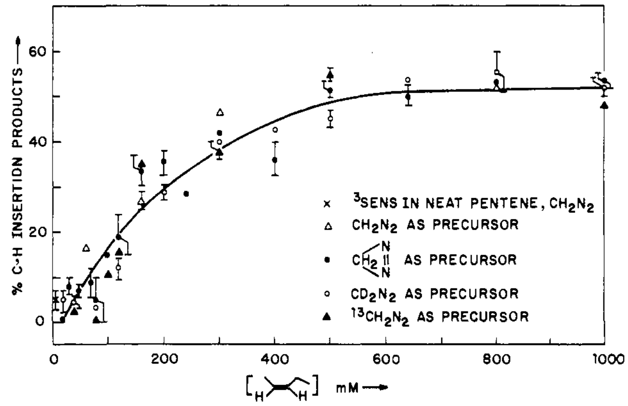


Figure 4. The yield of C–H insertion products (i.e., C_6 alkenes) as percentage of total products formed by reaction of diazirine (●), diazomethane (△), diazomethane-d_2 (○), and diazomethane-${}^{13}C$ (▲) with *cis*-2-pentene in C_6F_{14} solvent at 0 °C. (×) = benzophenone triplet sensitized decomposition of diazomethane in *cis*-2-pentene at 0 °C.

Stern–Volmer Competition of the Reaction of Acetonitrile with ${}^1CH_2$. Nanosecond pulsed laser excitation of diazirine or diazomethane in acetonitrile solution has been shown to result in reaction of ${}^1CH_2$ with acetonitrile to yield the methyl nitrile ylide **1** as a transient which possesses a strong absorption at 280 nm (eq 4).[17] Addition of substrates such as the 2-pentenes or

$$ {}^1CH_2 + CH_3CN \rightarrow \underset{\textbf{1},\ \lambda\ =\ 280\ \text{nm}}{CH_3\overset{+}{C}N\text{-}\overset{-}{C}H_2} \qquad (4)$$

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[15] A suitable triplet sensitizer was not found for decomposition of diazirine in 2-pentene and chloroform, although triplet sensitization decomposition of diazirine has been studied by CIDNP[14] in solution and by product analysis in the gas phase.[36] The possible reason is the very low concentration of diazirine in the product analysis experiment and the relatively slow rate constant for bimolecular triplet energy transfer from benzophenone to diazirine.

[16] Diazirine is used because diazomethane is readily decomposed by radicals.[14]

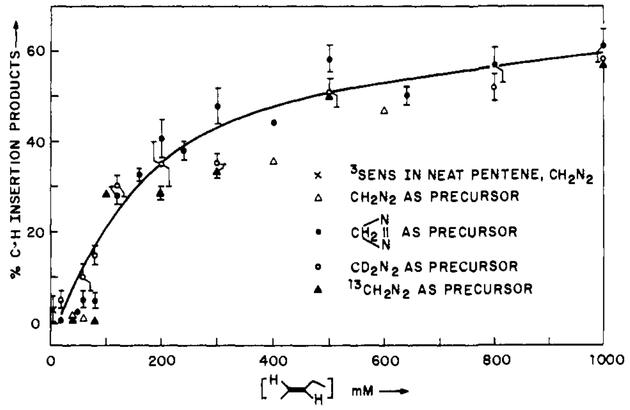

Figure 5. The yield of C–H insertion products (i.e., C_6 alkenes) as percentage of total products formed by reaction of diazirine (●), diazomethane (△), diazomethane-d_2 (○), and diazomethane-^{13}C (▲) with *trans2*-pentene in C_6F_{14} solvent at 0 °C. (×) = benzophenone triplet sensitized decomposition of diazomethane in *trans*-2-pentene at 0 °C.

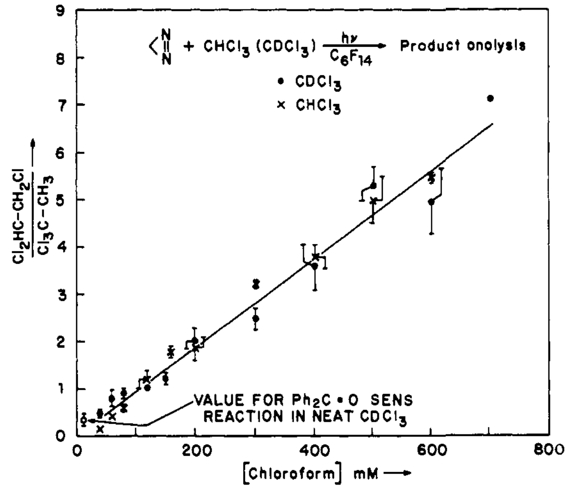

Figure 6. The ratio of the yield of C–Cl to C–H insertion product from photolysis of diazirine with various concentrations of chloroform (×) and chloroform-*d* (●) in C_6F_{14} solvent at 0 °C. Benzophenone triplet sensitized decomposition of diazomethane in chloroform (△) and chloroform-*d* (○) solvent at 0 °C.

Table II. Product Yields from Methylene Reaction with 2-Pentenes and Chloroforms in Solution at 273 K

	direct $h\nu$ (neat)[a]	^{3}Sens* (neat)[b]	direct $h\nu$ (dilute)[c]
cis-2-pentene			
	40 ± 3	44 ± 3	41 ± 4
	<1	51 ± 3	52 ± 4
C–H insertion products[d]	60 ± 3	5 ± 3	7 ± 2
trans-2-pentene			
	<1	18 ± 1	18 ± 2
	38 ± 4	79 ± 1	79 ± 2
C–H insertion products[d]	62 ± 3	3 ± 3	3 ± 3
chloroform-*d*			
$Cl_2DC-CH_2Cl/Cl_3C-CH_2D$	>24	0.29 ± 0.03	0.49 ± 0.03
chloroform			
Cl_2HC-CH_2Cl/Cl_3C-CH_3	>20	0.4 ± 0.1	0.29 ± 0.04

[a] Direct irradiation in neat *cis*- or *trans*-2-pentene or chloroforms ($h\nu$ > 300 nm). [b] Triplet sensitized photolysis of diazomethane in neat solution (benzophenone, 313 nm). [c] Direct irradiation in C_6F_{14} solution containing quenchers less than 0.05 M ($h\nu$ > 300 nm). [d] All C_6 alkene products.

chloroform as quenchers causes a decrease in the yield of the ylide, which allows a Stern–Volmer analysis to be made. The relative rate constants for reaction of the substrate and of acetonitrile with $^1CH_2$ can be evaluated from the slopes of Stern–Volmer plots as shown in eq 5 in which I_0/I represents the yield of the nitrile ylide observed in the pulsed laser experiment, and the rate constants are defined in Scheme III. The values of the relative rate constants derived from this analysis are 1.6 ± 0.1 and 1.4 ± 0.1 for chloroform and 2-pentenes as substrates. The relative rate constants for other substrates are shown on Table III. The similarities of these reactivity ratios for such widely differing reactions and the fact that each is close to unity provide strong support for the near diffusion controlled reactivity of $^1CH_2$.

Scheme III

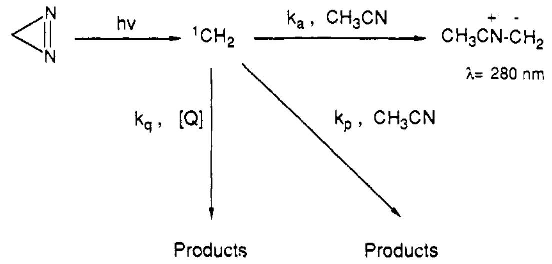

Table III. Stern–Volmer Constants for the Reaction of Methylene with Various Quenchers in Acetonitrile at 298 K

quencher	K_{SV} $(k_q/(k_a + k_p))$[a]
carbon tetrachloride	1.9 ± 0.1
chloroform	1.62 ± 0.08
chloroform-*d*	1.67 ± 0.08
methylene chloride	1.18 ± 0.02
methanol	1.89 ± 0.08
methanol-d_1	1.49 ± 0.08
methanol-d_4	1.53 ± 0.08
water	1.1 ± 0.1
deuterium oxide	0.88 ± 0.07
isoprene	2.2 ± 0.2
cis-2-pentene	1.54 ± 0.08
trans-2-pentene	1.37 ± 0.07
benzene	0.88 ± 0.05
hexafluorobenzene	0.1 ± 0.1
ether	1.21 ± 0.05
tetrahydrofuran	1.12 ± 0.05

[a] See Scheme III for the definition of k_q, k_a, and k_p.

$$\frac{i_0}{I} = 1 + \frac{k_q[Q]}{(k_a + k_p)[CH_3CN]} \tag{5}$$

Discussion

Mechanistic Interpretation of the Dilution Effect on the Reaction of Methylene with 2-Pentenes and Chloroform. The results reported in Tables I–III and in Figures 2–5 are consistent with the postulate that $^1CH_2$ is produced by direct photolysis of diazomethane or of diazirine, that $^1CH_2$ undergoes intersystem crossing to $^3CH_2$ upon dilution with perfluorohexane, and that $^3CH_2$ is scavenged by 2-pentene. A working reaction mechanism consistent with the product studies is shown in Scheme I, where $^1CH_2$ is shown to react with *cis*-2-pentene to produce a *cis*-cyclopropane stereospecifically and a series of CH insertion products and where intersystem crossing leads to $^3CH_2$ which reacts with *cis*-2-pentene to yield cyclopropanes nonstereospecifically and essentially no CH insertion products.

From the working mechanism, the ratio of the rate constants for reaction of $^1CH_2$ with 2-pentenes (^1k_p) to the rate constant for intersystem crossing (k_{ST}) can be evaluated from the data in Figures 2–5. To make this evaluation we take the product distribution obtained from the direct photolysis of diazomethane or

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(17) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415.

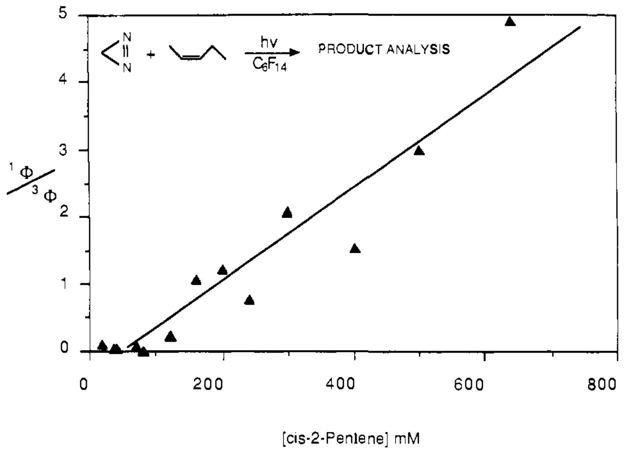


Figure 7. Plot of ratio of the singlet to triplet product quantum yields as a function of *cis*-2-pentene concentration (diazirine as the precursor). The errors are 15–20%.

Table IV. Rate Constant Ratio $^1k_p/k_{ST}$ Obtained with Various Quenchers in Perfluorohexane Solution at 273 K

quencher	$^1k_p/k_{ST}$ (M^{-1})
cis-2-pentene	10 ± 3
trans-2-pentene	9 ± 1
chloroform	7 ± 1
chloroform-*d*	7 ± 1

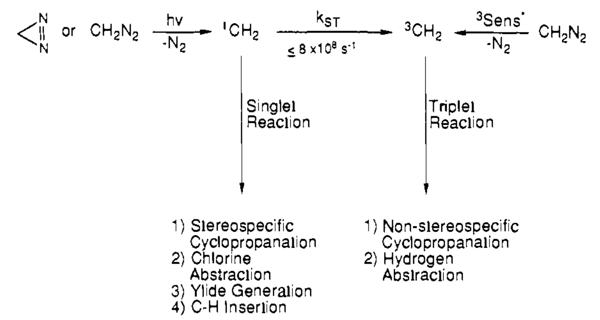
of diazirine in neat 2-pentene as representative of the reaction of $^1CH_2$ with 2-pentene, and we take the product distribution obtained from the triplet-sensitized photolysis of diazomethane as representative of the reaction of $^3CH_2$ with 2-pentene. The product quantum yields of singlet and triplet methylene at a given concentration of 2-pentene can then be evaluated from the product distribution (see Appendix A for a derivation of the relationships). Plots of singlet to triplet quantum yield ratios vs. the concentration of substrates yield the rate constant ratios $^1k_p/k_{ST}$ as the slopes (eq 6). Such a plot is shown in Figure 7 for *cis*-2-pentene as substrate. The analogous values for *trans*-2-pentene and chloroform as substrate are summarized in Table IV.

$$^1\Phi/^3\Phi = {}^1k_p[Q]/k_{ST} \qquad (6)$$

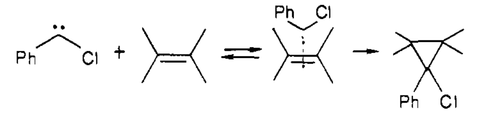
Mechanism of Intersystem Crossing of Methylene in Solution. The similarities of the results with different precursors of methylene, the similarities of the results of dilution with perfluorohexane and the triplet-sensitized decompositions in neat substrate, or the similarities of the slopes of the ratios of quantum yields as a function of dilution provide strong support for Scheme IV as incorporating all of the essential mechanistic features required to explain our observations.

The rate of intersystem crossing can now be evaluated by assuming that rates of reaction $^1CH_2$ with 2-pentene and chloroform in perfluorohexane solvent are diffusion controlled and by extracting k_{ST} from the ratio of rate constants $^1k_p/k_{ST}$ obtained from the slopes of the relative quantum yield plots (Table IV). That the reaction of $^1CH_2$ with 2-pentene and chloroform is diffusion controlled is supported by the observation that the Stern–Volmer analysis of $^1CH_2$ with acetonitrile as a standard substrate yields Stern–Volmer constants which are nearly identical for a wide variety of substrates of differing structures, including 2-pentene and chloroform (Table III). The viscosity of perfluorohexane at 0 °C is 1 cP,[18] from which a diffusion-controlled rate of 5.0×10^9 M^{-1} s^{-1} can be calculated.[19] From the lower value of 7 M^{-1} for the ratio of $^1k_p/k_{ST}$, an upper limit of 8×10^8 s^{-1} is thus obtained for k_{ST}, which is much lower than that expected from the gas-phase results with methylene. As mentioned in the introduction, from results on the quenching of $^1CH_2$ in the gas phase, deactivation of $^1CH_2$ is calculated to occur with a bimolecular rate constant of at least 2×10^9 M^{-1} s^{-1}, which implies a deactivation rate of no less than ca. 1×10^{10} s^{-1} in solution (for 5 M solvent). This value is at least one order of magnitude higher than the value we extract from our dilution experiments. Thus, it is clear that the results of gas-phase measurements with $^1CH_2$ cannot be extrapolated directly to the results in solution.

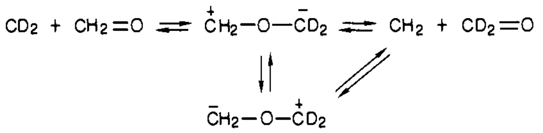
Scheme IV



Before we speculate on the origin of this contrasting behavior, let us consider the results of measurements of intersystem crossing of other carbenes in solution. The intersystem crossing of diphenylcarbene[20] and fluorenylidene[21] in solution are among the best documented because measurements have been made by direct time resolved techniques. In nonpolar solvents the k_{ST} values for fluorenylidene and for diphenylcarbene have been determined to be ca. 7×10^9 s^{-1} and 1.0×10^{10} s^{-1}, respectively. A significant "solvent effect" is observed on the rate of intersystem crossing of these carbenes. In polar solvents, the rate of intersystem crossing slows down significantly: 2.5×10^9 s^{-1} for fluorenylidene and 3×10^9 s^{-1} for diphenylcarbene. These results have been intepreted[20] in terms of a significant solvation of the singlet carbene, a result expected from theory if the singlet carbene possesses a dipolar structure. It is not clear whether the results with aryl carbenes have direct relevance to methylene. However, we speculate that a solvent effect could come about if during the act of decomposition of the carbene precursor by direct photolysis or shortly thereafter the resulting $^1CH_2$ is complexed by the perfluorohexane (e.g., by association with the *n* electrons of a fluorine atom). This complexation would probably lead to reaction with most other solvents, but the inertness of the CF bond allows the complex to persist. Such reversible complexation is probably similar to that suggested of phenylchlorocarbene with alkenes[22] (eq 7) and methylene-d_2 with formaldehyde[23] (eq 8). However, since the CF bond of perfluorohexane is relatively inert toward CH_2, intersystem crossing can occur within the CH_2/perfluorohexane complex, but it is slowed down because the complexing reduces the extent of spin–orbit coupling, which is expected to be the major mechanism for intersystem crossing. The complete lack of isotope effects (^2H or ^{13}C) of the intersystem crossing rate is consistent with the



(7)



$$CD_2 + CH_2{=}O \rightleftharpoons \overset{+}{C}H_2{-}O{-}\overset{-}{C}D_2 \rightleftharpoons CH_2 + CD_2{=}O \qquad (8)$$
$$\overset{-}{C}H_2{-}O{-}\overset{+}{C}D_2$$

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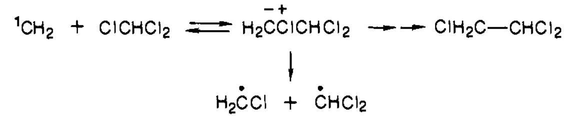
absence of significant contribution of hyperfine coupling to the intersystem crossing rate.

Reactivity of Methylene in Solution. Merging of Complexation and Reaction. Because of its inability to distinguish between different types of aliphatic CH bonds in its solution reaction with alkanes, methylene was termed "the most indiscriminate reagent known in organic chemistry".[11] This epithet was given to methylene at a time when the occurrence of two low-lying spin states of methylene was just beginning to be widely recognized. It is now clear that $^1CH_2$ is the state that is being examined in these studies, with little if any intersystem crossing to $^3CH_2$ being possible because of the extreme reactvity of $^1CH_2$ and relatively slow intersystem crossing of $^1CH_2$. In the case of reaction of $^1CH_2$ with 2-pentenes, insertion into alkyl, allylic, and vinyl CH bonds all occur competitively, while addition to the C=C double bond is somewhat preferred (Table I). On the other hand, $^1CH_2$ does show considerable discrimination between the CCl bonds and CH bonds of chloroform. A proposed mechanism for $^1CH_2$ reaction with chloroform is shown in eq 9, where a reversibly formed dissociable intermediate[24] either undergoes rearrangement to form CCl insertion product or undergoes cleavage to form radicals. That CCl insertion is the main product for $^1CH_2$ reaction with $CHCl_3$ implies that the production of radicals is a minor decay pathway. However, this pathway is sufficient to produce a significant CIDNP effect.[14] The selectivity of $^1CH_2$ toward CCl bonds and CH bonds of chloroform comes about after the intermediate formation, probably because chlorine migration in the complex intermediate is more favored than hydrogen migration.[25] The relative rates of $^1CH_2$ reaction with various substrates and with acetonitrile are quite similar. This similarity is consistent with the expected diffusion-controlled reactivity of $^1CH_2$ toward organic substrates in the solution phase. However, it is noteworthy that the rate of $^1CH_2$ reaction with hexafluorobenzene (C_6F_6) is about ten times slower than that with other quenchers. This rate is consistent with the known diminishment of alkene reactivity on fluorine substitution.[38] The decreased reactivity of the electrophilic $^1CH_2$ toward fluorinated alkenes is attributed to the lowering of π-electron density of the electronegative fluorines. The specific mechanism responsible for CCl insertion in no way determines the validity of our analysis. For example, an electron-transfer mechanism may actually be involved.



$$^1CH_2 + ClCHCl_2 \rightleftharpoons H_2\overset{-}{C}\overset{+}{Cl}CHCl_2 \dashrightarrow ClH_2C{-}CHCl_2 \quad (9)$$

$$H_2\overset{-}{C}\overset{+}{Cl}CHCl_2 \longrightarrow H_2\dot{C}Cl + \dot{C}HCl_2$$

The absolute reactivity of $^3CH_2$ appears to be considerably lower than that of $^1CH_2$, which has recently been confirmed by the gas-phase results.[26] In the gas phase, the bimolecular rate constant of methylene quenching by ethylene is 9×10^{10} M^{-1} s^{-1} for $^1CH_2$,[4] while it is only 4×10^5 M^{-1} s^{-1} for $^3CH_2$. Furthermore the selectivity of $^3CH_2$ in its reactions with 2-pentene in solution is considerable with cyclopropane formation being strongly favored over other possibilities. The products from the isomerization of cyclopropanes (or 1,3-diradical intermediates) were not observed within our detection limit, which implies that thermal isomerizations of cyclopropanes or 1,3-diradicals are less prevalent in solution.[37] In the case of chloroform as a substrate $^3CH_2$ favors hydrogen atom abstraction over chlorine atom abstraction.

Another point of interest relates to the possibility of $^3CH_2$ to $^1CH_2$ intersystem crossing in solution, a process that has been invoked to explain gas-phase data.[26] Our results provide no suggestion of such a process. Especially telling is the triplet-sensitized reaction of diazomethane with the 2-pentenes which leads nearly exclusively to cyclopropanation products, while direct excitation of diazomethane leads mainly to hydrogen insertion products. This result contrasts with those found for diphenylcarbene and fluorenylidene for which substantial triplet to singlet intersystem crossing occurs.[20,21] However, the results are readily understood in terms of the relatively large singlet–triplet splitting of methylene (9 kcal/mol, Figure 1). In diarylcarbenes this gap decreases to only several kcal/mol or so, allowing thermal population of the singlet carbene from the ground-state singlet carbene.

The differing reactivity (absolute bimolecular rate constant) and selectivity (relative bimolecular rate constant) of the singlet and triplet states of carbenes appears to be a common feature of these energetic species. This difference is conventionally explained on the basis of different electronic configurations for the two states in addition to the difference of their spin configurations. The latter feature usually does not enter directly into reactivity/selectivity profiles at the stage of an elementary reaction step, but becomes important in determining the possible pathways followed by primary intermediates formed by reaction of the carbene with the substrate. Thus the general characteristics of $^1CH_2$ reactivity are determined by its "zwitterionic" orbital configuration which imbues it with a ferocious electrophilicity.[27] This electrophilicity, we believe, is closely linked with the solvent effects for singlet carbenes. Thus, depending on the extent of bonding and the ability of the CH_2 moiety in a complex to react in a manner characteristic of $^1CH_2$, the concepts of reaction and complexing begin to merge. Such a merging concept has substantial analogy in the formation of charge-transfer species and exciplexes from electronically excited states which merges into full electron transfer reactions.[28] Any primary intermediate formed by electrophilic attack by $^1CH_2$ is spin paired and can usually find pathways to rapidly collapse to molecular products. In the same way the general characteristics of $^3CH_2$ reactivity are determined by its "biradical" orbital configuration which imbues it with a radical reactivity comparable to that of simple alkyl radicals. The reactions of alkyl radicals with typical organic substrates are usually orders of magnitude less than diffusion controlled,[29] so the reactions of $^3CH_2$ with such substrates are expected to also be less than diffusion controlled. Furthermore, triplet geminate radical pairs or biradical primary intermediates appear to be virtually obligatory in the reactions of $^3CH_2$ with organic substrates, thereby leading to nonstereospecific reactions and the efficient escape of geminate pairs from the primary radical cage.

Conclusion

On the basis of a combination of dilution and triplet-sensitization experiments, evidence for the intersystem crossing of $^1CH_2$ to $^3CH_2$ in perfluorohexane is obtained. Analysis of the products from the reactions of $^1CH_2$ and $^3CH_2$ with 2-pentenes and with chloroform as a function of dilution, and using the assumption of diffusion-controlled reactivity of $^1CH_2$ with the substrates, allows the evaluation of the rate of $^1CH_2$ to $^3CH_2$ intersystem crossing to be $\leq 8 \times 10^8$ s^{-1}. This value is much smaller than that which is expected from extrapolation of the gas-phase quenching of $^1CH_2$. The difference between the gas-phase and the solution-phase results is ascribed to complexing of $^1CH_2$ by perfluorohexane solvent to produce a weakly bound species with a slower intersystem crossing rate than that for $^1CH_2$ in the gas phase. Although $^1CH_2$ appears to react with many substrates at the rate of diffusion, selectivity is observed, implying the existence of diffusion-controlled complexes from which reaction occurs. Our results imply that it may not be possible to measure the rate of reactions of "free" methylene in solution.

Experimental Section

Acetonitrile (MCB, OmniSolv), methanol (EM, OmniSolv), methyl alcohol-*d* (Aldrich, 99.5+% atom D), methyl-d_3 alcohol-*d* (Aldrich, 99.5% atom D), deuterium oxide (MSD, 99.8+% atom D), and benzene (EM, OmniSolv) were used without further purification. Perfluorohexane (Alfa), *cis*-2-pentene (Aldrich), *trans*-2-pentene (Aldrich),

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chloroform (EM, OmniSolv), deuteriochloroform (Norell, Inc., 99.8% D), carbon tetrachloride (Fisher), methylene chloride (Fisher), isoprene (Aldrich), and hexafluorobenzene (Aldrich) were fractionally distilled prior to use. Diazirine[30] and diazomethane[31] were synthesized in a given solvent prior to use. The concentrations of diazirine[32] and diazomethane[33] were determined by their UV-vis absorption spectra. The two cyclopropanes, *cis*- and *trans*-1-ethyl-2-methylcyclopropane, were prepared as in the literature.[34] Other VPC standard compounds (e.g., C_6 alkenes) were obtained from Aldrich and Wiley Organics.

A C_6F_{14} solution containing diazirine (ca. 0.005–0.01 M) and various concentrations of *cis*-2-pentene (*trans*-2-pentene or chloroform) was purged with argon at −78 °C for 15–20 min and then was irradiated for 20 min in tubes cooled to 0 °C in a Dewar. Pyrex glassware was used for both diazirine and diazomethane. When diazomethane (ca. 0.01 M) was used, the solution was degassed with 3 freeze–pump–thaw cycles before photolysis. Irradiation was performed with an Oriel 1000 W Xe–Hg lamp. After photolysis, the reaction mixture was analyzed by VPC (SE-30 capillary, 50 m; 0.19 picric acid on Graphpac glass column, 6 ft). The C_6 products from the 2-pentene experiments were identified by comparison of VPC retention times with the authetic materials. Other products, many in trace or minor quantities, were observed upon VPC analysis of the 2-pentene system but were not specifically analyzed. The objective of this work is limited to a clarification of the major C_6 products, which conventionally have drawn the most attention and which are most closely related to the interesting processes. Triplet-sensitized photolysis of diazomethane in neat solvent was carried out at 0 °C with irradiation at 313 nm (0.25-m high-intensity monochromator, Kratos, Model 252) in the presence of benzophenone (ca. 0.015 M). The samples were degassed with 3 freeze–pump–thaw cycles before photolysis. The products were analyzed by VPC as described before. The laser flash photolysis system is the same as previously described.[35]

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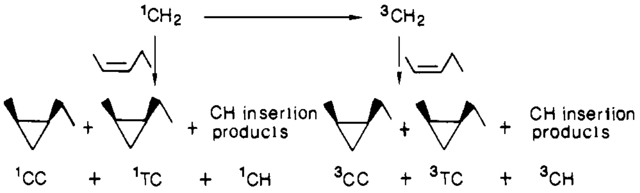
Appendix A

The ratio of singlet to triplet product quantum yield at a given concentration of substrate is calculated as follows with *cis*-2-pentene as an example. The reaction scheme is shown below, in



which ^1CC, ^1TC, and ^1CH represent the *cis*-, *trans*-cyclopropane and the CH insertion products obtained from $^1CH_2$ reaction with *cis*-2-pentene, and ^3CC, ^3TC, and ^3CH represent the *cis*-, *trans*-cyclopropane and the CH insertion products obtained from $^3CH_2$ reaction with *cis*-2-pentene. The product distribution from pure $^1CH_2$ (^1CC:^1TC:^1CH) was obtained from direct photodecomposition of diazirine in neat *cis*-2-pentene in a ratio of 0.40:0:0.60, while the product distribution from pure $^3CH_2$ (^3CC:^3TC:^3CH) was obtained from triplet-sensitized decomposition of diazomethane in neat *cis*-2-pentene in a ratio of 0.44:0.51:0.05 (Table II).

quantum yield of singlet products: $^1\Phi$

quantum yield of triplet products: $^3\Phi$

The product distribution of *cis*-, *trans*-cyclopropane and the CH insertion products at a given concentration of *cis*-2-pentene was obtained in a ratio of *a*:*b*:*c*, respectively. The *a*, *b*, and *c* were calculated in such a way that $a + b + c = 1$. Therefore, the singlet-to-triplet product quantum yield ($^1\Phi/^3\Phi$) can be calculated from the amount of trans cyclopropane by the equation shown below.

$$\frac{^1\Phi}{^3\Phi} = \frac{0.51 - b}{b - 0}$$

The analogous analysis can be applied to the CH insertion products. In theory, the quantum yield ratio can be calculated from the yield of *cis*-cyclopropane, the yield of *trans*-cyclopropane, and the yield of CH insertion products, respectively. However, in practice, for *cis*-2-pentene the quantum yield ratios are calculated from the yields of the *trans*-cyclopropane and the yields of the CH insertion products, respectively. For *trans*-2-pentene, the quantum yield ratios are calculated from the yields of the *cis*-cyclopropane and the yields of the CH insertion products, respectively.

Registry No. Methylene, 2465-56-7; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; chloroform, 67-66-3.

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